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Heavy Metals Evaluation of Groundwater Resources of Amaeze, Ishiagu, Ebonyi State, Southeast Nigeria.

Mgbeafuruike, E. U[1], Onuoha, P. I[1], Ovu, S. C.[2] Omeokachie[3], A. I[1]., Alieze, I. V[2]. and Obasi, P. N[2]

[1] Department of Geology, Alex Ekwueme Federal University, Ndiufu Alike Ikwo Ebonyi State.

[2]Department of Geology and Exploration Geophysics, Ebonyi State University. P.M. B 053, Abakaliki Nigeria.

[3] Department of Geological Science Nnamdi Azikiwe University Awka, Anambra State Nigeria.

Corresponding Author: Obasi, P. N; Email:obasiphilip26@gmail.com. Phone number: +2348060636246

Abstract.

Heavy metals evaluation of Amaeze, Ishiagu, Ebonyi State was carried out. The area lies between longitude 5º 55' N - 6º 00 'N and latitude 7º 30' E - 7º 35' E, about 20km South East of Enugu, 10km South West of Afikpo in South East Nigeria. The area belong to the Asu River Group (Albian) and the Ezeaku Group (Turonian). Ten (10) groundwater samples were collected from hand dug wells and boreholes and were analyzed using Atomic Absorption Spectrophotometric (AAS). The result of hydrogeochemical analysis reveals that the heavy metals concentrations in water in the study area are: Cd^{2+}, Pb^{2+}, Cu^{2+}, Cr^{3+} Ag^{+}, Zn^{2+}, Se^{2+} , V^{+} , Co^{2+}, Ar^{2+}, Ni^{2+} and Mn^{2+}. While physical parameters tested includes; pH, TDS, Ec and Turbidity. These heavy metals were found to have high concentrations (Co^{2+} , Ar^{2+} , Mn^{2+} , Ni^{2+} and Se^{2+}). These concentrations are above the USEPA and WHO, 2011 permissible values for safe domestic water supply. The high concentration is as a result of the dissolution of the ions into groundwater sources from ore bodies and also from infiltration processes into groundwater. Groundwater resources around Amaeze needs to to be protected for adequate industrial and domestic uses. Pipe borne water should be provided after effective geochemical evaluation of the area.

Keywords: Hydrochemical; Heavy metals; Mining; Groundwater; Amaeze

1.0 Introduction

Groundwater is one of the most precious natural resources on the planet, and its relevance in sustaining healthy populations in society is driving up demand (Obasi and Akudinobi, 2020; Igwe, et al., 2017; Obiorah, et al., 2018). On a global basis, groundwater is regarded critical in the development of industrial estates, tourist hubs, urban and agricultural populations (Niu et al., 2017, Xaincang, et al., (2020); Laxaman. et al., (2021); Azadeh, et al., (2020). The importance of groundwater in the conservation of global food security has been highlighted (Wada et al., 2014 and Obasi et al., 2021). However, depending on the intended goal, the level and quality of available water resources might become a worldwide concern, limiting a region's long-term development and ecological balance (Azada, et al., 2020). Eyankware et al., 2021 has emphasized that groundwater is preferred to surface water because it is readily free from surface contamination, and it is also considered to be less prone to contamination when compared to surface. Further, in most scenarios, groundwater is contaminated by infiltration from surface pollution such as leakage from septic tanks, mining activities, and indiscriminate waste disposal, among others. Niu et al., (2017) and Xaincang, et al.,(2020) noted that several factors are responsible for the alteration of groundwater resource. Hydrochemical evaluation of water resources is pertinent to acertain the chemical, physical and biological compositiom of water. This very necessary as the composition of water determines its domestic, industrial or agricultural uses. Many authors, including Okolo et al., (2018); Obasi., et al (2021, 2022); Obasi (2020); Moye et al (2017), Rubio et al, (2000); Nieto et al, (2007) Eyankware et al, (2020, 2021, 2022) have used different approach to evaluate surface and groundwater resources in different parts of the Africa and Nigeria. The study area, Amaeze is located in Ishiagu. And Ishiagu lies between longitude 5º 55' N - 6º 00 'N and latitude 7º 30' E - 7º 35' E, about 20km South East of Enugu, 10km South West of Afikpo in South East Nigeria. About 4km to South East of Ishiagu are several ridges of deposit of complex sulphide ore which extend all through the lower Benue trough. It is one of the economically important towns in Ebonyi State. Its economic relevance is basically due to agricultural and mining activities of lead/zinc and associated deposits. These minerals were discovered in the area in the 1950s according to Bogue (1952). This has attracted a lot of attention from government establishments and mining companies to the area. There have been continuous excavations, uncontrolled dumping of mine wastes and gangues, frequent discharge of mine wastewaters into agricultural farmlands and stream channels. All these introduces heavy metals into the environment and can find their way into groundwater sources. It is therefore, against this background that the hydrochemical evaluation of groundwater in Amaeze is necessary. The assessment of the quality of groundwater with respect to heavy metals in Amaeze and environs in Ishiagu area has been carried out. This work has established the distribution patterns of Cr, Mn, As, Ag, V, Pb, Zn, Cu, Cd, Ni and Co in water in the area.. The water quality with respect to physical parameters like Turbidity, total dissolve solid (TDS), potential of Hydrogen (pH) and Electrical conductivity (EC) of the study area has been evaluated.

2.0 Geology and physiography

The Geological Survey of Nigeria (GSN) was amongst the first group to carry out study on the geology of the southeastern Nigeria, which included parts of Ishiagu. The lead-zinc mineralization belt in the area has been studied by a number of workers. Farrington (1952) surveyed the lead-zinc belt, which is associated with lower Cretaceous folding and igneous activities in southern Nigeria. Gravity surveys by Cratchtley and Jones (1965) along the belt of occurrence of the brines reported that the brine springs are most frequently found near the axes of anticlines in fractured and mineralized areas.. Nwachukwu (1972) investigated the tectonic evolution of the southeastern portion of the Benue Trough where he noted that lead-zinc mineralization dominates the Albian shale and has fewer occurrences in the Turonian shale. Ezepue (1984) presented the major and trace element content of lead-zinc mineralization at Ishiagu with emphasis on the temperatures of formation. He also studied the geologic setting of the lead-zinc deposits of Ishiagu in relation to tectonic fissures which influenced the loci of mineralization. He noted that there are close associations between mineralized veins, igneous intrusion and up fluxing points of saline groundwater.

Locally, the area is underlain by the Asu River Group and Eze-Aku Group. The area is mainly characterized by well bedded shale, grey to black in colour (weathered to brownish material in some part of the formation), blocky, calcareous and in most locations interbedded with sandstone and mudstones. The sediments have been folded and fractured particularly following the series of tectonic episodes which have acted on them. Dolerite intrusion and lead-zinc mineralization were also observed in the area. This has been attributed to magmatic activities which have baked the shales. The terrain has 280ft (84m) as its highest contour and 200ft(60m) as the lowest contour above datum plane (global mean sea level), with a well drained drainage pattern generally flowing NE-SW: Ikwo River, Ivo River, Odu River and Ihetutu streams (Figure 1). The main river Ivo takes its source from the Udi-Okigwe cuesta and then splits into smaller streams such as Ikwo, Ngado, Ihetutu and Eku rivers that create dendritic drainage pattern in the study area. Two prevalent seasons in the are are wet and dry seasons. The months of wetness are from March to October. The average rain fall in this area is about 2125mm, during the period of raining season and slightly above 250mm in the driest month. However, occassional variation of the month have observed at the end of the other. The period of dry season there is scarcity of water, middle of the season is characterized by harmattan (period of extreme coldness), which is experienced within the months of December to January. The mean annual temperature range of the dry season is about 27ºC and occurs in the month of February to early March. Generally, the vegetation in Ishiagu and its environs consist of trees, shrubs and grasses.

3.0 Methodology

2.1: Water Sample Collection

Ten (10) water samples were randomly collected from groundwater resource from boreholes and handdug wells. Each sample was collected using one (1) liter plastic water bottle which was thoroughly rinsed with same sample water in order to avoid contamination from the container. The coordinates and elevations of the sample location were recorded using GPS. The samples were labeled properly with the location names, and were conveyed to the Hydrochemistry laboratory at the same day of collection. Total of sixteen parameters were analyzed from the water samples. Physical parameters such as pH, Conductivity, Turbidity, Total Dissolved Solid and heavy metals which include lead, copper, vanadium, cadmium, chromium, selenium, zinc, manganese, silver, cobalt, and Arsenic.

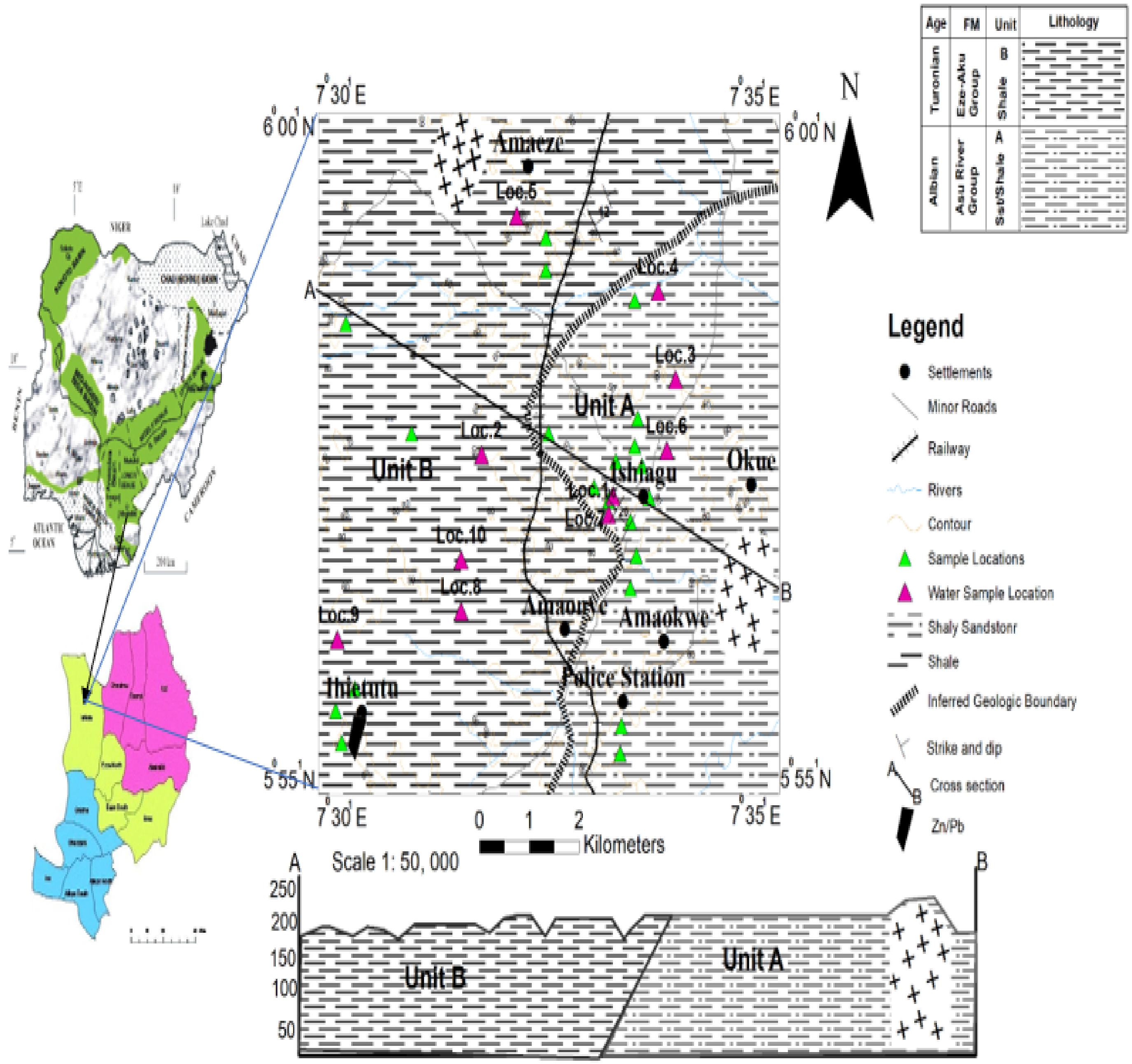

Fig 1: Geologic map of Ishiagu and environs showing sample location

2.2: Laboratory/ Water Analysis

Electrical conductivity and pH of the water samples were measured by electrometric method, using laboratory pH meter [according to American Public Health Association, (APHA) 2510B guidelines Model DDS-307(APHA; 1998)] and conductivity cell [according to American Public Health Association, (APHA) 2510 B guideline Model DDS-307(APHA; 1998)]. The heavy metal analysis was done using Varian AA240 Atomic Absorption Spectrometer (AAS) according to APHA, 1995 guidelines.

3.0 Result and Discussions

The result of the concentrations of groundwater has been presented in table 1.

3.1 Physical Parameters

The physical parameters analyzed include pH, Total Dissolved Solid (TDS), electrical conductivity and turbidity.

pH

This is the measure of the hydrogen ion concentration in water. The pH concentration of the study area ranges from 5.15– 6.12. The WHO (2012) recommendation of pH value for drinking water is between 6.5- 8.5. The pH values of all the samples are within the WHO (2012) recommendations and therefore safe for drinking. The slightly acidity pH values in these locations are due to the dissolution of minerals into the water and also as result of the minimal leaching of chemicals from dump at the mining sites into groundwater sources. The pH value of water is important as it helps to control major activities that take place in the environment (water) and it is also an essential parameter in water treatment (Chapman, 1989). It can also be used to deduce the extent of effluent plume discharge in water bodies.

Table 1: Results of heavy metals analysis of Groundwater of Ishiagu and environs.

Parameter	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
Silver (ppm)	ND	ND	0.070	0.024	0.021	0.062	0.055	0.003	0.007	ND
Vanadium (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cobalt (ppm)	0.333	0.084	0.333	0.233	0.318	ND	0.228	0.197	0.250	0.195
Arsenic (ppm)	0.765	1.222	0.882	0.953	1.333	0.761	0.968	1.194	0.911	0.880

Manganese(ppm)	ND	2.864	0.591	0.529	0.533	3.900	1.941	0.001	ND	0.008
Copper (ppm)	0.004	ND	ND	ND	ND	0.189	0.052	0.026	0.013	0.008
Zinc (ppm)	1.9171	0.7894	0.3890	0.2657	0.2021	1.1475	0.7769	0.5900	0.6690	0.3336
Chromium (ppm)	ND	ND	0.026	0.004	0.017	ND	ND	ND	ND	ND
Cadmium (ppm)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel (ppm)	0.046	0.81	0.049	0.039	0.055	0.064	0.096	0.055	0.087	0.054
Lead (ppm)	ND	ND	ND	ND	ND	0.035	0.002	0.003	0.065	0.103
Selenium(ppm)	0.556	0.612	1.448	1.307	1.212	1.313	1.401	0.389	0.114	0.128
pH	6.12	5.30	5.78	5.15	5.16	5.28	5.66	6.02	5.43	5.60
Turbidity (NTU)	44.00	34.20	30.11	15.11	10.32	28.30	32.20	38.20	39.20	35.11
Conductivity	9,41	7.18	4.39	8.58	6.61	11.25	3.35	2.70	7.07	13.16
Total dissolved solid (mg/l)	4.77	4.59	2.19	4.29	3.30	5.62	1.67	1.35	3.53	6.58

ND= Not detectable

TOTAL DISSOLVED SOLID (TDS)

Total Dissolved Solid (TDS) refers to the total solid particles that are dissolved in water. The total dissolved solid in the water sample of the study area ranges from 2.19 – 6.58 mg/1. The WHO TDS recommendation for domestic water is 1000 mg/L. The TDS concentration in the study area is within the WHO recommendation value. According to Todd, 1980, the water samples analyzed in the study area is fresh water because they fall within the limit of fresh water concentration.

TURBIDITY

Turbidity is a measure of the suspended and colloidal matters in water and this constitutes the transparency of water bodies. Such suspensions and colloidal matters could be clays, silts, organic matter and microscopic organisms. The turbidity of the surface water in the study area ranges from 10.32 - 44.00 (NTU). From the WHO (2004) standard, turbidities exceeding 5 NTU is not good for domestic use. From the result of the analysis on turbidity, the surface water in the study area has turbidity values outside the WHO recommendations. The high turbidity values in the study area are due to the organic matter contents in the water, the clay and silt content of the water and the washing of other solid particles into the water.

ELECTRICAL CONDUCTIVITY

Electrical conductivity of water is the ability of water to conduct electric current and this is possible due to the presence of solids in solution, which is referred to as Total Dissolved Solid (TDS) in water. The electrical conductivity of water in the water samples of the study area ranges from 2.70-13.16µS/m with mean value of 7.634 µS/m . The WHO (2011) recommendation of conductivity for domestic water is 1000µS/m. from the result; the conductivity of water in the study area is within the WHO recommendation for domestic water. Most dissolved inorganic substance in water is in the ionized form and these contribute to the specific conductance. A measure of conductivity gives a practical estimate of the variation in the dissolved constituents in the given area.

3.2 Heavy Metals

Heavy metals analysed are lead, copper, mercury, cadmium, chromium, selenium, aluminum, zinc, manganese, silver, cobalt, and Arsenic. These ions are discussed below with their various concentration values in the water of the study area.

Arsenic ion (As^{2+})

The concentration of As in the study area ranges from 0.765-1.333mg/l with a mean value of 0.9861mg/l. The WHO (2004) recommendation of As for drinking water supply 0.01mg/l. This implies that the Arsenic ion (As) concentration in the study area is above the WHO recommendation value for surface water. The high value of arsenic in the study area indicates that there are activities such as mining in the environment. Arsenic can exist in many natural forms such as sulphide or metal arsenides or arsenates. High concentration of As in surface water posses a serious health problems. Arsenic emanates from the dissolution of ores. It is also associated with ores containing metals such copper and lead, volcanic eruptions are another source of arsenic. In water, it is mostly present as arsenate, but in anaerobic conditions, it is likely to be present as arsenite (Almela et al., 2002). It is usually present in natural water at concentrations of less than 1-2mg/l. However, in waters, particularly groundwaters, where there are sulphide mineral deposites and sedimentary deposites deriving from volcanic rocks, the concentrations can be significantly elevated upon 12mg/l (WHO,2002). Arsenic is found in the diet, particularly in fish and shellfish, in which it is found mainly in the less toxic organic form(Garvey et al., 2013).

Transport and partitioning of the arsenic in water depends upon the chemical form(oxidation state and counter ion) of the arsenic and on interactions with other materials present.

Lead ion (Pb^{2+})

The concentration of lead ion of the World health organization ,WHO (2004) recommendation standard of Pb for drinking water is 0.01mg/l. The concentration of Pb ranged from 0.002 to 0.103mg/l in the study area. High concentration of lead causes lead poisoning which is dangerous to human health especially infants. It can also cause nervous system depression, nervousness and patty (Nnabo et al,2011). The amount of lead dissolved in the plumbing system depend on several factors, including pH, temperature, water hardness and standing time of the water, with soft, acidic water being the most plumb solvent (WHO, 2008). Owing to the decreasing use of lead-containing additives in petrol and lead-containing solder in the food processing industry, concentrations in the air and food are declining, and intake from drinking - water constitutes a greater portion of total intake of lead (Sawyer, *et al*., 1998).

Manganese ion (Mn^{2+})

The concentration of manganese ion in the groundwater system of the study area rages from 0.001 - 3.900mg/l. The concentration of Mn is above the WHO recommendation in all the location tested but highest in sample 6. The WHO recommendation value is (0.5mg/l) for manganese in a safe drinking water. This high concentration is attributed to the dissolution of manganese from the chalcopyrite and siderite ores in the area. This is controlled by the solubility, pH, Eh (oxidation - reduction potential), and the characteristics of the avaliable anions in water (Clewell et al., 2003). Aschner et al., 2007 emphasized that the metal may exist in water in any of four oxidation states; however, Mn (II) predominates in most waters (pH 4-7), but may become oxidized under alkaline conditions at pH>8 (EPAA, 1984). The principal anion associated with Mn (II) in water is usually (CO_3^{2}). This increases the concentration as the carbonate composition of the shales are readily avaliable for reaction.

Cadmium ion (Cd^{2+})

The hydrochemical investigation of water samples reveals the total absence of Cd in the samples. Cadmium not detected may be as a result of non dissolution of Cd ions. Cadmium occcurs naturally in the environment. Additional release of cadmium to the environment occur from natural sources and from processes such as combustion of fossil fuel, incineration of municipal or industrial wastes, or land application of sewage sludge or fertilizer WHO, (2004) reveals that smoking is a significant additional sourse of cadmium exposure in humans. Occurrence levels in drinking water are usually less than 1 mg/l (Elinder, 1985)

Generally, cadmium will bind strong ly to organic matter and this will, for the most part immobilize cadmium (Autier and White, 2004). Cadmium in water tends to be more avaliable when the pH is low (acidic) (Elinder, 1992). In surface water and ground water, cadmium can exist as the hydrated ion or as ionic complexes with other inorganic or organic substances. While soluble forms may migrate in water, cadmium is relatively nonmobile in soluble complexes or adsorbed to sediments, which may leach into water (Elinder, 1985; EPA, 1979).

Zinc ion (Zn^{2+})

Natural water usually contain very low levels of zinc less than 0.1mg/l. The World Health Organization, WHO (2011) recommended value for zinc in a safe drinking water is 5mg/l. The concentration of zinc ion ranges from 0.2021 to 1.9171 mg/l respectively. This value of zinc ion concentrations in the study area is within the recommended value for zinc ion in drinking water. Zinc is released into the environment both from natural and antropogenic sources; however ,release from antropogenic sources are greater than those from natural sources.

Apart from the dissolution of zinc in the water, which increases with acidity, zinc is immobile in water. In water, zinc occures primarily in the +2 oxidation state, it dissolves in acids to form hydrated zn^{2+} cations and in strong base to form zincate anions, which are hydroxo complexes. In most waters zinc exist as primarily as the hydrated form of the divalent cation. However, the metal often form complexes with a variety of organic and inorganic ligants (EPA, 2003, 2005).The transport of zinc in the water is controlled by anion species. In natural waters, complexing agents, such as humic acid, can bind zinc. Divalent zinc ion, often replaces magnesium in silicate mineral of igneous rocks; consequently weathering if this zinc containing bedrock gives rise to Zn^{2+} in solution (EPA, 2005).

Copper ion (Cu^{2+})

The concentration of copper in the study area ranges from 0.004 - 0.189mg/l. The United State Environmental Protection Agency (WHO, 2004) recommendation of Cu ion in surface water is 1.3 mg/l. The concentration of copper ion in the study area are within the permissible value of copper in drinking water. Concentration of Cu in surface water above the USEPA recommendation has a negative effect on human body, as it causes gastrointestinal disorder and kidney and liver problem. The chalcopyrite (which is endowed in the area), breaks down into cooper and pyrite but copper has low mobility and reacts slowly with water. This can be attributed to the low concentration of copper in the area.

Chromium ion (Cr^{3+})

The concentration of Cr^{3+} in water in the study area ranges from 0.004 - 0.026, although many samples are undetected. The USEPA recommended permissible value of Cr^{3+} in drinking water is 0.1mg/l. The value of this ion is within the USEPA recommendation value but high concentration of this ion above the permissible value causes allergic dermatitis (USEPA). The reduction of chromium ions under anaerobic conditions occurs rapidly, with the reduction half-life ranging from instantenous to a few days (Seigneur and Constantinous, 1995). However, the reaction of chromium (IV) by organic sediment and soil is much slower and depends on the type and amount of organic material and on the redox condition of the water. The reduction half-life of chromium (IV) in water with soil sediment ranges from 4 to 140 days, which the reaction typically occuring faster under anaerobic rather than aerobic conditions.

Selenium ion (Se^{2+})

The concentration of Se^{2+} in the study area ranges from 0.128 – 1.448mg/l. The USEPA recommended value of Se^{2+} for safe water supply is 0.5mg/l. The concentration of this ion in water in the study area is above the USEPA recommended value. The source of this ion in water of the study area is from the dissolution of ion from the lead and zinc mine in nearby community into the water. Elemental selenium that cannot dissolve in water and other insoluble forms of selenium are less mobile and will usually remain water, poising smaller risk of exposure. However the selenium compounds that can dissolved in water are sometime very mobile, and surface waters can receive selenium from the atmosphere by dry and wet deposition, from adjoining water that my contain selenium, from runoff, and from subsurface drainage .

Silver ion (Ag^+)

The concentration of Ag^+ ion in water in the study area ranges from 0.003 - 0.070mg/l with a mean value of 0.035mg/l. The USEPA recommended value of Ag^+ for safe domestic water supply is 0.1mg/l. The value of this ion in water in the study area is within the USEPA recommendation value. The water in the study area is safe for domestic water supply. The source of silver ion in the study area is also from the dissolution of the ion into water from the lead zinc mine. The only sign of silver over load is argyria, a condition in which skin and hair are leavily discoloured by silver in the tissue (WHO, 2008).

Cobalt ion (Co^{2+})

The concentration of cobalt ion in the study area varies between 0.084 - 0.333mg/l with a mean value of 0.241mg/l. The concentration of cobalt ion in the study area is above the United State Environmental Protection Agency, USEPA (2008) recommended value for drinking water of 0.07mg/l. Constant exposure to cobalt powder has diverse effect on the sight and hearing ability of humans, liver, pancreas and heart disorders. However, in spite of all this defects cobalt performs some medical functions such as in hip replacements, radiotherapy and for sterilizations of medical equipments. Industrially, it serves as a pigment to produce distinct blue colour and battery making.

Nickel ion (Ni^{2+})

Nickel ion concentration of the groundwater resources of the study area varies between 0.039- 0.81mg/l with a mean value of 0.135mg/l. However the World Health Organization recommended value for nickel for drinking water is 0.1mg/l. The concentration of nickel ion the groundwater system in the area is within WHO (2011) except in location 2 with concentration of 0.81mg/l. Its high concentrations in sample 2 in the study area may be based on the fertilizer in the study area which enters the surface water from the runoff and finally finds its way to the groundwater. The human body contains about 10mg/l of Nickel, its inhalation and exposure to a higher degree is the greatest risk of developing health problems such as a dermatitis upon contact. Also the presence of iron-rich sulfide that reachily settle out tailings effluents from sulfide are acidic due to the bacterial generation of sulfuric acid from the sulfide minerals in the tailing clernens and landolph, 2003, suggested that dessication of sediments leads to ornatation of iron sulfides and subsequent acidification of the sediments which increases mobilization of heavy metals like nickel, leading to groundwater concentration of Ni.

Vanadium (V^+)

Vanadium ion was not detected in all water samples analysed. The United State Environmental Protection Agency (USEPA, 2012) recommendation of Cu ion in surface water is 1.3 mg/l. The concentration of vanadium ion in the study area is zero and are within the permissible value of vanadium in drinking water. Concentration of V in groundwater above the USEPA recommendation has a negative effect on human body.

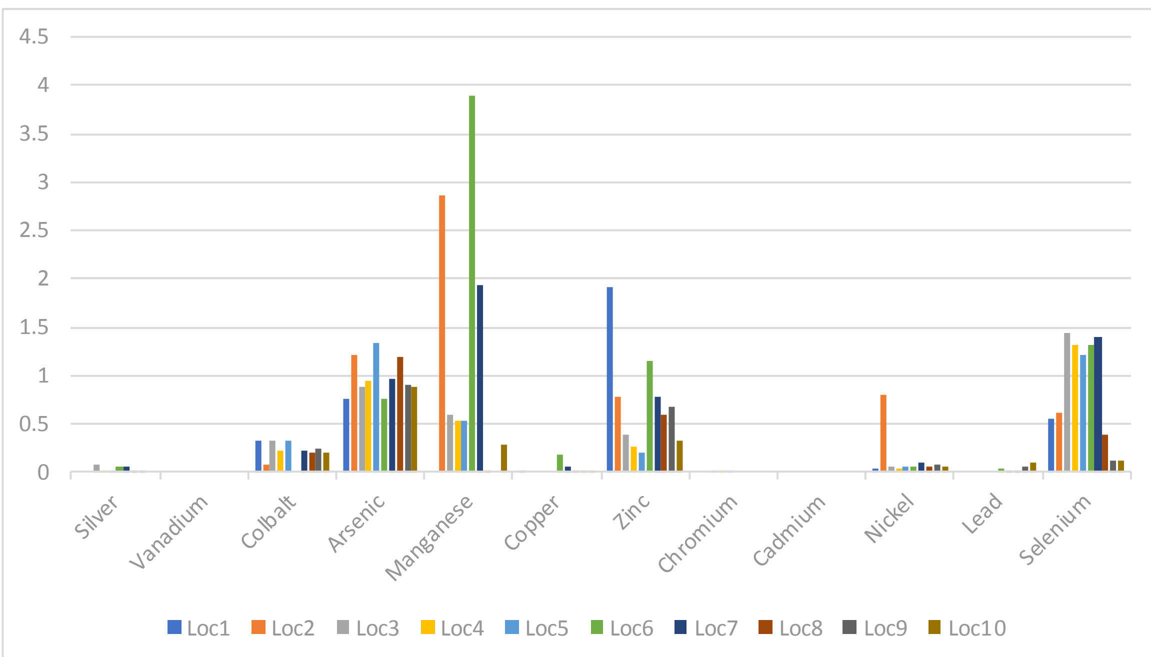

Fig 2: Frequency of heavy metals occurrence in the Ishiagu ning area

5.0 Conclusion

Geology and groundwater quality assessment of Amaeze, Ishiagu, southern Nigeria was carried out. Ten samples were collected from groundwater sources and analysed using Atomic Absorption Spectrophotometric method.

Geologically, study area (Ishiagu and its environs) is part of the Lower Benue Trough and is underlain by Albian shales (indurated and fissile) of Asu River Group and sandstone , diorite intrusion and lead-zinc mineralization were also observed in the area which serve as major economic mineral potential of the area. The shale in the study area have distinct characteristics and colours. These have been generally group into two lithologic units: Shale/sandstone interbed unit and Shale unit.

Hydrochemical evaluation of groundwater shows that the water contain heavy metals with mean range of (lead 0.000mg/l, copper 0.004mg/l, cadmium 0.000mg/l, chromium 0.016mg/l, selenium 0.827mg/l, zinc 0.713mg/l, manganese 1.129mg/l, silver 0.038mg/l, cobalt 0.260mg/l, Arsenic 1.031mg/l, vanadium 0.000mg/l and nickel 0.199mg/l) while physical parameters and mean average include; P^h 5.592, Turbidity 26.748, conductivity 7.634 and TDS 3.828mg/l. Concentration of As^{3+} ,Mn^{2+} ,Se^{2+} , Co^{2+} and Ni^{2+} in some locations are above the WHO, 2011 permissible guidelines for drinking water, especially for surface water in the area while Pb^{2+} , Cd^{2+} , Cr^{3+} , Zn^{2+}. are below and within the WHO, 2011 and USEPA, 2004. The area is prone to chronic health and environmental hazards but geochemical investigation of stream sediments and soil should be carried out to conclude these.

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