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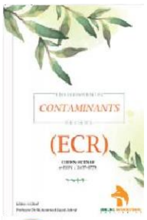

RESEARCH ARTICLE

TRACE METAL CONCENTRATIONS AND PHYSIOCHEMICAL CHARACTERISTICS OF GROUNDWATER AROUND IKWE - ONA REFINERY AND SURROUNDING ENVIRONMENT, AKWA IBOM STATE, NIGERIA

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ABSTRACT

This study was aimed at assessing the groundwater physicochemical characteristics and concentrations of toxic metals from hydrocarbon impacted communities in Ikwe-onna and Ibeno Akwa-Ibom State, Nigeria. A total of 45 water samples were collected from 15 boreholes within the study area using strict/standard sample collection procedure. Samples were taken to the laboratory, prepared and analyzed for toxic metal content using the ttomic absorption spectrophotometer (AAS). All physical parameters were analyzed *in-situ* while chemical properties were analyzed in the laboratory. Statistical analysis was done using SPSS. The concentration of Lead in groundwater ranged from 0.02 to 0.65 mg/l. Average range of iron obtained was 0.03 – 0.50mg/l while the average range of cadmium recorded from the 15 sampling locations was from 0.064±0.05 to 0.145±0.0099 mg/l. The mean range of Zinc was from 0.0457±0.00067 – 0.2513±0.025 mg/l. Manganese mean concentration ranged from 0.0917±0.074 – 0.2667±0.058mg/l. mean range of copper range from 0.01 to 0.43mg/l. Mean values for Arsenic were between 0.0012±0.00072 to 0.0061±0.0087mg/l. Al level in groundwater from Ikwe-Onna as 0.01 to 0.13mg/l. Results of physicochemical parameters indicates that temperature and dissolved oxygen were slightly higher than the regulatory standards. This study recommends frequent quality evaluation of groundwater to prevent water quality deterioration.

KEYWORDS

groundwater, trace metals, hydrocarbon, boreholes, Ikwe-Onna, Akwa Ibom State

1. INTRODUCTION

Toxic metals are chemical elements with a metallic structure, a high density, and a high toxicity level even at low concentrations. Common examples of heavy metals include the chemical symbols Cd, As, Cr, Pb, and Zn (Adeyemi and Ojekunle, 2021). These metals are found in the earth's crust and are notoriously difficult to degrade. Some of these metals are referred to as "trace elements," such as iron, zinc, copper, manganese, iodine, chromium, selenium, molybdenum and cobalt, which are required for basic human metabolic function (Aliasgharpour and Rahnamaye 2013; Al-Fartusie and Mohssan, 2017). But if they accumulate in your body, whether from breathing them near a factory that produces them or ingesting food containing them, you could become ill (Prashanth, et al., 2015; Skalnaya and Skalny, 2018). When it comes to toxicity, the bioaccumulation of certain metals in biological systems over time is more dangerous than the chemical's concentration in the environment.

Compounds tend to build up in living things when they are taken in and stored at a faster rate than they are broken down (metabolized) or taken out. The water supply and waste water from industries, consumer waste, acid rain, and even natural processes can all contribute to the introduction of metals into surface and ground water (Salem, et al., 2000). Higher dissolved concentrations of iron and manganese are harmful to human neurological and muscular systems and can make people look unhealthy as well (Tredoux and Cave, 2004; Tredoux and Cave, 2004; WHO, 2021). The data supports this conclusion. The water around the Ikwe Ona refinery contains a wide range of trace metals and chemical properties. Research estimates the volume of water on the surface of the earth to be more than 70.9% of the earth surface. The use of water spans over different forms of life (Foster, 2001; Howard et al., 2003). As much water as there is in the world, there is still a problem with the quality and accessibility of that water in rural areas of developing nations (Faremi and Oloyede, 2010).

The health implications of contaminated water are associated with several human diseases such as Diarrhea is responsible for an estimated 1.8 million deaths a year, or 4.1% of all disease-related deaths worldwide (Kariuki et al., 2012). An estimated 88% of this burden is attributable to things like unclean or unsafe water sources, inadequate sanitation, and poor hygiene (Udousoro and Umoren, 2014). Only 58 percent of Nigerians in the country's cities have access to potable water, according to a new report. Nearly everyone gets their drinking water from wells, boreholes, or surface water. As a result of population growth, urbanization, and pollution, this is a major issue. Negative anthropogenic activities are the primary cause of contaminated groundwater in many parts of the world. Hence the need to study the extent of ground water contamination in the study area to ascertain the risk of human exposures by drinking of such ground water and give possible recommendations. This research is aimed

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at assessing groundwater physicochemical characteristics and contamination of toxic metals from hydrocarbon impacted communities in Ikwe-onna and Ibeno Akwa-Ibom State.

2. LITERATURE REVIEW

When humans do something bad to water, it alters its physical, biological, and chemical properties (Selvinaz et al., 2015). Many plants and animals found in the ocean can be used in agriculture and new industries, as well as in the pharmaceutical industry. All of these industries have important advantages and services to offer (Selvinaz et al., 2015). It is impossible to overstate the importance of water to human life. Contamination of water supplies can have a devastating effect on businesses, as well as the death of living organisms (Garba, et al., 2008). Pollution is the most common cause of this, but there are many others. In Nigeria, the water sources closest to the population are becoming increasingly isolated (Garba, et al., 2010). Material that is not meant to be in waterways, lakes, wells, streams, boreholes, or even new water in homes and businesses can result in contamination of water. Humans and other collaborative frameworks could be harmed by these materials.

With regard to the rate at which biological and chemical processes occur in water, temperature is directly related. Many people have claimed that the temperature of the water has an effect on the amount of oxygen it contains. Aquatic plants, crustaceans, and other organisms are harmed by a decrease in the amount of oxygen in the water as temperatures rise. Dissolved oxygen is another nutrient that crustaceans require in order to remain healthy (DO). The concentration of hydrogen ions in water is expressed as a negative logarithm (pH). When minerals are formed, changed, or dissolved, it is critical to the chemical reactions that take place (Ebele et al., 2016). Most aquatic organisms are accustomed to neutral conditions, so the acidity of the water is a major factor in their survival. When it comes to microbial metabolism, growth, and development, pH has a significant impact on almost all enzymes, hormones, and proteins. It also has a major impact on mineral formation, alteration, and dissolution (Ebele et al., 2016; Yao, et al., 2001).

To understand the metabolic processes of many aquatic organisms, it is important to know the pH of the water. The pH of a body of water is a good indicator of how clean or polluted it is (Jenderedjian, et al., 2007). In part, this is because there is a high concentration of organic matter in the soil (Udom et al., 2002). Because so many of an aquatic organism's metabolic processes are pH-dependent, changes in pH can have a significant impact on their well-being (Okorafor et al., 2013). Different physicochemical parameters have playa major role in determining the quality of a water source, such quality play a major in determining the risk associated with the consumption or ingestion of such water by human. The interactions between groundwater and surface water are extremely difficult to predict (Kurokawa et al., 2001). Groundwater aquifers can be contaminated by non-point sources, which do not directly affect surface water.

Contamination of groundwater aquifers can occur from a variety of sources, including those that do not directly affect surface water (Ekubo et al., 2011). Point and non-point contamination may not occur in all cases of chemical spills and infiltrations. In the event that it gets into the aquifer below, which is known as "poison tuft," it is extremely dangerous (Lai et al., 1994). A hydrologic transport model or a ground water model can be used to accomplish this. The crest, or crest front, can be used as an example. Look into the soil and topography of the site, as well as the flow of groundwater and surface water, to see how contaminants get there and how they are transported (Mazumder et al., 1996).

3. THE STUDY AREA

The communities of Ikwe and Ibeno in Nigeria's Akwa Ibom State were studied for this project. Ikwe is home to the Ikwe-Onna Refinery Limited. Most Onna residents make their living off the sea and land due to the island's proximity to the Atlantic. Because fishing is the main source of income in the region, this is the case. The coordinates in decimal degrees for its longitude are 7°52′0′′ and its latitude is 4°39′0′′. Off the shore of these towns you'll find significant oil and gas drilling operations. Projects are being led by companies like Exxon Mobil and Total Energy Plc. Scientists from a wide range of disciplines have studied the ripple effects of major oil and gas firms' operations on the world at large. Environmental damage from the oil spill was discovered by local researchers in and around Onna. Ibeno is the name of an LGA in the Nigerian state of Akwa-Ibom. Its exact coordinates are 4.568693 longitude and 7.976396 latitude, and it is bounded south by the Atlantic Ocean, north by Onna, Esit Eket, and Eket, and west by Eastern Obolo Local Government Area (figure 1).

The southernmost part of Akwa Ibom State is located in the Ibeno Local Government Region. More than 1,200 square kilometers of shoreline is its distinguishing feature. From Okposo I in the east, near the Mbo Local Government Area and the Bakassi Peninsula, to Atabrikang village in the west, this mountain range stretches for a good long way. The local governments of Eket, Esit Eket, Onna, and Eastern Obolo all border it. The Atlantic Ocean can be found to its south. Fishing is a major economic driver for the locals. The region under investigation is located in Nigeria's Niger Delta, a highly industrialized region of the Gulf of Guinea. People are concerned about the effects of oil and gas operations, including waste disposal, gas flaring, oil leaks, and noise pollution. The groundwater quality in the area is significantly impacted by these operations, as is well acknowledged. Akwa-Ibom state is home to Ibeno, a town.

Eket, Onna, Esit Eket, and Eket make up the north and east of the region, while the Atlantic Ocean, which runs from west to east, separates it from Eastern Obolo LGA, which lies to the west. Akwa Ibom State's southernmost LGA, Ibeno, is home to a population of about 200,000 people. It has a coastline that extends for more than 1,200 miles. The village of Atabrikang is located near the Mbo Local Government Area on the western side of Okposo I. Eket, Esit Eket, Onna, and Eastern Obolo are home to people. The Atlantic Ocean forms its southern border. Fishing is a major source of income for the residents of the area. There is a lot of industrial activity in Nigeria's Niger Delta region, which is located in the Gulf of Guinea. Oil and gas activity in the area generates a lot of pollution, including noise, gas flaring, oil spills, and waste. Ground water quality in the area is thought to be greatly affected by these factors, hence the need for this research work to monitor the concentrations of Trace Metal and Physiochemical Characteristics of Groundwater around Ikwe - Ona Refinery and Surrounding Environment.

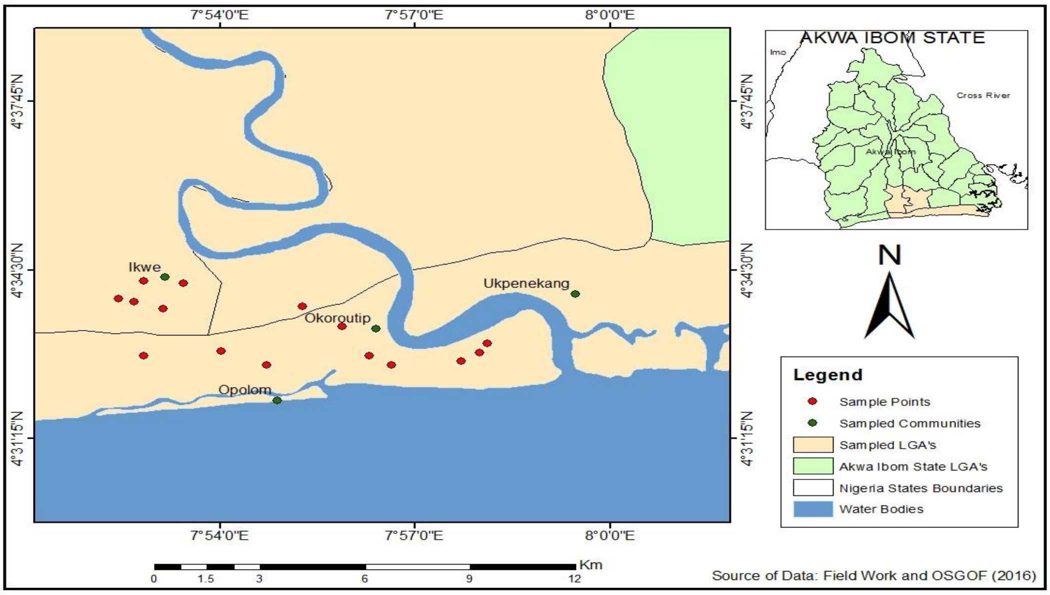

Figure 1: Map of the Study Area

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4. MATERIALS AND METHODS

4.1 Sample Collection

Global Position Systems (GPS) waypoints were used to locate the sampling locations and then plotted on a sampling map. For a total of 15 sampling points, the local government investigated three different communities in the study area. In order to test the water beneath the surface, these boreholes were used. All of the plastics and glasses in this experiment were cleaned with 0.05 m hydrochloric acid. Rinsing them with the distilled water was the final step. They were then dried in a clean, dust-free environment. Water from the location where the bottles were taken to be cleaned was used to rinse twice with distilled water (Borehole). Three times as many water samples were collected from the 15 boreholes in the study area throughout the three months when the wet season moved to the dry season (October to December 2020). At the site in Port Harcourt, Nigeria, 45 samples were collected and sent to Giolee Global Services Limited to be prepared and tested in the lab. It was important to note the date, time and location of each water sample, as well as the name of the person who collected it.

4.2 Sample Treatment and Digestion

The concentrations of potentially harmful metals in the water samples were determined using atomic absorption spectrophotometry. The water was measured out and put into lab test bottles before being transported elsewhere for analysis. After that, we transferred 50 mL of the subsample into a 250 mL beaker fitted with a well and a watch glass to use as the digesting vessel. The final concentration was 1.01 mL/mL. After that, we added HNO_3 and 0.50 mL plus 0.05 mL of concentrated HCl to each sample. The answer was concealed behind the watch glass. Then, for another two to two and a half hours at 95 to 5 degrees Celsius, it was digested in the fume hood. The samples were removed from the heat and allowed to cool for at least 30 minutes in an effort to lessen the amount of potentially harmful vapors they released. The samples were reassembled with 50 mL of distilled water and vigorously shaken after the watch glass was removed. The quantity of metal in the solution was determined by placing it in a 100 ml plastic container and analyzing it with an atomic absorption spectrophotometer (AAS).

4.3 Physicochemical Analysis

Many factors were examined in this study such as temperature of the aquifer water; salinity; total dissolved solids and turbidity; biochemical demands for oxygen; as well as dissolved oxygen. When calibrated correctly with the appropriate standard solutions, Extech's multi-parameter digital instrument was then used to measure in the field, temperature, turbidity, pH, electrical conductivity and total dissolved solids (DO: 700 model). Samples were stored in an ice chest until they could be sent to the laboratory for analysis, where they were tested for dissolved oxygen and biochemical oxygen demand, as well as other parameters. The concentrations of potentially harmful metals in the sampled water were determined using atomic absorption spectrophotometry. After the water volumes were scaled appropriately for the test, they were transferred to laboratory test bottles and taken for analysis.

4.4 Temperature

The Extech multi-parameter digital thermometer was used to determine water temperature (DO: 700 model). The thermometer's reading was stable because the instrument's sensitive part was submerged in water. The average of the three readings was calculated and recorded. Three readings were taken.

4.5 Turbidity

In the field, an Extech digital meter was used to measure the water's turbidity at a depth of 15 centimeters below the surface (DO: 700 model). The thermometer's sensitive portion was submerged in water to stabilize it, and readings were taken. The average of three measurements taken at each station was used to calculate and record the turbidity of the ground water (APHA, 1998, and in Nephelometric Units) (NTU).

4.6 Dissolved Oxygen (DO)

In order to determine the amount of dissolved oxygen (DO) in the water, one can use either the Azide method or Winkler's method (APHA, 1998). The water was allowed to fill a 70-ml DO bottle that had been labeled and washed thoroughly. To get rid of any air bubbles in the sample bottle, this was done. The sample was diluted with Wikler-I and Wikler-II solutions. The alkali and iodide reagents were properly mixed with the sample after a stopper was placed on it to remove air bubbles. Samples of water that had been treated with Winkler I and II were given 0.5 ml of concentrated sulfuric acid. To ensure that the precipitate was completely dissolved, a stopper was added and the reaction was vigorously mixed. A 0.025 N Na2S2O3 solution was added to a portion of the sample in an Erlenmeyer flask. Sodium thiosulphate is the active ingredient in this mixture. For as long as possible, the titration continued, and the end point was recorded (ASTM, 1999).

4.7 Biochemical Oxygen Demand (BOD)

It was done the same way as with the DO, but the samples were kept at 20 °C for 5 days. It's the same procedure that was used to determine the dissolved oxygen concentration for the incubation period's DO samples. BOD samples were diluted, and the DO of the diluted water was measured, to ensure that there was enough oxygen for the bacteria to grow. The dissolved oxygen level was measured on day 5, and the BOD5 was calculated as shown above. The DF x is a powerful new weapon (A - B) Where:

A is Initial DO of dilution water,

B is DO after 5-day incubation and

DF is dilution factor of sample to water.

5. RESULTS AND DISCUSSION

5.1 Physicochemical Parameters

Table 1: Range and mean of physicochemical parameters of Ikwe-Onna groundwater

Parameters	Minimum	Maximum	S.E	DPR/FMEnv limit
Colour (TCU)	8.90	19.50	0.467	0.5
pH	5.70	8.70	0.116	6.5-9.2
Temperature (^{0}C)	28.60	35.60	0.259	25-30
Turbidity (NTU)	5.30	11.30	0.231	15
Salinity (ppt)	4.8	11.30	0.245	
Total Suspended Solids (mg/l)	8.10	16.20	0.380	50
Total Dissolved Solids (mg/l)	16.30	190.70	6.793	500
Conductivity (µs/cm)	0.60	13.20	0.528	2000
Biochemical Oxygen Demand (mg/l)	1.21	6.20	0.34	10
Dissolved Oxygen (mg/l)	1.98	7.70	0.33	3.0-5.0
SO_4^-	1.10	2.96	0.09	100
NO_3	1.28	2.67	0.10	50
Cl_2	0.06	0.75	0.04	250
Total Alkalinity	9.02	22.40	0.72	120

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Table 2: Range of Toxic metals of Ikwe-Onna groundwater

Parameter (mg/l)	Minimum	Maximum	S.E	P-value	DPR/FMEnv limit	
Arsenic (As)	<0.00	0.01	0.00045	0.832	0.01	
Lead (Pb)	0.02	0.65	0.0219	0.016	0.05	
Aluminium (Al)	0.01	0.13	0.0036	0.900		
Zinc (Zn)	0.04	0.28	0.0103	0.000	5.00	
Iron (Fe)	0.03	0.50	0.0183	0.038	0.1	
Copper (Cu)	0.01	0.43	0.0183	0.000	0.05	
Manganese (Mn)	0.01	0.38	0.0136	0.259	0.05	
Cadmium (Cd)	0.01	0.17	0.0075	0.848		

5.2 Colour

Results for Colour ranged from 8.90 – 19.50±0.467TCU throughout the study period **(**figure 2 and Table 1). The lowest mean colour reading 9.73±0.69TCU observed in station 6 while the highest colour reading(18.89±0.49TCU) was observed in station 13. There was no statistically significant difference between the stations when one-way analysis of variance (ANOVA) was performed at (p<0.05).

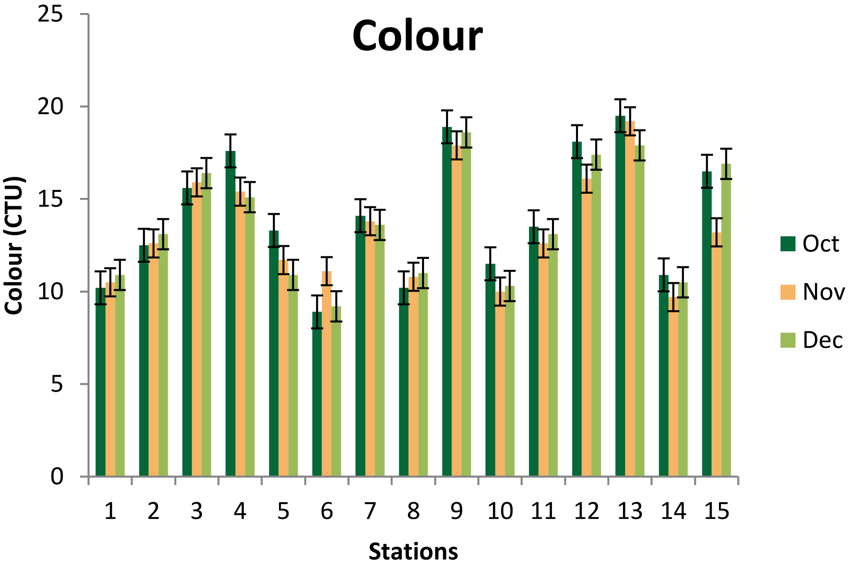

Figure 2: Colour at different stations of Ikwe-Onna, Nigeria.

5.3 Temperature

The mean temperature range of the study area was 29.30±0.30^{0}C to 34.87±0.47^{0}C **(**figure 3 and Table 1). higher than the values of 26.5 to 27.5°C reported by from Akure Ondo State Nigeria, they also reported dissolved oxygen range of 0.9 to 2.4 mg/L which is less than the report of the present study (Akinbile et al., 2011). the range of mean temperature recorded in this study is typical of tropical waters and its consistent with reported values and 26.05^{0}C to 32.1^{0}C and 28.1±0.2°C and 29.5±0.4°C on Andoni River and in Bantaji and RafinKada settlements of Wukari Local Government Area, Taraba State, Nigeria respectively (Emoyoma, et al., 2019); Oko, et al., 2017). Increased temperatures is dependent on the type and level of polluting material (Nwaichi et al., 2012). The results of the present study were slightly higher than the range of 25-30^{o}C for ground water stipulated by DPR/FMEnv. The kinds of organisms present and their rates of movement are critical due to the high temperature of the water. Fish and other aquatic life can be greatly impacted by changes in water temperature or dissolved oxygen (DO) levels. As water temperature rises, so does the movement and reproduction of aquatic organisms. When the temperature rises, the rate at which chemical reactions take place increases. Aquatic organisms may be adversely affected by toxic complexes that form.

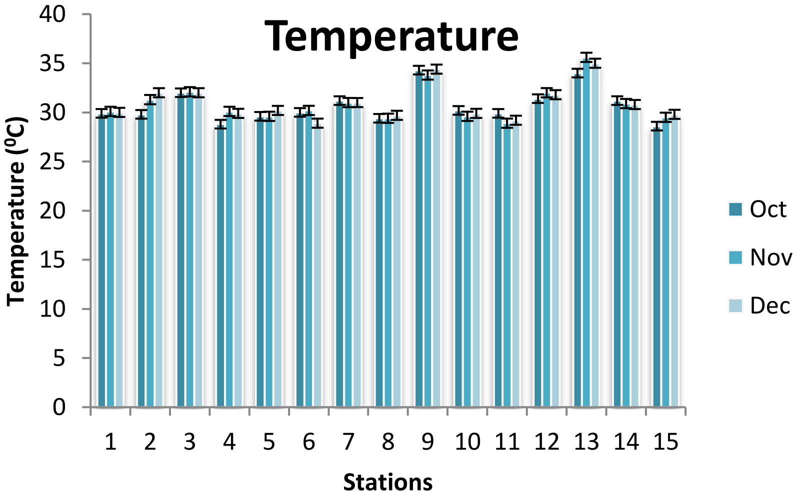

Figure 3: Temperature at different stations of Ikwe-Onna, Nigeria.

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5.4 pH

In the present study, pH ranges from 5.90 to 8.47 (figure 4 and Table 1). The pH values obtained from the study area to large extent is within the recommended range of 6.50 to 8.50 for standard acceptable pH of ground water (WHO, 1993) Scientific research has documented research data to support their assertion that high pH levels are undesirable, according to research, high pH have a high probability of imparting the taste of the water to become bitter. Elevated pH levels are also associated with poor functioning or effectiveness water chlorination, this development is known to increase the quantity of chlorine as well as increase chlorine exposure time or contact time with the disinfectant (Chandra et al., 2012).

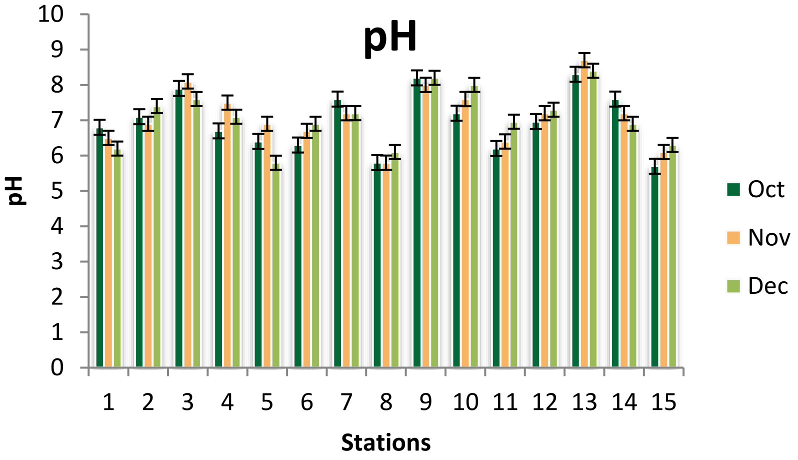

Figure 4: pH at different stations of Ikwe-Onna, Nigeria.

5.5 Biological Oxygen Demand

Organic matter and inorganic material such as sulfides, iron, and nitrogen are broken down using oxygen. Doing this requires a lot of oxygen. The measured BOD values fell within the permissible range (figure 5 and Table 1). So much organic matter can be broken down by microbial metabolism even if water doesn't kill or kill bacteria, as this experiment demonstrates (Clesceri, et al., 1995; Ebele et al., 2016).

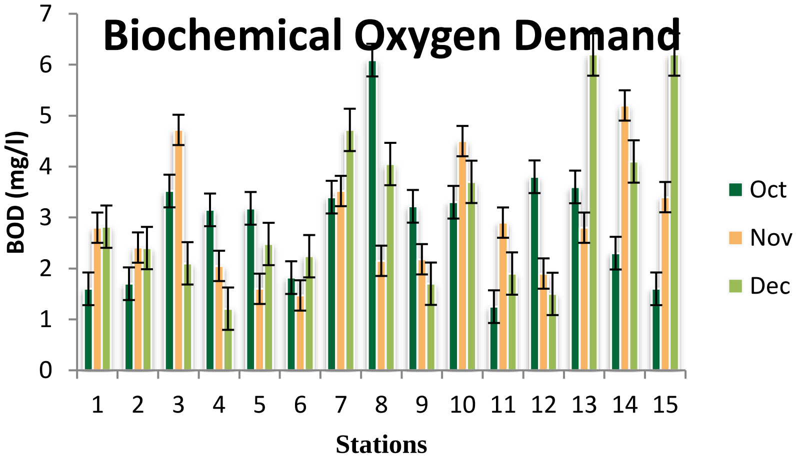

Figure 5: Biochemical Oxygen Demand at different stations of Ikwe-Onna, Nigeria.

5.6 Dissolved Oxygen

Concentration of Dissolved oxygen (DO) in ground waters depends on the physical, chemical and biochemical activities in the water. DO values 2.97±0.93-6.02±0.84mg/l (figure 6 and Table 1) recorded during the study period had a slight variation from FMENV permissible limit of 5.0mg/l (Table 1). however, it is in-line with the values 3.9±0.4mg/l to 4.7±0.46 reported by (Oko et al., 2017). Aquatic life relies heavily on DO for survival, and it can also be used to determine the quality of a river.

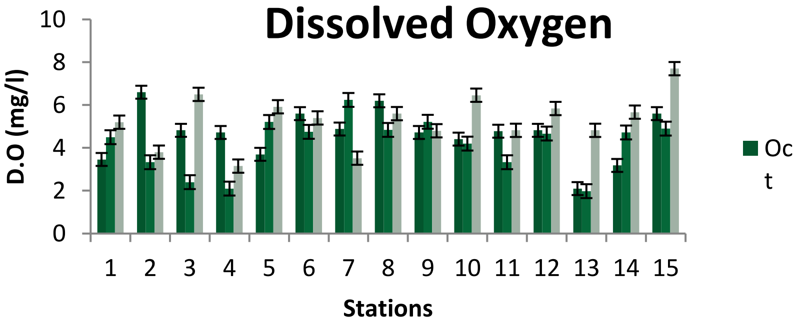

Figure 6: Dissolved Oxygen at different stations of Ikwe-Onna, Nigeria.

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5.7 Turbidity

Mean values for Turbidity of 5.67±0.27 – 11.03±0.07 NTU (figure 7 and Table 1) values are below DPR/FMEnv permissible limit of 15NTU. Various suspended and colloidal solids contribute to turbidity, which is hazardous to human health and the environment, as reported by (Nwaichi et al., 2012). Before it enters the distribution system, clean groundwater must be tested for turbidity to ensure its safety. In order to reduce the amount of turbidity, filtration is an excellent option (Nwaichi et al., 2012).

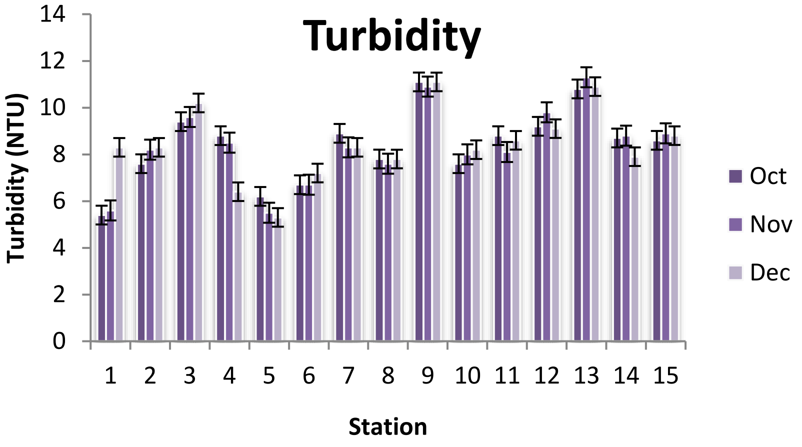

Figure 7: Turbidity at different stations of Ikwe-Onna, Nigeria.

5.8 Salinity

Salinity recorded across the stations showed slight or no variations throughout the period samples as presented in figure 8 and Table 1. The figure shows that variations in salinity values ranged from $4.80^{0}/_{00}$–$11.30^{0}/_{00}$. The highest mean value of $11.03 \pm 0.07^{0}/_{00}$ was recorded in station 9 while the minimum mean value $6.03^{0}/_{00}$ was recorded in station 14. One-way Analysis of Variance revealed that salinity in the various stations of the month sampled were not significantly different ($p<0.05$)

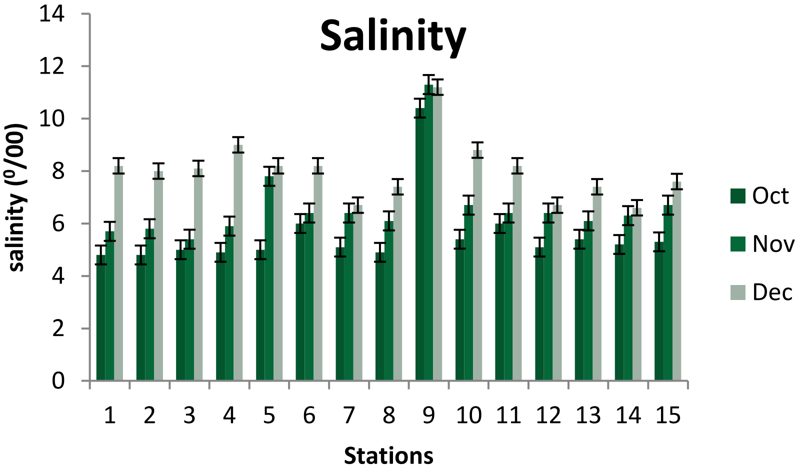

Figure 8: Salinity at different stations of Ikwe-Onna, Nigeria.

5.9 Electrical Conductivity

The result of the present study showed EC values of 0.60 to 13.20 µS/cm (figure 9 and Table 1) across the 15 stations were below the DPR/ FMEnv limit of 2000 µs/cm, the mean values showed no significant difference at P<0.05. The ability of a medium to allow an electric current to flow through it is known as conductivity; According to the total ion count, temperature, and other factors. Conductivity values were far lower than the 2000µs/cm DPR/FMEnv. the result of the present study is less than the reports of (1190, 550, 890 and 450 µS/cm) (Popoola et al., 2019).

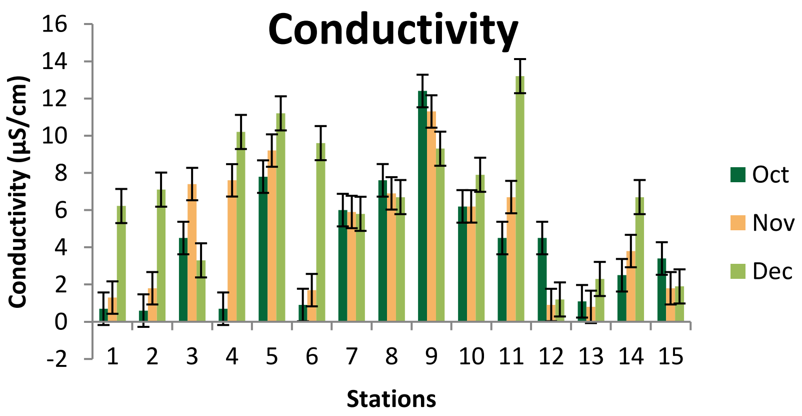

Figure 9: Conductivity at different stations of Ikwe-Onna, Nigeria

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5.10 Total Alkalinity

The alkalinity of groundwater from the study area ranged from 9.02-22.40 **(**figure 10 and Table 1) from the 15 sampling units in the study area, this result is in line with the reports of 9.0±0.2 9.5±0.5, however, this results were less than the results of 175.49 reported by (Oko et al., 2017; Batayneh et al., 2012). In this study, the DPR and NSDWQ thresholds were set at 120 and 150, respectively. This study's findings fell between 120 and 150. This low alkalinity level indicates that the groundwater in the area where the study was conducted is clean.

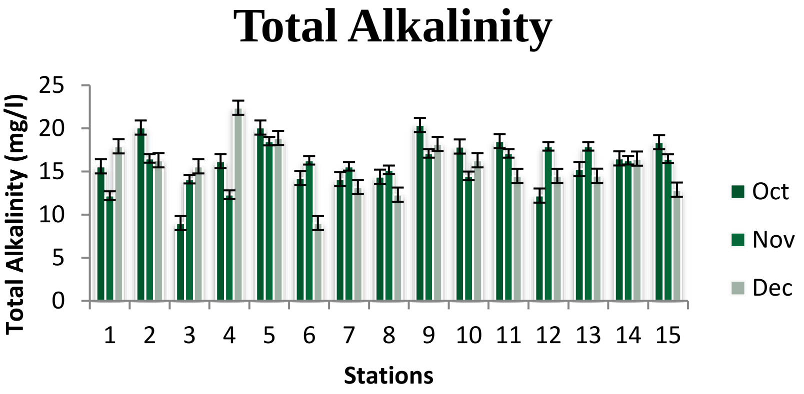

Figure 10: Total Alkalinity at different stations of Ikwe-Onna, Nigeria.

5.11 Total Suspended Solids (TSS)

Total suspended solids TSS concentration collected across the stations and the months revealed that there were variations throughout the period samples as presented in figure 11. Table 1 shows that variations in TSS values ranges from 8.10mg/L – 16.20mg/l. Station 8 recorded the least mean value (8.33±0.14mg/L) while highest mean value (15.8±0.20mg/l) was recorded in station 13. One-way Analysis of Variance revealed that TSS is not significantly different (p>0.05).

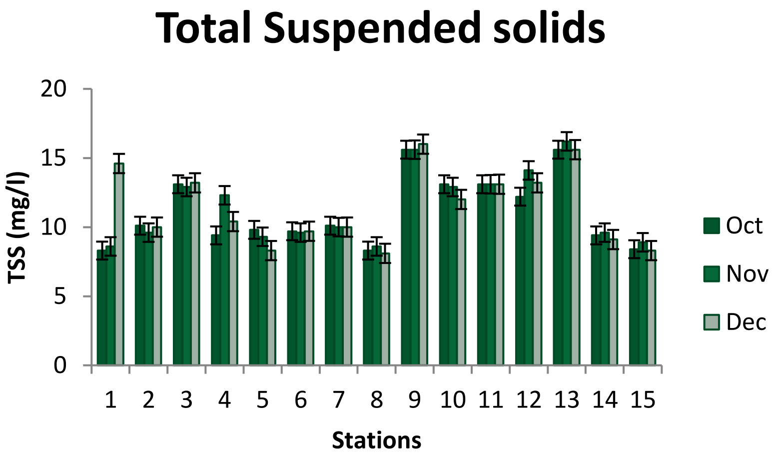

Figure 11: Total Suspended Solids at different stations of Ikwe-Onna, Nigeria.

5.12 Total Dissolved Solids

How much wastewater from sewage plants or other ion sources is in your water can help determine total dissolved solids (TDS) (Ebele et al., 2016). Suspended and dissolved solids are common tests of polluted waters. However, mean total dissolved solids results of 30.4±0.72 – 174.73±8.81mg/l **(**figure 12 and Table 1) are below the FMEnv permissible limits of 500mg/l. reported mean results of total suspended solids in groundwater of 559.2, 589.7, 319.5 and 247.5 mg/L, this values are higher than results of the present study, according to their study, high TDS levels in IW1 and IW2 was an indication of saline water contamination of groundwater (Popoola et al., 2019). The implication of the low level of TDS in this study is that the groundwater is not polluted by TDS. A group researchers previously reported high level of TDS, according to them, high levels of TDS were a result of low number of runoffs and domestic sewage (Yusuf et al., 2017).

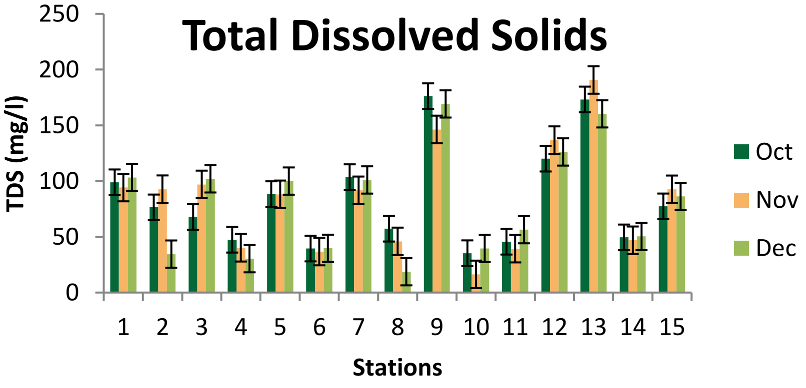

Figure 12: Total Dissolved Solids at different stations of Ikwe-Onna, Nigeria.

5.13 Chloride (Cl^-)

Chlorides are known to exist as salts of potassium and sodium, their concentrations are usually dependent on the type of water these salts are. Chlorides are normal or stable salt component of water. The chlorides mean range concentration from the study area ranged from 0.06-0.75 **(**figure 13 and Table 1). This value were less than the reports of which ranged from 52.2 to 88.6 mg/l. the result of the current study is less than the maximum permissible values of 250 and 600 mg/L specified by the NSDWQ and the WHO, respectively (Popoola et al., 2019).

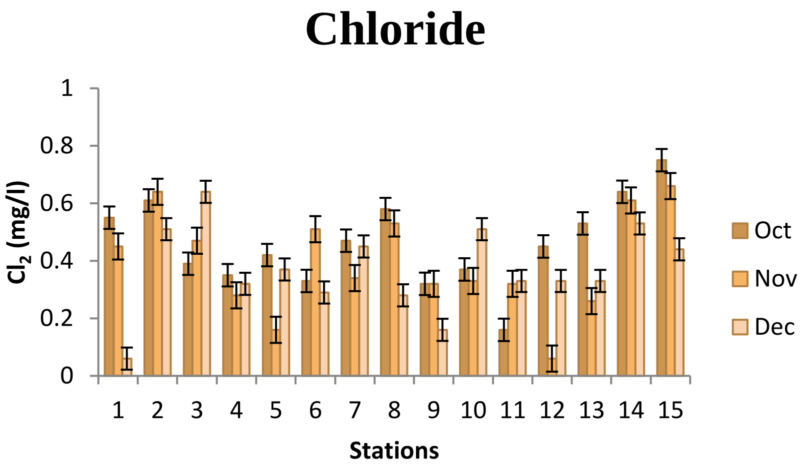

Figure 13: Chloride ion at different stations of Ikwe-Onna, Nigeria.

5.14 Nitrate ($NO_3{}^-$)

The nitrate content of the water from the study showed that, the range nitrate is 1.28 to 2.67 **(**figure 14 and Table 1). These results are in line with the findings of who reported the range of of 0.33 and 2.37 mg/l. these values are below the stipulated standard by the WHO permissible value (5 mg/L) (Popoola et al., 2019).

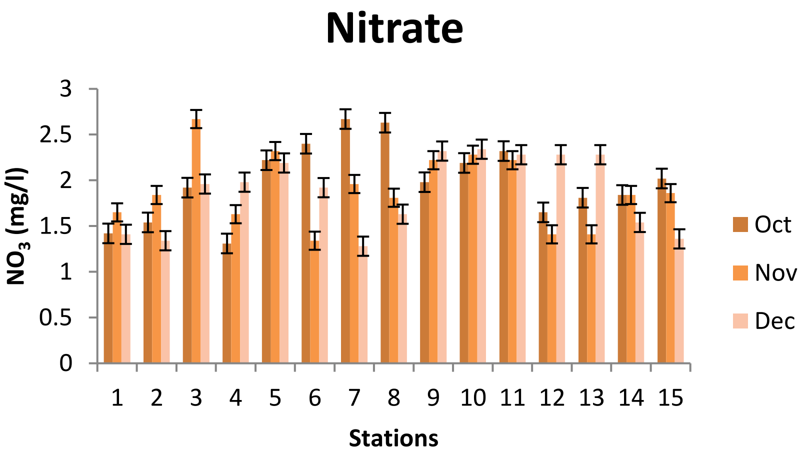

Figure 14: Nitrate ion at different stations of Ikwe-Onna, Nigeria

5.15 Sulphate ($SO_4{}^{2-}$)

$SO_4{}^-$ concentration from the study area was reported as 1.10 to 2.96 **(**figure 15 and Table 1). These values are less than the results of (Popoola et al., 2019) which reported higher mean values for mean sulphate from their study samples. The result of the present study is far less than the standard content as stipulated by WHO, NSDWQ, EPA, 250 and, respectively. A rise in water pH is linked to acidosis when high concentrations of sulphates build up in the water (Asamoah and Amorin, 2011).

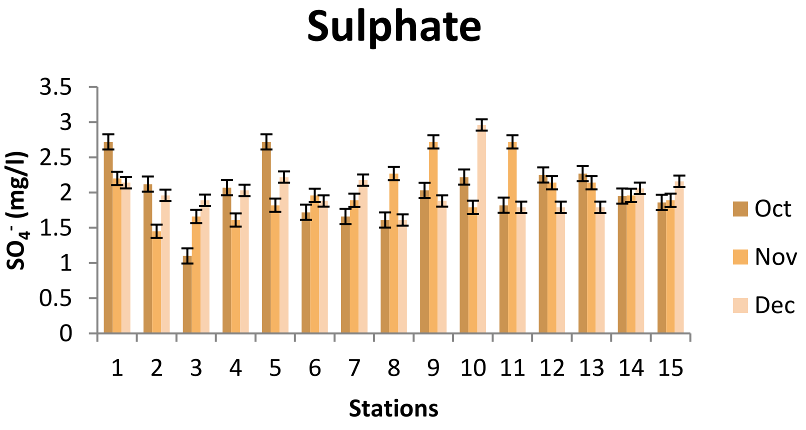

Figure 15: Sulphate ion at different stations of Ikwe-Onna, Nigeria.

5.16 Toxic Metal Concentrations

5.16.1 Lead (Pb)

The concentration of Lead in groundwater during the study period ranged from 0.02 to 0.65 mg/L (Table 2) these values are slightly above the permissible limit of 0.05mg/l by (FMENV, 2002) however, reported a higher Pb value of 0.1487±0.2531 to 0.1086±0.1846 mg/l. lead is the most significant toxic metal among all the metals under here, it characterize by high toxicity and harmful nature even when it is in very low concentrations (Oko et al., 2017; Gregoriadou et al., 2001). Lead had very high bioaccumulation ability in body tissues results to high human health. Elevated levels of lead in water above recommended the permissible levels could result to serous human implications ranging from; hypertension, impeded brain development in foetus, impacted calcium metabolism, and possible carcinogenic effects.

5.16.2 Iron (Fe)

Magnetite, taconite and haematite are natural forms of Iron which exist in rocks, soil and minerals making about 5% of the Earth's crust according to (Popoola et al., 2019). Average range of iron obtained from this study was 0.03 – 0.50mg/l (Table 2), These values are slightly above the WHO recommended groundwater level of <0.3mg/l. the result was however lower than the results of Fe 0.0263±0.0003 0.0225±0.0009 reported by (Oko et al., 2017). This result is also lower than the range of 0.15 and 3.26 mg/l reported by (Popoola et al., 2019). Low levels of Fe have been linked to anaemia in humans. liver-damage disease has also been linked with the consumption of water with elevated concentration of Fe in drinking water. A group researchers reported Fe to be associated with diabetes mellitus, arteriosclerosis and other neurodegenerative diseases (Bhaskar, et al., 2010; Brewer, 2010).

5.16.3 Cadmium (Cd)

According to the presence or contamination of groundwater by cadmium is as a result of leaching contaminated sources such as mining, paints, electroplating, petrochemical, plastics and fertilizer industries (DeZuane, 1997). The health consequences of cadmium poisoning have also been documented by scientific research. In the present study, the average range of cadmium recorded from the 15 sampling locations was from 0.064±0.05 to 0.145±0.0099mg/l (Table 2), these values are higher than the reports of who reported 0.0013±0.0002 to 0.0010±0.0002 mg/l ground water cadmium level in his research (Oko et al., 2017). The study's findings suggest that the groundwater at the study site may contain high levels of cadmium. This may be due to the effects of nearby oil and gas operations.

5.16.4 Zinc (Zn)

Dohare, et al., (2014) reported that, approximately 0.05 g/kg of zinc exists naturally as component of the earth crust. The mean range of Zinc from the present study was from 0.0457±0.00067 – 0.2513±0.025mg/l (Table 2). This result is below the minimum and maximum zinc levels of 0.911 mg/L and 0.182 mg/l reported by (Popoola et al., 2019). In addition, the WHO allows for maximum concentrations of 3, 5, and 15 mg/l. It is prohibited to exceed a DPR/FMEnv. concentration of 5.0 mg/l. They might have to travel to other areas to get enough of the natural form of zinc, sphalerite, which does not dissolve in underground water bodies when it is leached into them (Broadley et al., 2007).

5.16.5 Manganese (Mn)

Manganese is a critical component of biological systems, influencing pH, oxidation, and reduction reactions, according to (Shand et al., 2007). The result of the present study showed that manganese mean concentration ranged from 0.0917±0.074 – 0.2667±0.058mg/l (Table 2), this value is above the regulated permissible standard of the WHO, NWQS, the DPR/ FMEnv for groundwater (0.05 mg/l). In the area where the research was conducted, manganese is found in the groundwater. The findings of this study are also superior to those of who conducted a similar investigation 0.0066±0.0058mg/l to 0.0066±0.0047 mg/l, and 0.079 mg/l to 0.481 mg/l (Oko et al., 2017; Popoola et al., 2019).

5.16.6 Copper (Cu)

Measured mean range of copper range from 0.01 to 0.43mg/l (Table 2). These values is above the permissible limits of the DPR and WHO of 0.05mg/l in drinking water source. The trace values obtained suggest the precipitation sources of copper into the groundwater. The result of the present study is higher than the copper levels (0.0003±0.0001mg/l to 0.0004±0.0001 mg/l) reported by (Oko et al., 2017). In spite of this, reported concentrations of 0.18 mg/l and 0.44 mg/L (Popoola et al., 2019).

5.16.7 Arsenic (As)

Recorded mean values for Arsenic were between 0.0012±0.00072 to 0.0061±0.0087mg/l (Table 2). The value obtained for Arsenic are below the DPR/FMEnv of 0.01mg/l indicating low pollution. These values were also higher than the reports of 0.0008±0.0001mg/l to 0.0007±0.0002mg/l (Oko et al., 2017). This result suggests that, there may be no contamination of the ground water from the study area by Arsenic (As).

5.16.8 Aluminum (Al)

The result of the current study report Al level in groundwater from Ikwe-Onna as 0.01 to 0.13mg/l, this result is however lower than the stipulated permissible limit of 1.0mg/l by the (WHO, 2005). This data is lower than Momot and Synzynys, 2005 reported 0.2-0.65 mg/l in Toxic aluminium and heavy metals in groundwater of middle Russia. The result of the current study shows that, the water from the study may not be contaminated by aluminum.

5.17 Groundwater Trace Metal Concentrations

The mean trace metal concentrations in mg/L with standard error of the water samples from the study area is recorded in Table 2. The concentration of Arsenic (As) varied significantly across the stations ranging from <0.001 – 0.0061±0.0087mg/l. Mean Arsenic was highest in station 11 and least in station 3. Analysis of showed significant difference at p>0.05 (p=0.832). The concentration of Aluminum (Al) ranged from 0.01- 0.13mg/l. The mean concentration was highest in station 4 (0.0347±0.017mg/l) and lowest in station 6 (0.0723±0.011mg/l). Analysis of variance showed significant difference at p>0.05 (p=0.900). Lead (Pb) concentration showed little or no variation with a range of 0.02 – 0.65mg/L. The highest mean value was observed in station 5 (0.437±0.109mg/l) and lowest in station 1 (0.0483±0.027). Analysis of variance showed no significant difference at p<0.05 (p=0.016). The concentration of Zn showed no variance significantly across the stations ranging from 0.11 – 0.33mg/l. Mean concentration of Zn was highest in station 13 (0.28±0.003mg/l) and least in station 4 (0.127±0.009mg/l). Station-to-station variations in Cu concentrations were insignificant.

It spanned a range of.18 to.33. Station 9 had the most and station 5 had the least (Table 2). The concentration of Fe across the stations ranged from 0.08 – 0.48mg/L. Mean Fe concentration was least in station 9 (0.14±0.043mg/l) and highest in station 10 (0.327±0.06mg/l). Analysis of variance showed significant difference in concentration across the stations (p>0.05). Manganese concentration ranged from 0.01 to 0.38mg/l. Mean concentration was highest in station 6 (0.2617±0.578mg/l) and lowest in station 1 (0.0917±0.074mg/l. Concentration of Cd showed significant difference across the stations (Table 2). Mean concentration of Cadmium was least in station 1 and highest in station 9. Magnesium concentration ranged between 0.45-3.12mg/l. Mean range was lowest in 2 (0.803±0.13mg/l) and highest in station 10 (1.72±0.63mg/l). Analysis of Variance across the stations showed no significant difference at p>0.05 (p=0.725).

6. CONCLUSION

The results of physicochemical parameters from the study area indicates that, temperature and dissolved oxygen were slightly higher than recommended standards, however, mean pH range values. Biological Oxygen Demand, Turbidity, Conductivity, total dissolved solids and Alkalinity were all below recommended standards. Results of the trace elements indicated that mean chlorides, nitrates, and sulphate concentration across the sampling points is less than the maximum permissible values specified by the NSDWQ and the WHO, respectively. The concentration of Lead, Iron, Cadmium, Copper and Manganese was all above recommended permissible limit of WHO, and DPR/FMEnv, contrastingly, the mean range of Zinc, Arsenic and Manganese in the study area was below the permissible standard values of 3.0 to5.0mg/l of the WHO, NWQS, the DPR/ FMEnv. Because of the region's heavy reliance on oil and gas, the groundwater in the study area may contain higher levels of cadmium. Drinking ground water from the research region is associated with many risks that aren't related to cancer, as the current study reveals that cadmium and lead are major causes of chronic non-cancer risks. Ground water in the study location is unsafe for human consumption since the answers to both "hazardous metals HQ" questions are greater than one.

AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation and data collection were carried out by Nwankwoala, H.O; Oyegun, V. O; and Azuonwu Obi. Data analysis was performed by Okujagu

Diepiriye Chenaboso; Ohwoghere-Asuma, O; and Akakuru, O.C. The first draft of the manuscript was written by Okujagu Diepiriye Chenaboso and all authors reviewed and commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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DATA AVAILABILITY

All data used are included in this article

CONFLICT OF INTEREST

The authors declare that they have no known competinig finalcial interest or personal relationships that could have appeared to influence the work reported in this paper.

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