

Hydrogeochemical Characterization of Groundwater of Field Y, Offshore Niger Delta

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ABSTRACT

Hydrogeochemical analyses were carried out on groundwater samples in order to understand the hydrochemistry of the water. The results revealed that groundwater has a high electrical conductivity, which could be as a result of more chemicals dissolved in the water and total hardness observed in all samples shows that the water isn't hard water. Major cations and anions were identified using Piper Trilinear diagram Durov diagrams and Stiff diagrams. The parameters studied include; Ph, Electrical conductivity, Temperature, Total Suspended Solid, Salinity as Chloride, Sulphate, Total Hardness, Total Hydrocarbon Content, Nitrate, Phosphate, Alkalinity, Calcium, Sodium, Magnesium, Potassium, Iron, Zinc. The major cations are: Sodium (Na⁺), Potassium(K⁺), Calcium (Ca²⁺), while the major anions are: Bicarbonate (HCO₃), Carbonate(CO₃), Sulfate (SO₄⁻), and Chloride (Cl⁻). TDS is the major physical parameter that is dominant in the Durov diagram, although the analysis in the Durov, Piper and Stiff diagram shows that $Ca₂ +$ and HCO₃, are the major cation and anion respectively which implies that the groundwater in the study area are $Ca₂⁺$ and HCO₃. It was also observed that the quality of groundwater was suitable for domestic purpose and agricultural purpose.

Key Words: Groundwater, Cations, Anions, Piper, Durov, Stiff

INTRODUCTION

In many nations, groundwater is the main source of water for home, agricultural, and industrial applications, and its contamination has been acknowledged as one of the most significant issues (Belkhiri et al., 2010). In the course of its migration, groundwater interacts with the minerals that make up the rocks as it passes through the pore spaces within the rocks (Amadi et al., 2012; Boateng et al., 2016). Any location's groundwater quality is dependent on the aquifer through which it moves, taking into account the hydrological cycle and flow direction (Offodile 1983; Amadi et al., 2010; Boateng et al., 2016). Groundwater quality is seriously threatened by growing human activity and intense use of natural resources (Foster, 1995). Evaluation of the quality of groundwater can be a difficult task.

The groundwater quality in the area is quickly declining, according to studies by Etu-Efeotor & Odigi (1983), Amajor (1986), Amadi, et al., (1989), Etu-Efeotor, (1981); Udom, et al., (1999); Nwankwoala, et al., (2007); Nwankwoala & Udom, (2008), and Nwankwoal Groundwater is becoming a primary source of water due to population growth and increasing urbanization, so it is crucial to comprehend the hydrogeochemical processes that occur in the aquifer system. The main source of water supply in the area's hydrogeo chemistry and various types of water are evaluated in this study, along with the properties of the groundwater. Additionally, the most important factors influencing water quality and ionic processes that affect the region's aquifer systems' groundwater composition will be researched. In order to anticipate the water character of the groundwater, this study also offers the chance to see a complete profile of the distribution and dynamics of the dominating hydrogeochemical facies. Therefore, in order to implement policies that will stop the progression of this issue, a full investigation of the phenomenon is required. It is understood that effective management of coastal groundwater resources requires on accurate predictions of how the saltwater-freshwater interface will behave in response to both natural and human development activities, in addition to planning and regulation.

In the past ten years, there has been a significant increase in the requirement to assess the quality of water

utilized by humans (Olatunji, et al., 2005; Nwankwoala et al., 2007). Additionally, it has been demonstrated that the chemistry of underground water is influenced by geology (Abimbola, et al., 2002; Olatunji, et al., 2001). More significantly, studies have also revealed that the quality of groundwater is influenced by the secondary products, the type of surface runoffs, and the mineralogical composition of the underlying rock (s) (Tijani, 1990). If particular information on water quality, which is required for sustainable resource development and management, is lacking, the supply cannot be declared to be safe because the chemical components of groundwater are known to pose some health hazards (Amajor, 1986; Amadi). Due to a general lack of hydrologic and hydrogeologic data, the hydrochemical processes and properties of the local aquifer systems are typically unknown, which makes planning and managing groundwater abstraction more difficult. Large uncertainties also exist in the understanding of the main processes controling the evolution of groundwater in the area.

The primary chemical components of groundwater govern the quality of the water and how it should be used. The criteria used to measure the quality of groundwater are the concentrations of these constituents expressed as cations and anions in milligrams per liter (mg/L), and the fluctuation in concentration across space will be used to identify and characterize areas with low quality groundwater. A highly helpful criterion in assessing water quality generally is the total dissolved solids (TDS), which is a measurement of the total quantity of minerals dissolved in water. TDS is an expression of the amount of ions dissolved in water. According to Todd and Mays (2005), water with a TDS of 500 mg/L or higher is preferable for both residential and industrial usage. Water with a TDS of 1,000 mg/L or more is considered saline and unusable. Other water quality measurements that depend on the ions dissolved in water include the hardness and specific electrical conductivity of the water. Ions are consequently essential for evaluating groundwater.

The chemical makeup of groundwater is recognized to pose various health hazards, hence the availability cannot be deemed safe in the absence of detailed information on water quality, which is necessary for the sustainable management and development of resources. Due to a general paucity of hydrologic and hydrogeologic data, the hydrochemical processes and characteristics of the aquifer systems in some areas of the Eastern Niger Delta are essentially unknown, which makes planning and managing groundwater abstraction more difficult. The primary mechanisms governing the evolution of the groundwater in the region are likewise subject to significant uncertainties. In the course of its migration, groundwater interacts with the minerals that make up the rocks as it passes through the pore spaces within the rocks (Amadietal., 2012; Nwankwoala&Udom, 2013; Boatenget al., 2016). Groundwater quality in any locality takes after the chemical composition of the aquiferthrough which it migrates in accordance with the hydrological cycle and flow direction (Amadietal., 2010).

Taking into consideration the fact that the aquifers of the transition zone of the Niger Delta are shallow, consisting predominantly of sand, gravel and ignitic materials and that they vary from unconfined at the surface to semi-confined at depth {Nwankwoala and Ngah, 2014}, these shallow aquifers are therefore vulnerable to contamination from crude oil leakage and spills, sewage disposal on land, solid waste disposal on land, infiltration from industrial wastes, and urbanization spreading into recharge areas due to the presence of the petroleum industry and other industries within the delta, altering the quality of groundwater. With these factors in mind, it is therefore difficult to monitor and detect groundwater pollution, and even more difficult to control it and may persist for decades without being detected. Identification and delineation of locations where groundwater quality is significantly below recognized norms require evaluation of the groundwater quality control parameters and their spatial relationships. According to Guler et al. (2002) and Cloutier et al. (2008), geographical variability in chemical constituent concentration and/or composition can provide information about the connectedness and heterogeneity of aquifers as well as the physical and chemical processes that govern water chemistry. Since the early 20th century, graphic and statistical methods have been developed to aid in the classification of different types of water and the evaluation of water quality using the concentrations of chemical constituents. These techniques are the most frequently used to analyze patterns in hydrologic and hydrogeochemical processes in both surface and groundwater systems. Graphical techniques are frequently used to analyze groundwater. Examples include Piper diagrams, Stiff pattern diagrams and Durov diagrams

Piper diagrams are used to categorize different types of waters, it shows the classification of water samples from various lithological environment. It also demonstrates the chemical character of the water samples using

the dominant cation and anion to tell the dissimilarities and similarities of the groundwater sample. It is used as an effective graphical representation of chemistry in water samples in hydrogeological studies. The percentage values of six ion groups are considered in the plot, and they are calcium, magnesium and sodium plus potassium cations, and sulfate, chloride and carbonate plus hydrogen carbonate anions.

Stiff pattern diagrams, which are used to compare waters with various characteristics visually, it is useful in the analysis of groundwater ion concentration. It plots milli-equivalent concentrations of cation on the left side of the diagram and shows anion concentrations on the right.

Durov diagrams, which are used to graphically illustrate cation/anion concentrations in relation to TDS and PH.

Principal component analysis (PCA), a data transformation method based on the assumption that a multivariate dataset exists, and hierarchical cluster analysis (HCA), a data classification technique most commonly used in Earth sciences, are two of the most widely used multivariate statistical methods (Guler and Thyne, 2002).

Aim and Objectives

The purpose of this research is to use statistical techniques to ascertain the concentrations of the chemical components of the ground water and their spatial relationships within the study area.

The following are the paper's objectives:

- 1. To identify the water types (hydrogeochemical facies) in the study area
- 2. To comprehend the groundwater flow regime and its impact on the groundwater's chemical make-up.
- 3. To identify the areas where the quality of the groundwater is acceptable.
- 4. To assess how human activity has impacted the local groundwater quality.

Location and Accessibility

The study area is the Niger-Delta, which is in southern Nigeria and is situated between latitudes 4º 21' 43.2" N -7 ° 40' 52.8" N and longitudes 5 ° 8' 42" E -9 ° 30' 7.2" E. It covers an area of about 84,640 km2 spatially and includes the states of Bayelsa, Cross River, Rivers, Edo, Delta In most places, the gently sloping lowland topography of the Niger Delta region is less than 10 degrees, and the highest point of the lowland, which is well-drained, forms a mosaic with an altitude of between 15 and 25 meters (Musa et al., 2014). The area has a flat monotonous low relief, interspersed by several wetlands.

METHODOLOGY

Materials

- a. Chemical Reagent
- b. Compass clinometer
- c. Global Positioning System (GPS)
- d. Conductivity meter
- e. Thermometer
- f. Sample containers
- g. Field notebook
- h. Masking tapes and Marker pens

i. Hand gloves

Methods

The samples were collected in the field, transported, and subjected to a variety of laboratory analyses. Every technique was carried out in accordance with SOPs. Samples were obtained manually through sampling. They were gathered at random, and each sample was geo-referenced. Alternatively, samples were taken from handdug wells and boreholes. A total of ten samples were collected in the research region. Before collecting samples, turbidity, conductivity, pH, and temperature tests were conducted at each location.

For sample collection, plastic containers with a capacity of 2 liters each were employed. Before being filled, the containers were first rinsed with groundwater. It was allowed to run for five minutes before samples were taken from the tap-borehole.

Within 24 hours of collection, all collected samples were transferred to the laboratory ratory for analysis. Immediately after collection, all samples were stored in thermo coolers with ice to maintain a temperature of $4^{\circ}C$.

The thermometer, pH meter, and electrical conductivity meter were used to measure the water sample's temperature, pH, and electrical conductivity in-situ. The coordinates and elevation of the spot were recorded by the GPS. After that, the samples were transferred to a lab for analysis within the allotted retention time.

Figure 1: Map of study area showing sampling points

RESULTS

The result obtained from the laboratory analysis of the collected water samples are discussed and interpreted. The interpretations were made based on DPR and WHO drinking water quality standards.

Table 2: Physico-chemical parameters of groundwater samples

Table 3: Summary statistics of groundwater physical and chemical characteristics

DISCUSSION

Table 4: Pearson's Correlation Matrix

Pearson's correlation matrix shows the relationship between the parameters. Correlations such as those indicated in the table suggest that the relationship between the parameters is very strong and that such relationships depend heavily on each other. For example, an increase in pH (increase towards basicity) would

result in an increase in bicarbonate concentration and a decrease in pH will result in a decrease in bicarbonate concentration. Ammonium correlates highly with phosphate implying that their source may be the same and they increase and decrease together.

(pH)

The groundwater quality data for the study area is presented in Table 1. The hydrogen-ion concentration (pH) of the groundwater in the study area ranges from **6.51-6.98.** The WHO 2022 maximum permissible limit for pH is within the range of **6.5-9.2**. pH is a measure of the negative logarithm of the hydrogen ion concentration of a solution. It is a measure of the acidity and alkalinity of a liquid. pH less than 7 is acidic, and pH above 7 is basic (Alkaline).

In the study area the pH range was slightly less than 7, which means the water is slightly acidic, this may be due to infiltration of rain into the subsurface. Extremes of pH can affect the palatability of water and affect distribution systems due to their corrosive effects.

Electrical Conductivity (EC)

The electrical conductivity of the grand water samples ranged from **434-687** with a mean of **564.6.**

Electrical conductivity (EC) actually measures the ionic process of a solution that enables it to transmit current. According to WHO standards, EC value should not exceeded 400 μS/cm, however the groundwater samples range is above 400μS/cm, although NIS (2007) gives a permissible limit of 1000μS/cm.

The conductivity of water reflects its ability to conduct an electric current. EC has no direct significance to health.

Total Suspended Solids (TSS)

The concentration of TSS ranges from **1.52-3.7mg/l** in the study area. The highest TSS value in the study area is **3.7mg/L.** This value is significantly higher than the WHO 2022 standard for TSS in water of 0.5mg/L.

Temperature

The temperature in the study area ranges from 27.2-30.8 ºC**.** However the DPR, WHO maximum permissible limit is 25-50ºC. The rate of chemical reactions generally increases at higher temperature. Water, particularly groundwater, with higher temperature can dissolve more minerals from the surrounding rock and will therefore have a higher electrical conductivity. Temperature affects the rate of dissolution of oxygen. Temperature has no effect on health (NIS) The study of temperature is critical and essential as some key constituents of water either change their form or alter their concentration.

Salinity

The salinity values of the groundwater in all the 10 locations ranges from 10.52mg/l to 119.12mg/l. These values are significantly lower than the WHO 2022 standard of 250mg/L.

Sulphate

The values of the sulphate concentration level ranged from 6.44mg/l to 9.81mg/l. The DPR, WHO maximum permissible limit is 100mg/l, This falls within the permissible limit. Sulphates occur in rocks, geologic formation, discharges and so on. Sulphates have a laxative effect, especially when combined with magnesium or sodium. Water containing sulphates in excess will also attack the fabric of concrete sewer pipes.

Total Hardness

The total hardness in the study area, ranges from **31.00mg/l to 39.00mg/l.** The DPR, WHO maximum

permissible limit is **400mg/l.** However, hardness levels in the range of 0-60mg/l is said to be soft. Hardness is a natural characteristic of water. Hardness in water may enhance its palatability and consumer acceptability for drinking purposes. The toxic effects are remarkably less in water with a significant degree of hardness. One of the disadvantages of hard water is that they can cause blockage of pipes and severely reduce their boiling efficiency.

Total Hydrocarbon Content (THC)

The values of the total hydrocarbon content ranges from **1.52** to **3.47.** This value is significantly lower than the WHO 2022 standard for THC in water of 10mg/L.

Nitrate

The nitrate values range from **0.013mg/l to 0.072mg/l** which is below the WHO 2022 maximum permissible limit of 50mg/l.

Nitrate is the primary form of nitrogen in groundwater; it is soluble in water and can easily pass through soil to the groundwater table. Nitrate in water could be as a result of nitrogenous fertilizer used in the area. Nitrate may occur due to oxidation of ammonia, agricultural fertilizer run-off.

Phosphate

The values of the sulphate concentration level ranges from **0.007mg/l to 0.029mg/l.**

The DPR, WHO 2022 maximum permissible limit is not specified, but the WHO (2006) put the permissible limit of phosphate concentration at **5mg/l.** Since the water range in the study area lies below the WHO 10mg/l. Phosphorous has no implications on human health.

Alkalinity

The alkalinity values ranges from **7.11mg/l to 9.22mg/l**. The DPR, WHO maximum permissible limit is 200mg/l.

The total Alkalinity in water was determined in accordance to the American Public Health Association (APHA) 2320B. 100ml of the sample was measured into a clean conical flask and 2- drops of phenolphthalein indicator. The mixture was titrated with $0.02M$ of H_2SO_4 until the pink colour disappears. The volume of acid was recorded as Aml. 3-5 drops of indicator of methyl red and bromocresol green in 95% pure alcohol added and titrated with $0.02N$ H₂SO₄ and at the end point, when the colour changed from blue to pink, the total volume Vml of H2SO⁴ added was noted.

Calcium

The calcium ranges from **2.32mg/l to 4.11mg/l.** The maximum permissible limit according to WHO (2011) and NIS (2007) is500mg/l. Calcium is largely responsible for water hardness, and may negatively influence toxicity of other compounds. In limed soils, calcium may immobilize iron. Calcium is very important as concentrations in high levels may be beneficial. Calcium is the most important element in the human body and an adequate intake is essential for normal growth and health. Calcium occurs in rocks, bones and shells. Abundance of calcium causes problems associated with hardness.

Sodium

The sodium values of the groundwater ranges from **11.91mg/l to 16.22mg/l**, which is lesser than the WHO maximum permissible limit of 150mg/L.

The DPR, WHO 2022 maximum permissible limit is **150mg/l,** the range of sodium in the study area, is way below the permissible limit.

Elevated levels of sodium and chloride can impart a salty taste, interfere with the watering of certain plants, and increase corrosivity, which in turn can affect household plumbing.

Magnesium

The values of magnesium ranges from **10.26mg/l to 14.58mg/l.** The DPR, WHO maximum permissible limit is 200mg/l. Magnesium dissolves from mineral of feldspar and mica like calcium.

Potassium

The potassium values of the study area ranges from **1.89mg/l to 3.21mg/l.** The DPR, WHO maximum permissible limit is not specified. However, the WHO (2006) maximum permissible limit is **200mg/l**, so therefore, the water is safe for drinking and other domestic use. The presence of this ion could be probably resulting from the dissolution of feldspar, mica and clay minerals.

Iron

The values of iron in the study area, ranges from **0.521mg/l to 0.876mg/l.** The DPR, WHO maximum permissible limit is 0.3mg/l. Iron occurs naturally in the aquifer but levels in ground water can be increased by dissolution of ferrous boreholes and handpump components. The health impacts of excess iron concentration are primarily organoleptic but there has been medical concerns about high levels of iron in drinking water. Excessive iron concentration in soluble form may cause staining to clothes during laundry and change the taste of vegetables during cooking.

Iron is found in geological formation. The Benin formation which is the water bearing aquifer, from where the groundwater seeps into the wells are ferrigenous, and contains minerals such as, marcarsite, hematite, geoethite, and limonite. The mobility and subsequent downward infiltration of these minerals through the porous and permeable formation account for the presence of iron the water from the study area (Amadi et al 2014).

Zinc

The zinc values in the study area, ranges from **0.131mg/l to 0.312mg/l**. The DPR, WHO maximum permissible limit is **15mg/l**. So, it is safe to say that the values in the study area are below the maximum permissible limit, this means it is safe for drinking and other domestic use.

Figure 2: Showing that the major physical parameter that is dominant is TDS

This program reads concentration data from the Utilities datasheet and builds a Durov diagrams, which demonstrate the relationship between various ions within hydrochemical samples. Total Dissolved Solids (TDS) values are depicted with proportionally scaled circles, similar to those in the Piper Diagram program. Contours are also available for TDS data and relative sample density. Concentrations entered in the source data file in units of milligrams per liter are converted to milli-equivalents per liter for display on the diagram.

The Durov Diagram is an alternative to the Piper Diagram. In the two triangles, it plots the major ions as percentages of milliequivalents. The totals of both the cations and anions are set to 100% and the data points in the two triangles are projected onto a square grid which lies perpendicular to the third axis in each triangle.

The analysis of the Durov diagram show that the groundwater in the study area has Ca^{2+} and HCO_3^- as their major cation and anion respectively. It also shows that the major physical parameter that is dominant in the study area is TDS.

Piper Diagram

Piper diagrams consist of three parts: Two trilinear diagrams along the bottom and one diamond-shaped diagram in the middle.

The trilinear diagrams illustrate the relative concentrations of cations (left diagram) and anions (right diagram) in each sample. For the purposes of a Piper diagram, the cations are grouped into three major divisions: Sodium (Na⁺) plus Potassium (K⁺), Calcium (Ca²⁺), and Magnesium (Mg²⁺). The Anions are similarly grouped into three major categories: Bicarbonate (HCO₃⁻) plus Carbonate (CO₃²), Sulfate (SO₄²), and Chloride (Cl⁻). Each sample will be represented by a point in each trilinear diagram; unique symbols may be selected for each sample and can be referenced in a symbol index at the top of the diagram. Symbols may also be accompanied by labels.

Concentrations entered in the source data file in units of milligrams per liter are converted to milli-equivalents per liter for display on the diagram.

The diamond field is designed to show both anion and cation groups. For each sample, a line is projected from its point in the cation and anion trilinear diagrams into the upper region; where the lines intersect, the symbol is plotted. Circles may be plotted around each point to illustrate total dissolved solids (TDS) for the sample. The total dissolved solid computation will include all components listed in the data file ("standard" ions and additional ions).

Figure 3: Showing the analysis of the Piper diagram shows that the groundwater in the study is a Mg^{2+} and SO_4^2 water.

Stiff Diagram

Stiff diagrams plot milli-equivalent concentrations of cations on the left side of the diagram and of anions on the right. Each ion is plotted as a point, and the points are connected to form a polygonal shape. The ions are plotted in a consistent order (Na+K across from Cl; Ca across from HCO3 + CO3; Mg across from SO4) so that each polygon becomes that sample's "signature". Additional ions, if present, are plotted in the order that they are listed, below the standard ions.

Figure 4: Stiff Diagram

The analysis of the Stiff plots also supports that the groundwater in the study is a Ca^{2+} and HCO_3^- water.

CONCLUSION

Almost all the parameters that were analyzed were observed within the range of accepted standards by the WHO for domestic use, drinking water.

Electrical conductivity has the highest mean value of 564.6 among all other parameters. The EC values are above the WHO permissible limit standard, and this could be as a result of more chemicals dissolved in water and the high conductivity can be reduced by removing the number of dissolved solids in the water through reverse osmosis, flocculation or distillation.

The water is slightly acidic, but this isn't an issue as it can be treated before use.

After the comparison of the analysis results with the WHO quality guidelines, the groundwater in the study area would be suitable for domestic use, livestock and agricultural use and also industrial use, after proper treatment.

The hydrochemical study shows that the groundwater in the study area is hard water/temporarily hard water and slightly acidic, due to the presence of the dominant cation (Mg^{2+}) and anion (SO₄²) and it has a high electrical conductivity, which might not be suitable for domestic use and household consumption, but it can be treated to be used for domestic purpose.

Water hardness can be treated with methods such as reverse Osmosis, ion exchange

The pH can be treated with a little lime by the users before usage and consumption.

The high electrical conductivity can be rectified by reducing or completely removing the dissolved solids in the water.

The iron content exceeded the WHO permissible limit of 0.3mg/l, too much iron can be treated by aeration or chemical oxidation followed by filtration.

The major cations present in the groundwater are Sodium (Na⁺), Potassium(K⁺), Calcium (Ca²⁺), Magnesium (Mg^{2+}) , and the groundwater contains mainly Mg^{2+} and $SO_4{}^{2-}$. The presence of HCO3- in groundwater makes it more alkaline which makes it suitable for drinking.

These cations are geogenic which means they originated from the soil and they are important to human health.

RECOMMENDATION

It is recommended that further monitoring of boreholes in the area should be carried out to figure out the cause of the high electrical conductivity

Frequent studies should be done in order to properly ascertain possibly evaluate the rate at which hydrogeochemical parameters change within the study area.

Non-corrosive materials and PVC pipes should be used for borehole construction in the study area due to the acidic nature of the water.

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