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LEVELS OF HEAVY METALS ON GROUNDWATER IN ABAKALIKI AND ITS ENVIRONS, SOUTHEASTERN NIGERIA

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ABSTRACT: The present study was aimed to assess the levels of heavy metals in Abakaliki and its environs, south eastern Nigeria. A total number of 15 water samples (12 boreholes and 3 hand dug wells of groundwater points) were collected from different locations of the study area and analyzed for the concentration of heavy metals: As, Cd, Cu, Ni, Pb, and Zn using Atomic Absorption Spectrophotometer of Perkin-Elmer Analyst 100 Model. The pH of the water samples were determined using Hanna digital pH meter. The result of the analysis showed that water samples from the area have pH range of 6.0-7.8 which falls within the acceptable limit of WHO, 2008 standard permissible limit for portable water. The concentration of these metals in groundwater were found in the ranges of As (nil-2.40mg/l), Cd (0.06-0.41mg/l), Cu (nil-3.10mg/l), Ni (0.08-1.15mg/l), Pb (0.10-0.90mg/l) and Zn (nil-1.35mg/l). The result also revealed that some water samples in some locations such as Hausa quarters, off Onwe road, Azu-Ebonyi, Mechanic village, Ogoja road and Building Materials contained As, Cd, Cu, Ni and Pb that exceeded permissible limit recommended by WHO standard. It also showed that the distribution of these metals was found in both the two sources of waters sampled (borehole and hand dug well) in the area. The reason for these heavy metals in groundwater could be as a result of hydrochemical activities within the rock formations that bear the groundwater in the area. As a result, adequate hydro geological studies should be carried out when locating boreholes in the area for health reasons and domestic use.

KEYWORDS: Groundwater, Asu River Group, Drinking Water, Mining Activities and Industrial Waste.

1 INTRODUCTION

With the rapid industrialization and economic development, heavy metals are continuing to be introduced to soils, sediments and groundwater through several pathways including application of fertilization, irrigation, mining and river runoff. Soils are usually regarded as the ultimate sink for heavy metals discharge into the environment through which, water percolates down to form groundwater. Moreso since water is necessary for the daily activities of animals and humans, however increase in population has led to increase in demand for portable water; inhabitants of the area depend solely on groundwater for domestic and other uses (Moses et al., 2014). Therefore, the environmental problem of soil, sediments and groundwater pollution by heavy metal has received increasing attention in the last few decades in both developing and developed countries throughout the world (Abida et al., 2009). The term “heavy metal” refers to any metallic chemical element that has relatively high atomic density greater than $4gm^3$ and is toxic at low concentration. Examples of heavy metals include lead, zinc, copper, cadmium, mercury, arsenic, chromium, titanium and nickel, (Marscher, 1995). Heavy metals are natural components of the Earth’s Crust. They cannot be degraded or destroyed. To small extent they enter our bodies through food, drinking water and air. As trace-elements, some heavy metals for example, copper, selenium and zinc are essential in maintaining the metabolism of the human body system. However, at higher concentration they can be toxic (Bruins et.al., 2000). Heavy metals can enter a water supply through anthropogenic means such as mining, fertilizer application, and industrial wastes or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater (simeonove et al., 2003).

1.1 Location Of Study Area

The study area lies at the intersection of the Enugu Afikpo and Ogoja roads. It is bounded by longitudes $8^{O}05^{'}E$ and $8^{O}10^{'}E$ and latitudes $6^{O}15^{'}N$ and $6^{O}20^{'}N$. The study area is located at southern part of Abakaliki as seen from the map of Ebonyi State Figure1. The areas were accessed through Enugu, Ogoja and Afikpo through a network of tarred roads which includes the Abakaliki Enugu express road, Abakaliki Afikpo express roads. The entire study area is approximately 81km^2. The villages and towns within the study area include: Ekaeru Inyimagu, Abakaliki, Ndiechi, Igbeagu, Azuiyiokwu, Ugboloke, Obugha Amachi, Agbaja, Agu Akpu and Nkwagu as shown in Figure 1.

2 Geology Of The Study Area

The study area is under in the Benue Trough, lead-zinc occurred in Ishiagu, Enyigba, Ameri and Ameka all in Albian sediment in Abakaliki. In the middle Benue Trough lead-zinc mineralization are found in Akwana and Arufu Albian sediment which is hosted in silicified limestone of Asu River Group. In the upper Benue Trough lead-zinc in Albian sediment are found in Albian and at the same time experienced magmatic intrusion. This folding and uplift at the Albian beds of south-eastern Nigeria led to the Formation of Abakaliki anticlinorium and Afikpo synclinorium.

The Albian sediment of southeastern Nigeria was first named Asu River Group by Reyment, (1965) from the river in Abakaliki called Asu. Therefore Asu River at Abakaliki is the type locality of the Albian sediment of south-eastern Nigeria. Faulting, folding and magmatic activity in south-eastern Nigeria started during the Santonian to early Campanian only affected the Albian sediment. That is the reason ore deposit, igneous and pyroclastic rocks of south-eastern Nigeria are found in the Albian sediment. The lead-zinc in Albian sediment Asu-River Group occur in Albian sediment in lower Benue Trough, upper Benue Trough, in middle Benue Trough and in lower Benue Trough the lead-zinc mineralization are found in Akwana and Arufu Albian sediment which is hosted in silicified limestone of Asu River Group.

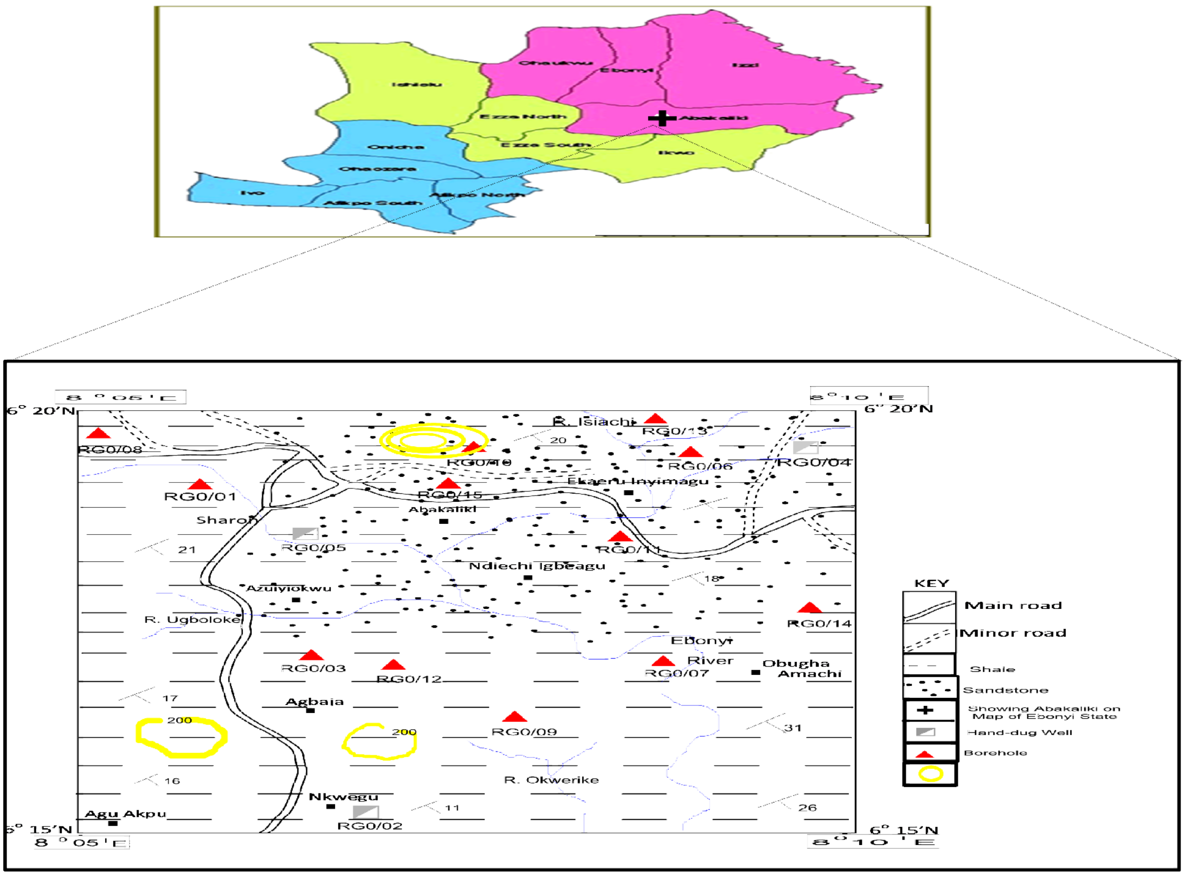

Figure.1 Showing the Geology of the Study Area and Water Sample collection Site

2.1 Hydrogeology Of The Area

The water resources of the study area seem to fall into two categories namely. Surface water (rivers, streams, dams and ponds) and groundwater (boreholes and hand-dug wells)

2.1.1 Surface Water

Source of surface water supply in the study area include streams, rivers and ponds. The shale nature of the area makes it prone to flooding. The few streams that drain the area are seasonal and dry up during the dry season. These can not serve as a good source of water supply. The water available from Ebonyi River unfortunately carries heavy load of suspended and dissolved materials. The materials make the water muddy and highly unfit for domestic use. Other rivers visited are Ochaha River and Iyiokwu River which are also not portable. However, rainwater, boreholes and hand dug-wells are the most available water to the inhabitants for use.

2.1.2 Groundwater

Though, the study area is lithologically shale in nature, groundwater supply in the study area is encouraging. This is because of the extensive fracture in the subsurface lithology which helps to host underground water. There are a quite number of functional boreholes and hand-dug wells as shown in (Plate 1 and 2) in the area, though not conclusively portable as a result of hardness nature of the water and other contaminations. Since the study area is dominantly shale with some micaceous sandstone intercalations, it indicates that the water is mainly from minor joints, cracks, and fractures within the shale and micaceous sandstone unit. Water movement is very slow in these shale rock which are units of poor permeability and there is long period of contact between rock material and water. Adsorption and ion exchange salts are incorporated into these rocks, particularly chlorides and sulphate. A fraction of these substances are locked up during deposition within void and cannot easily be leached out because of the low water velocity. The groundwater in the study area is therefore very rich in dissolved solid which is particularly attributed to high $S0^{2-}_4$ and Cl content. Generally, the groundwater in the area is hard which could be shown from its inability to easily foam with soap and coating of the boiling containers. This is likely to be caused by mineralization and occurrence of brine as associated with Pb-Zn minrealization the area (Olade, 1976).

Plate 1: Inhabitants Sourcing for Water from Borehole along Water Works Road, Abakailiki

Plate 2: Inhabitants Sourcing for Water from Hand-dug Well at Mechanic Village

3 MATERIAL AND METHOD

The water samples for analysis were collected at fifteen different groundwater sources from Abakaliki and its environs. The collection was done on the month of November, 2012 when groundwater levels must have declined making it more concentrated by heavy metals. The water samples were randomly collected using 100 milli-litre of clean sterilized transparent plastic containers. The plastic containers were first rinsed with the water sample before collection. Water samples from hand dug wells were collected by drawing water from the well using a clean container and transferring it to a 100 milli-litre clean sterilized bottle, while that of boreholes were collected from running taps in a 100 milli-litre clean sterilized bottles in the study areas.

The water samples were acidified at the site with three drops of ultrapure 1:1 HNO_3 to avoid precipitation of the metals before laboratory analysis. Selective metals such as Pb, Ni, Cd, Cu, As and Zn were determined by atomic Absorption spectrophotometer of Perkin-Elmer Analyst 100 model. At each point of water sample collection, the longitude and latitude of the area where the borehole or hand dug well was sited, were measured with the aid of the Garmin-Etrex (GPS).

The pH of the water samples was determined using Hanna digital pH meter. The pH meter was immersed into a clean plastic bowl containing the water sample. The clean plastic bowl was first rinsed with the water before immersing the pH meter. This was done if the water source is from hand-dug wells. If the water source is from a borehole, the tip of the pH meter is placed in contact with the water flowing out from the pumped borehole. The pH readings were taken after stabilization of the pH meter.

The water samples collected in the transparent plastic container were labeled using a masking tape according to their sampling points.

4 RESULT

The result of the analysis of water samples collected in the area and its bar charts are shown in (Table 1) and (Figure 5 to 10) respectively.

Table 1: Result of Groundwater Analysis from Abakaliki and its Environs in mg/l.

Sample no.	Latitude	Longitude	Address	Cu		Zn		As		Cd		Ni		Pb		pH
				$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	
RG0/01	N06^{0}17’48.8”	E008^{0}553.1”	Hausa Quarters (BH)	0.9	0.1	0.09	0.1	2.4	0.16	0.07	0.13	0.1	1.34	0.7	1.22	7.3
RG0/02	N06^{0}15’05.9”	E008^{0}06’36.5”	Nkwagu com. Pri.Sch (HDW)	1	1.1	0.06	0.09	Nil	Nil	0.38	0.2	1.4	0.36	0.5	0.13	6.4
RG0/03	N06^{0}18’57.6”	E008^{0}05’48.1”	Off Onwe Road (BH)	0.8	0.1	0.32	0.05	0.1	1.34	0.26	0.14	0.28	2.35	0.9	0.1	7.8
RG0/04	N06^{0}18’29.3”	E008^{0}09’06.9”	Azu-Ebonyi (HDW)	1.3	0.14	0.13	0.1	0.2	0.62	0.4	0.12	0.56	0.96	0.5	0.16	6.8
RG0/05	N06^{0}20’24.8”	E008^{0}08’44.8”	Sharon (HDW)	1.5	0.21	Nil	Nil	0.1	1.34	0.14	0.23	1.15	2.54	0.6	0.25	6.0
RG0/06	N06^{0}18’41.5”	E008^{0}07’45.5”	Mechanic village (BH)	2.9	0.49	0.1	0.23	0.6	0.21	0.06	0.32	0.23	2.01	0.1	1.34	6.2
RG0/07	N06^{0}19’01.5”	E008^{0}06’17.4”	Onwuegbunna street (BH)	3.1	0.42	0.03	0.09	1	0.22	0.16	0.15	0.25	2.22	0.6	0.17	6.6
RG0/08	N06^{0}18’56.7”	E008^{0}07’08.5”	57 Ogoja Road (BH)	1.5	1.99	0.3	0.03	Nil	Nil	0.3	3.04	0.18	0.16	0.1	1.34	7.2
RG0/09	N06^{0}19’06.9”	E008^{0}06’51.8”	No 3 Abatete Street (BH)	3.1	0.38	1.05	0.15	Nil	Nil	0.41	0.17	0.18	0.16	0.6	1.22	7.1
RG0/10	N06^{0}19’30.4”	E008^{0}07’33.7”	Cas Campus (BH)	2.3	0.08	1.35	0.25	0.7	5.9	0.12	2.89	0.08	0.13	0.1	1.34	6.7
RG0/11	N06^{0}19’42.3”	E008^{0}07’15.0”	Ikaeru (BH)	0.8	0.10	1.01	0.32	Nil	Nil	0.16	0.07	0.12	0.07	0.7	1.22	6.6
RG0/12	N06^{0}19’30.6”	E008^{0}06’55.1”	Water Works Road, (BH)	Nil	Nil	0.87	0.09	0.5	0.45	0.27	0.16	0.09	0.16	0.1	1.34	6.3
RG0/13	N06^{0}18’38.6”	E008^{0}6’15.9”	Building Material (BH)	2.4	0.16	0.96	0.1	Nil	Nil	0.18	2.3	0.08	0.34	0.3	0.11	6.1
RG0/14	N06^{0}18’46.4”	E008^{0}6’11.9”	No 14. Amasiri Street (BH)	1.7	1.22	0.16	2.7	Nil	Nil	0.07	0.16	0.44	0.14	0.6	0.36	7.6
RG0/15	N06^{0}18’48.4”	E008^{0}6’12.9”	No 16 Awgu Street (BH)	Nil	nil	0.09	0.18	Nil	Nil	0.18	0.11	0.74	1.01	0.9	0.1	6.9
Total				23.3	6.51	5.49	4.48	5.60	10.24	3.16	10.19	5.88	13.95	7.30	11.45	
WHO (2008) Maximum Limit mg/l				2		3		0.01		0.003		0.07		0.01		

Key

$\bar{x}$= mean — *Cd=Cadmium* — *RGO = Robinson George Ojobor*

σ= standard deviation — *Ni= Nickel* — *BH = Borehole*

Cu=Copper — *Pb=Lead* — *HDW = Hand Dug Well*

Zn= Zinc — *pH=Power of Hydrogen*

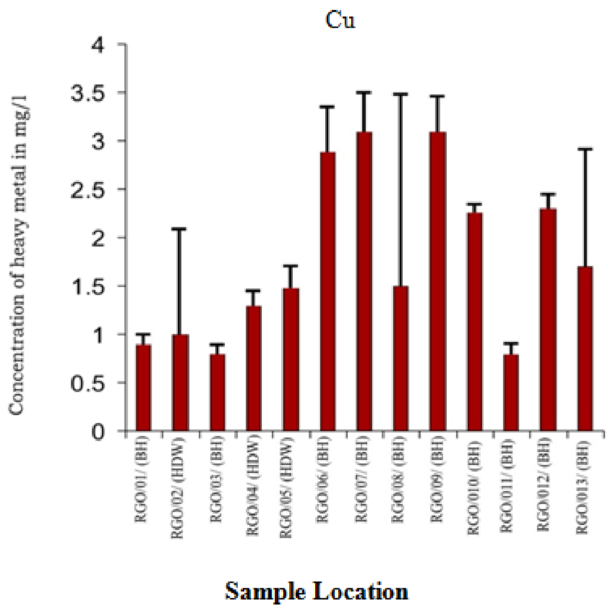

Fig 4: Barchart Representation of Copper Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

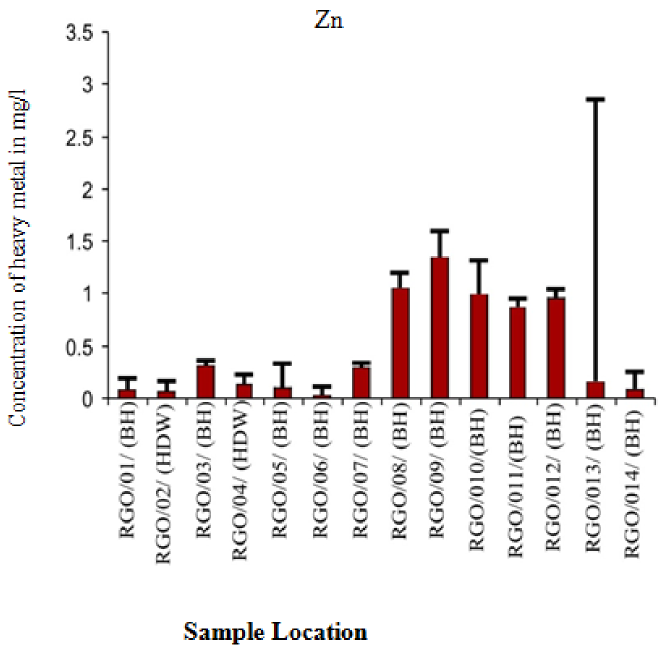

Fig 5: Barchart Representation of Zinc Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

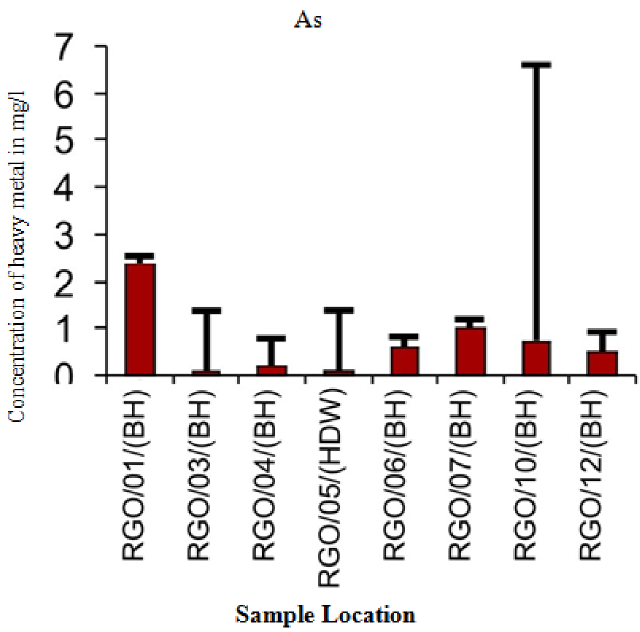

Fig 6: Barchart Representation of Arsenic Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

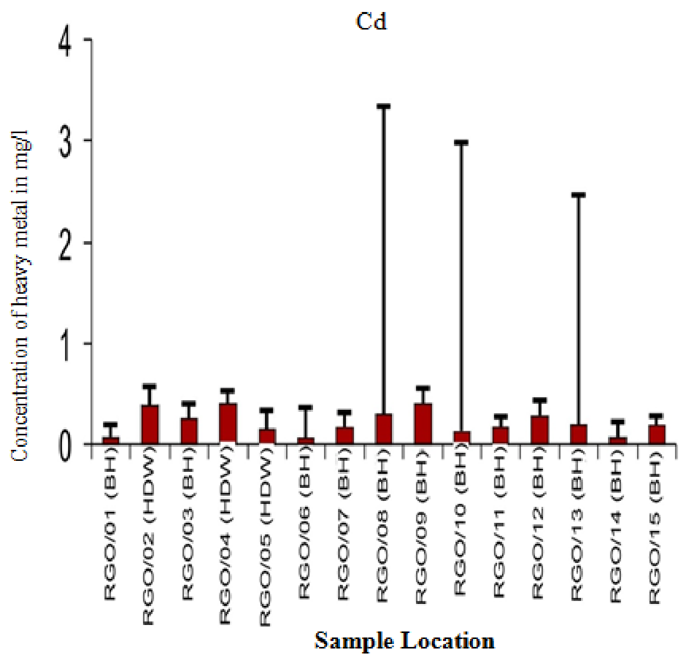

Fig 7: Barchart Representation of Cadmium Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

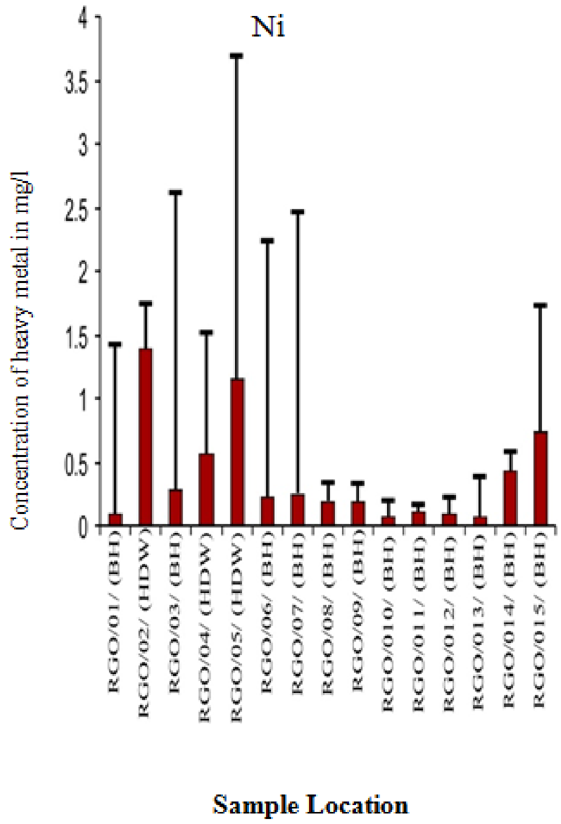

Fig 8: Barchart Representation of Nickel Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

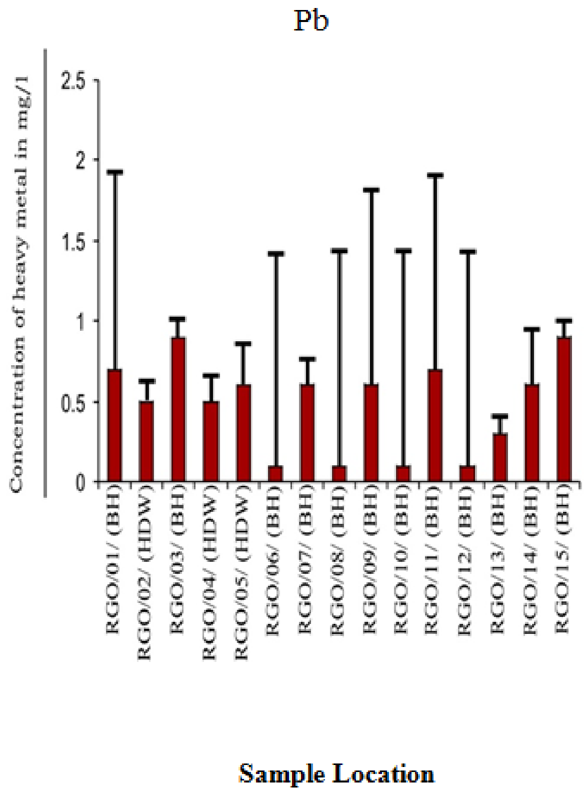

Fig 9: Barchart Representation of Pb Concentration with Error Bars in mg/l in Groundwater from Abakaliki and its Environs.

Table 2: Maximum Limits of Metal Permissible in Water Established by the World Health Organization (2008).

Parameters	Limits (mg/l)
Cu	2
Zn	3
As	0.01
Cd	0.003
Ni	0.07
Pb	0.01

5 Discussion

The standard for the comparison used in this study is the standard guideline for the World Health Organization (2008) permissible limit for portable water. The comparison of the results obtained from the analysis and the recommended limit of these parameters from the World Health Organization (2008) showed deviations in some parameters with the recommended values for portable water which are discussed below:

5.1 pH

The pH of natural water is a measure of its net alkalinity or acidity. It is a measure of the total hydrogen ion concentration of the water.

From (Table 1), the maximum pH of 7.8 was recorded in sample location RGO/03 while minimum pH of 6.0 was also recorded in sample location RGO/05. No acidic water was recorded, as no pH value fall below 6.0. The fall within World

Health Organization (2008) acceptable pH range for portable water is 6.5-8.5.The absence of acidic water in the study area is probably due to non-hydrolysis of lateritic deposit; (Ezeigbo, 1989).

5.2 LEAD

Lead had maximum concentration value of 0.9mg/l (± 0.5mg/l) in location RGO/03 and RGO/15 (off Onwe Road and No. 16 Awgu Street). The minimum lead concentration of 0.10mg/l (± 1.34mg/l) was in location RGO/ 06, 08, 10 and 12 as shown in (Table 1). The range of these values were above the standard limits recommended by WHO permissible limits for portable water set at 0.01mg/l as shown in (Table 2). In all the sampled locations, lead were found to exceed the standard recommended limit by WHO,2008.

The presence of lead in groundwater in the area could be as a result of lead-zinc mineralization, use of lead arsenate as pesticide and lead storage batteries in the study area (Olade, 1976).

5.3 ZINC

Zinc as observed from (Table 1), had maximum concentration value of 1.35mg/l (± 0.25mg/l) in location RGO/10 (CAS campus) and minimum concentration value of 0.03mg/l (± 0.09mg/l) in location RGO/7 (Onwuegbunna street). The concentration of zinc in the study area fall within the permissible limit set by WHO, 2008 for portable water as 3mg/l (Table 2).

The decrease in zinc contamination in the groundwater in the area is as a result of non-oxidation of zinc sulphide minerals (Edmond, 1973) and probably due to zinc co-precipitation with calcium as carbonate phosphate complexation with organic matter of low solubility and adsorption of clay minerals on manganese or iron oxide (Jenne, 1968).

5.4 COPPER

This has maximum concentration value of 3.10mg/l (± 0.42mg/l) in location RGO/09 (No. 3 Abatete street) and minimum concentration value of 0.8mg/l (± 0.10mg/l) in location RGO/11 and 03 (Ikaeru village and off Onwe road) as observed from (Table 1). The following sampled locations in the study area comprising location RGO/01 (Hausa quarters) 0.9mg/l (± 0.10mg/l), RGO/02 (Nkwegu Com. Pri. Sch) 1.0mg/l(± 0.1mg/l), RGO/03 (off Onwe road) 0.8mg/l (± 0.10mg/l), RGO/04 (Azu-Ebonyi) 1.3mg/l (± 0.14mg/l), RGO/05 (Sharon village) 1.5mg/l (± 1.99mg/l), RGO/08 (57 Ogoja road) 1.5mg/l (± 0.21mg/l), RGO/11 (Ikaeru village) 0.8mg/l (± 0.1mg/l) and RGO/14 (Amasiri street) 1.7mg/l(± 1.22mg/l) are within acceptable values recommended by WHO standard for drinking water set at 2mg/l (Table 2). Locations RGO/12 and 15 had no trace of copper. The reason for the absence of copper in the area may be as a result of non-adsorption of copper unto soil constituents and its precipitation with zinc, manganese and cadmium (Richard and Nriagu, 1978).

5.5 CADMIUM

Cadmium as observed from (Table 1), had maximum concentration value of 0.41mg/l (± 0.23mg/l) recorded in location RGO/09 (No. 3 Abatete street) and minimum concentration value of 0.06mg/l (± 0.32mg/l) recorded in location RGO/06 (Mechanic village). Cadmium concentration in the study areas exceeded recommended limit of 0.003mg/l recommended by WHO for portable water. This increase is as a result of agricultural fields due to use of pesticide as well as cadmium containing phosphatic fertilizer used by farmers in the area (Lokeshwari et al.,2006), and the presence of Cd in Pb-Zn minerals in the area

5.6 NICKEL

The maximum concentration value of nickel in the study area was 1.15mg/l (± 2.54mg/l) recorded in sample location RGO/05 (Sharon village) and minimum concentration value of 0.08mg/l (± 0.13mg/l) recorded in location RGO/10 and 13 (CAS campus and building materials) respectively. From the above values, it was shown that the concentration of nickel within the area exceeded the recommended limit set by WHO, 2008 standards for portable water as 0.07mg/l. The increase of nickel in the area could be as a result of used and dumped electroplating and alloy products in the area (Table 2).

5.7 ARSENIC

The maximum concentration value of arsenic in the study area was recorded to be 2.40mg/l ($\pm$ 0.16mg/l) as recorded in sample location RGO/01 (Hausa quarters) and minimum concentration of 0.10mg/l ($\pm$ 1.34mg/l) as recorded in two sampled locations RGO/03 and 05 (off Onwe road and Sharon village) respectively. Seven locations, RGO/02, 08, 09, 11, 13 and 15 showed no trace of arsenic in the area. Other eight locations in the area are contaminated with arsenic, namely RGO/01, 03, 04, 05, 06, 07, 10 and 12 as shown in Table 1. The reason for the presence of arsenic in the area could be as a result of application of phosphate fertilizers which creates the potential for releasing arsenic into groundwater. Laboratory studies suggest that phosphate applied to soil contaminated with lead arsenate can release arsenic to soil water (Davenport and Peryea, 1991). Since the inhabitants in the study area are mostly farmers that make use of fertilizers to boost their crops production, this could probably lead to the high increase of arsenic in the groundwater of the area.

6 CONCLUSION

- Water is one the most essential substance needed to sustain human life, animals, plants and other living beings. From the above studies, it is concluded that the quantity of groundwater varied from place to place.
- However, the situation is not too worst but the higher concentration of heavy metals in some sampling stations indicates that without proper treatment water is not suitable for agricultural and domestic applications.

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