# The Hydrogeochemical Properties of an Abandoned Mining Location - A Case Study of Odagbo Coal Mine

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**Abstract:- A significant contributor to water contamination is acid mine drainage (AMD). In this study, the chemical composition of water samples in the coal mines at Odagbo, was assessed to determine the chemistry of the mine waters and potential for acid mine drainage (AMD). The water samples were all subjected to thorough geochemical investigation. The findings showed that all water samples taken in the mining area had relatively low PH values (range from 3.24 to 3.84) in aqueous solutions which shows high acidity value ranging from 150 to 1730 typical of AMD, with rising levels of TDS and $SO_4^{2-}$. Electrical conductivity (EC) measurements showed a moderately significant range of 123.0 to 170.3 µS $cm^{-1}$. It was evident that the water samples were $SO_4^{2-}$ enriched, with values ranging from 249.50 to 1703.04 $mgL^{-1}$ which indicates pollution of mine waters. Elevated $Ca^{2+}$, $Mg^{2+}$, and Fe were another characteristic of the AMD samples. As a result, the current case study will provide an updated scientific foundation for the detection of heavy metal contamination's source as well as suggest critical lines of inquiry for future research.**

***Keywords:-*** *Hydrogeochemical, AMD, EC, Pollution.*

## I. INTRODUCTION

The hydrogeochemical species of an element plays a significant role in its environmental chemistry. These species offer valuable insights into the mobility and consequent availability of the metal to organisms, as well as its potential toxicity, (Xiao et al., 2015; Jaishankar *et al.*, 2013; Nagajyoti et al.,2010; Fergusson, 1990). The rising demands for river water due to rapid industrialization, urbanization, and population growth in recent decades have resulted in a considerable decline in water quality, particularly in the vicinity of mining areas and in the lower basin. Consequently, water contamination remains a pressing concern in this region. Effective management and planning of groundwater necessitate regular monitoring of both the hydrochemical characteristics of water and the hydraulic properties of the aquifers that store the groundwater. The chemical composition of groundwater is influenced by various factors, including geology, the extent of chemical weathering, the quality of recharge water, and inputs from sources other than water-rock interactions. These factors, along with their interactions with groundwater, contribute to the complexity of groundwater quality (Domenico and Schwartz, 1990; Guler and Thyne, 2004; Sunne Vazquez et al., 2005). Bivariate statistical methods are analytical techniques that can be employed to examine groundwater composition. They help in adequately characterizing hydrochemical systems and have proven useful in addressing numerous environmental issues and enhancing our understanding of groundwater flow patterns (Meng and Maynard, 2001; Yidana et al., 2008a, b). Hence, the present investigation employed bivariate statistical analysis to comprehend the associations between water quality parameters in order to establish the predominant factors and mechanisms governing the chemical composition of groundwater in the designated region. Moreover, this examination will also provide an updated scientific foundation concerning heavy-metal contamination and its identification of sources, and may also propose significant avenues for future research utilizing multivariate statistical methodologies and geochemical modeling to ascertain the contamination status and potential origins of pollutants in the study area.

➢ *Description of the Study Area*

Odagbo comprises a coal reservoir, situated approximately 16km to the north-east of Ankpa in Kogi State (as shown in Figure 1). This deposit stretches from its eastern outcrop boundary near the tributaries of Okpokwu, Otokpa, and Okaba rivers to considerable depths beneath more recent sedimentary layers (Late Maastrichtian-Tertiary) in the western direction. Access to this area is possible by means of a 10km road branching off the Ankpa-Makurdi Federal Highway. This road traverses the Okaba and Odagbo communities within the Ankpa District. The mining operations are conducted at Odagbo, an open-pit coal mine located approximately 4 km away from Okaba. The mine comprises a 0.8 m thick (exposed section) bituminous coal layer, which is covered by an overburden of 3-6m (as depicted in Plain 1). The coal itself exhibits a very dark hue and is overlaid by a light grey silt shale (heterolithic), transitioning into light grey to brownish laminated and mottled siltstone at the uppermost section.

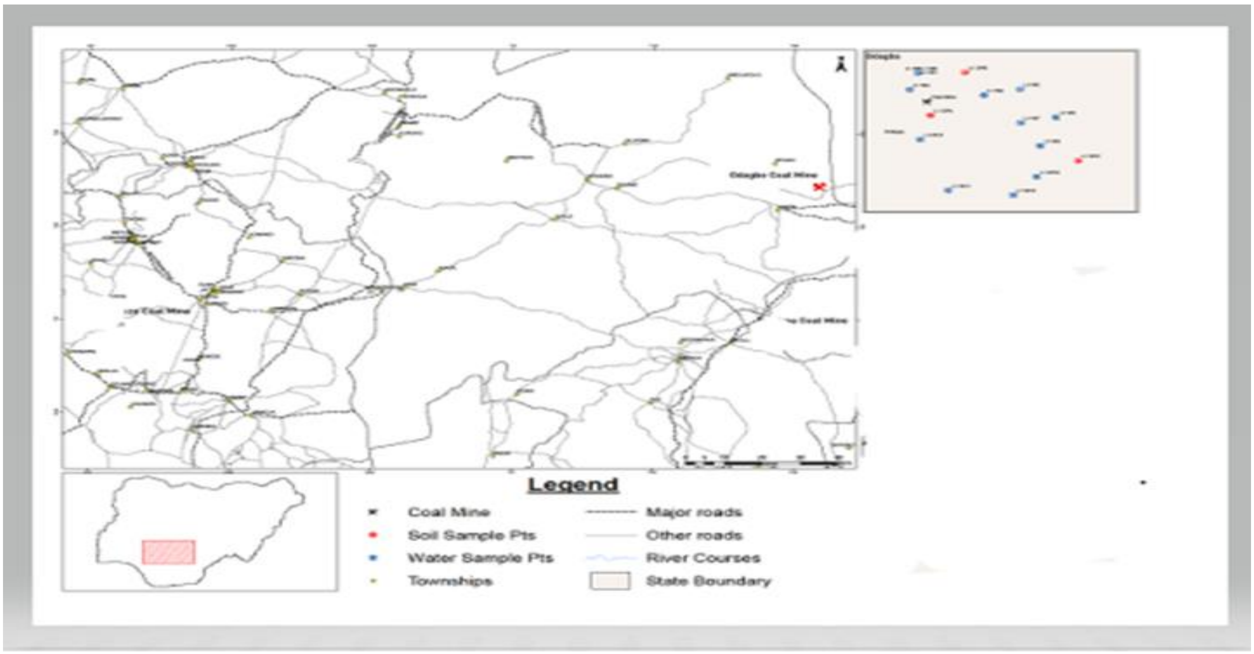


Fig 1 Location Map of the Study Area

## II. MATERIALS AND METHODS

➢ *Sample Collection*

A sum of 20 water samples were gathered from various regions within the mining site situated in Odagbo, Nigeria. These samples were obtained using sterilized polythene bottles with a capacity of 500 milliliters.

➢ *Physicochemical Analysis of Water*

The physicochemical characteristics of the water samples, such as pH and electrical conductivity, were examined. Total dissolved solids (TDS), total hardness (TH), and (EC), as well as total Alkalinity, nitrate, sulphate (SO4), sodium, calcium, magnesium (Mg), and sodium (Na), lead (Pb), copper (Cu), zinc (Zn), and iron (Fe). The evaluation adheres to the guidelines outlined by APHA (1995) as displayed in Table 1. TDS, EC, and other variables were on the field measurements. This is crucial because these criteria can alter while being transported.

Table 1 Techniques for the Determination of the Physicochemical Parameters

| Parameter | Method of Determination |
|---|---|
| pH | pH meter |
| EC | Conductometer |
| TDS | Gravimetric technique |
| TH | EDTA Titration technique |
| TA | Titrimetric |
| $NO_3$ | Discreet analyser |
| $SO_4$ | Discreet analyser |
| Cl | Argentometric technique |
| Zn, Mn, Cu, As, Pb, Co | ICP-AES |
| Mg, Fe, Ca, Na, Al, K, | ICP-MS |

**By inductively coupled plasma Optical / Atomic Emission Spectroscopy (ICP OES/AES) Inductively coupled plasma Mass Spectroscopy (ICPMS)

➢ *Acid Mine Drainage and Heavy Metal Contamination*

Heavy metal contamination is a significant environmental issue, particularly for rising medium-sized cities in emerging nations such as Nigeria. Heavy metal pollution of the soil and ultimately the food chain is a risk since heavy metals are typically not removable even after wastewater treatment at sewage treatment plants (Fytianos et al., 2001). This is why this study analyses a couple of heavy metals (As, Cr, Cu, Fe, Pb, Mn, Ni and Zn) at the Odagbo coal mine. The concentration of aqueous metals in receiving water bodies is frequently increased by mine drainage, and these metals can be transported to sediment by adsorption and precipitation mechanisms, Spellman et al., 2022 (Smith, 1999), while the pollution risk from heavy metals increases with time due to conversion from an inert state into an active state during weathering (Al-Oud *et al.,* 2011).

➢ *Geostatistical Techniques*

Numerous statistical techniques have been employed over time to assess both the hydrogeochemistry and water quality (Nelson and Ward 1981; Briz-Kishor and Murali 1992; Ramesh Kumar and Riyazuddin 2008; Routroy et al. 2013). Correlation and regression analyses in this study were carried out using Microsoft Excel software (2013)

## III. RESULTS AND DISCUSSION

➢ *pH*

Sulphuric acid from pyrite oxidation makes water corrosive and decreases pH. Acidic mining discharge and low-pH groundwater systems produce weakly acidic groundwater. Metal sulphide oxidation during mining can cause acidic discharge (Herbert, 1996; Keith et al., 2001; Santofimia and López-Pamo, 2013). Odagbo had a mean pH of 3.55, a maximum and minimum of 3.84 and 3.24, and a standard deviation of 0.18 (Table 2). The control sample was the most acidic. The WHO (2017) recommends 8.0 for drinking water. Awalla (2014) and Matthew et al. (2012) indicate that acid mine drainage may cause this situation in mining-area water sources. Concentration and strength determine acid and alkali effects. Strong, concentrated acids and alkalis are corrosive, whereas weaker ones are not. pH does not cause bad effects alone.

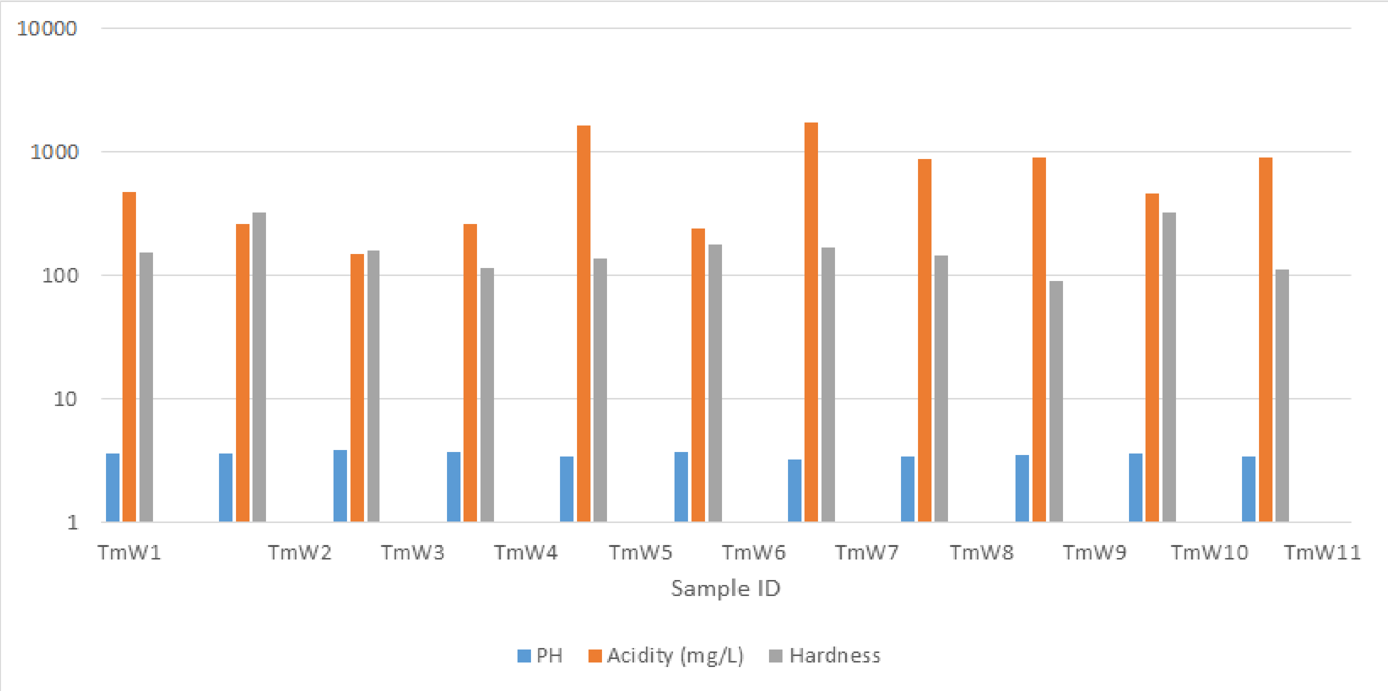


Fig 2 pH, Acidity and Hardness values at Odagbo Coal Mine

➢ *Sulphate Ion at Odagbo*

Acid mine drainage, caused by mining and mineral processing, pollutes water. Pyrite oxidation in air and water creates sulphuric acid and dissolved iron. AMD acidic streams will contaminate surface and groundwater with heavy metals. AMD pollutes water in mining nations. Sulphate's conservatism predicts acid mine drainage frequency and severity. Discrete analyzers measured sample sulphate ions. Sulphate ion concentrations ranged from 249 to 1581, with a mean of 915. 941.87 SD. WHO recommends 250 ppm or less sulphate. Health issues develop when sulphate concentrations for human consumption are disturbed (Backer, 2000). The research area's sulphate concentration may cause laxation.

➢ *Electrical Conductivity (EC)*

EC and sulphate ions are AMD-sensitive even after substantial dilutions. Sulphate, unlike other ions, is unaffected by sorption, precipitation, or pH changes, making it ideal for AMD tracing. Sulphate ions especially affect conductivity. Conductivity, which can be measured directly in the field, is appropriate for routine field screening of water samples for AMD contamination. Sulphate and conductivity are associated in all examined waterways, with AMD contamination strengthening the relationship. Odagbo EC (Table 3) ranges from 1.74 to 5.10, with a mean of 3.42 and a standard deviation of 2.38. These conductivity levels are below the WHO (2017) standard of 1000 µS/cm. Conductivity selects optimal dilutions for accurate sulphate analysis. No ion-specific electrode is available to continually measure sulphate in the field. Automated calorimetry can be employed, but due to iron oxides in AMD, natural humic acids in rivers, and other factors, field-based sulphate analysis is unreliable, imprecise, and expensive. Conductivity seems suitable for sampling and monitoring acid mine waters. Odagbo data reveal that small soluble particles did not considerably ionise the water.

➢ *Total Disssolve Solid (TDS)*

Electrometrically measuring total dissolved solids in water samples (APHA 2004). TDS measures water's total inorganic and organic salts and other components. Anions like carbonate, bicarbonate, nitrate, chloride, and sulphate, and cations like calcium, magnesium, and potassium are the main components. TDS's "Hardness" is the quantity of dissolved calcium and magnesium in water. Some ions are necessary, but others are detrimental. TDS levels peak at 1000.00 and 500.00 mg/L. TDS in Odagbo (Table 2) ranges from 1000.38 to 1980, with a mean value of 1586.13. Thus, people reject water with high TDS levels for taste and other reasons. Lower TDS water may include microorganisms that are detrimental to human health.

Table 2 Geochemical Parameters of Odagbo Mine Site

| Chemical Parameters | Odagbo mine | | | WHO (2017) | NIS(2015) |
|---|---|---|---|---|---|
| | range | Mean | SD | | |
| Temp. | 27.5-29.1 | 28.3 | 1.13 | Ambient | Ambient |
| Ph | 3.24-3.48 | 3.5 | 0.18 | 6.5-8.5 | 6.5-8.5 |
| TDS(ppm) | 1000-1980 | 1490 | 692.96 | 1000 | 500 |
| EC(µS/cm) | 1.74-5.10 | 3.42 | 2.38 | 1000 | 1000 |
| T. Hardness | 90.2-325.4 | 207.8 | 166.31 | 100 | - |
| Acidity | 150-1730 | 940 | 1117.23 | - | - |
| DO | 2.4-8.2 | 5.3 | 4.10 | - | - |
| Phosphate | 0.4-15.8 | 8.1 | 10.89 | - | - |
| Sulphate | 249.-1581 | 915 | 941.87 | 200 | 100 |
| Nitrate | 1.32-3.86 | 2.59 | 1.80 | 45 | 50 |
| Chloride | 0.94-2.27 | 1.605 | 0.94 | 250 | 250 |

➢ *Geostatistical Analysis of Odagbo Coal Mine*

The physicochemical characteristics and metal concentrations of the water samples collected at Odagbo are presented in Table 3. The pH levels of the groundwater samples in this region exhibit strong acidity, ranging from 3.24 to 3.84 with an average value of 3.55. Furthermore, the electrical conductivity (EC) of the water samples fluctuates between 1.74 to 5.1 with an average of 3.14ms/cm, reflecting the influence of saline-water intrusion. Regarding the dissolved oxygen (DO) concentrations, values exceeding 5mg/L indicate an oxygenated groundwater environment. However, the DO levels in the area vary from 2.4 to 8.2 with an average of 4.08 mg/L, suggesting that the groundwater is aerobic. Analyzing the metal concentrations in the groundwater, the order of abundance is as follows: Mn>Zn>Co>Ni>Fe>Al>Cr>Cu>Ca>Si>Mg>K>As>Pb>Na. Descriptive statistics, including the maximum admissible concentration (MAC), global standards, and health effects, are provided in Table 3. Notably, toxic heavy metals, such as arsenic (As), are present in the study area. The concentration of As in the groundwater ranges from 2.58µg/L to 14.39µg/L, with an average value of 7.98µg/L (Table 3). It is worth mentioning that these arsenic values are below the acceptable limit of 50µg/L set by the World Health Organization (WHO, 2017) and the United States Environmental Protection Agency (USEPA, 2012). The presence of As in the study area primarily stems from mining activities (Hunt and Howard, 1994).

Table 3 Geostatistical Parameters of Odagbo Coal Mine

| Parameters | Units | Minimum | Maximum | SD | Mean | MAC | USEPA (2012) | Health Effect |
|---|---|---|---|---|---|---|---|---|
| Ph | | 3.24 | 3.84 | 0.175 | 3.55 | 6.5-8.5 | 6.5-8.5 | Abdominal pain, diarrhea, nausea and vomiting |
| DO | mg/L | 2.4 | 8.2 | 2.02 | 4.08 | - | - | |
| EC | mS/m | 1.74 | 5.1 | 1.4 | 3.15 | 1400 | | Laxative effects |
| TDS | mg/L | 1000.38 | 1980 | 310.67 | 1586.13 | 1500 | - | Aesthetic |
| Cr | µg/L | 2.26 | 73.05 | 24.66 | 26.14 | 20 | | |
| Mn | mg/L | 2841.6 | 18645.99 | 4843.31 | 9196.09 | 50 | 50 | Staining, discoloration |
| Co | µg/L | 74.65 | 376.11 | 102.92 | 163.96 | - | | Cancer, polycythemia |
| Ni | µg/L | 55.39 | 320.42 | 88.82 | 135.7 | 150 | | Skin allerges |
| Cu | µg/L | 7.48 | 60.14 | 15.88 | 23.74 | 1000 | 1300 | Anemia, Liver damage |
| Zn | µg/L | 182.68 | 1097.26 | 304.87 | 452.31 | 75 | | Nausea and vomiting |
| As | µg/L | 2.58 | 14.39 | 4.15 | 7.98 | 10 | - | Increased risks of lung and bladder cancer and skin changes |
| Pb | mg/L | 0.9 | 6.68 | 2.03 | 3.29 | 10 | - | Dealth or permanent damage to the brain and kidneys |
| Al | µg/L | 1.38 | 85.92 | 32.88 | 38.66 | 200 | 200 | severe trembling, loss of memory, dementia |
| Fe | mg/L | 6.7 | 234.3 | 79.78 | 76.94 | 1000 | | Anemia, weight loss |
| Ca | mg/L | 9.94 | 57.61 | 13.33 | 32.97 | | | growth retardation, reproductive failure |
| K | mg/L | 1.72 | 17.43 | 4.57 | 7.65 | | | Diarrhea, chest tightness |
| Mg | mg/L | 3.86 | 22.4 | 5.35 | 13.75 | | | laxative effect |
| Na | mg/L | 1.32 | 5.39 | 1.17 | 2.98 | | | Corrosion, contamination of freshwater streams |
| Si | | 6.2 | 48.57 | 15.21 | 25.06 | - | - | Lung cancer |

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## IV. CORRELATION ANALYSIS

Bivariate analysis, which evaluates the direction and magnitude of the relationship between two variables, is known as correlation. The correlation coefficient's numerical value ranges from +1 to -1, based on the strength of the relationship. A value of 1 signifies a perfect correlation between the two variables. As the correlation coefficient approaches zero, the association between the variables becomes weaker. The sign of the coefficient indicates the direction of the relationship, with a positive or no sign representing a positive relationship and a negative sign representing a negative relationship. In order to conduct factor analysis, it is necessary to be aware of the correlation coefficients between the parameters. These coefficients were computed to measure the extent of variance between specific pairs of water quality measures.

Table 4 shows a positive association between pH and Ca, K and Na, which suggests that Ca, K and Na increase with increasing pH and vice versa. This demonstrates that as pH rises, hydrogen ions (H+), which normally take the place of calcium and iron in minerals like clay, become less abundant. This can be the result of an ion exchange process alone. Only Ca, K, Mg and Na exhibit a negative connection with EC. While there is a high positive connection with TDS, Zn, As, Al and Fe; and a low positive correlation with Pb. TDS exhibits discernible positive association with other factors except Ca, K, Mg, and Na where there is demonstrable negative correlation. Ca exhibits a positive affinity for pH, Fe, and Zn, while exhibiting a negative affinity for DO, EC, TDS, Pb, As and Al. Mg exhibits positive affinities for Fe, Zn, Ca and K while exhibiting negative affinities for pH, EC, TDS and DO. It is clear that parameters with higher ion character have a stronger association than parameters with lower ion character. In general, the variety in connection demonstrates how complex the quality of groundwater is and how interactions between rock and water affect it.

Table 4 Correlation Analysis of Hydrochemical Parameters of Odagbo Coal Mine

| | PH | DO | EC | TDS | Zn | As | Pb | Al | Fe | Ca | K | Mg | Na | NO3 | PO4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PH | 1 | | | | | | | | | | | | | | |
| DO | -0.75781 | 1 | | | | | | | | | | | | | |
| EC | -0.70667 | 0.528485 | 1 | | | | | | | | | | | | |
| TDS | -0.43987 | 0.653348 | 0.249152 | 1 | | | | | | | | | | | |
| Zn | -0.84497 | 0.415131 | 0.632353 | 0.168704 | 1 | | | | | | | | | | |
| As | -0.83764 | 0.606294 | 0.695522 | 0.558578 | 0.823833 | 1 | | | | | | | | | |
| Pb | 0.305382 | -0.18818 | 0.0433 | 0.338543 | -0.44682 | -0.09059 | 1 | | | | | | | | |
| Al | -0.89575 | 0.663907 | 0.656287 | 0.481307 | 0.827701 | 0.944317 | -0.25934 | 1 | | | | | | | |
| Fe | -0.78817 | 0.392374 | 0.439176 | 0.048188 | 0.931339 | 0.659044 | -0.53244 | 0.676847 | 1 | | | | | | |
| Ca | 0.102318 | -0.25748 | -0.48708 | -0.43474 | 0.072987 | -0.38839 | -0.53304 | -0.29272 | 0.292494 | 1 | | | | | |
| K | 0.612029 | -0.56371 | -0.70539 | -0.60449 | -0.59134 | -0.82956 | -0.09043 | -0.7283 | -0.41317 | 0.676963 | 1 | | | | |
| Mg | -0.18493 | -0.07227 | -0.22509 | -0.31397 | 0.370866 | -0.09884 | -0.62676 | -0.01379 | 0.539821 | 0.947611 | 0.44749 | 1 | | | |
| Na | 0.145621 | -0.22203 | -0.46909 | -0.40058 | -0.13773 | -0.48888 | -0.39353 | -0.38552 | 0.051174 | 0.902629 | 0.813795 | 0.822048 | 1 | | |
| NO3 | -0.72511 | 0.302571 | 0.407735 | 0.031192 | 0.921624 | 0.593891 | -0.52454 | 0.640339 | 0.959823 | 0.357138 | -0.37885 | 0.59358 | 0.072771 | 1 | |
| PO4 | 0.000763 | -0.33492 | 0.039534 | -0.06507 | 0.156659 | -0.0401 | 0.262503 | 0.031029 | 0.108097 | 0.154628 | 0.037157 | 0.153989 | -0.01796 | 0.331191 | 1 |

## V. REGRESSION ANALYSIS

The regression analysis predicts the values of the responses for a given set of predictors as well as the relationship between one or more responses (dependent variables) and one or more predictors (independent variables). These variables are typically quantitative, that is, interval or ratio-based.

- *The Straightforward Correlation between those Variables can be Expressed Mathematically as follows:*

$$Y=F(Xi) \quad \text{.......................................} \quad 1$$

Where the independent variables are expressed by X, while the dependent variables are represented by Y. If the relationship between Y and Xi is linear, the regression would be linear; otherwise, it would be nonlinear. Regression analysis' primary goal is to model the dependent variables as a function of an independent variable (Duleba and Olive, 1996). In the statistical study of water resources data, simple linear regression analysis is absolutely crucial (Khan 2011). The description of the relationship between the variables of interest and the other variables may be made with the help of the analysis. It is utilized to forecast the values of one variable utilising information from another variable that has more data. I utilized the basic linear regression of the form in Equation 2 (Khan 2011) to conduct the regression analysis using the significant positive correlation between some of the parameters in Table 4 at the 0.01 level ($r < 0.05$):

$$Y= P_o + P_1X \quad \text{.......................................} \quad 2$$

Where Y and X are the dependent and independent variables, respectively; Po represents the coefficient of regression's intercept; and $P_1$ represents the slope. Equations 4 and 5 presents the regression equations for various water quality metrics that were assessed using Microsoft Excel version 2016:

pH= -8.7271DO + 35.031…………………………………..3

K = 0.2073Na + 1.3988……………………………………4

Zn = 0.0028$NO_3^-$ + 0.8552………………………………5

The results of the regression analysis shows that pH can directly be calculated from DO. This shows a positive trend with $R^2$ of 0.5743. The value of $NO_3^-$ can be calculated by measuring Zn with a strong regression value of 0.8494. The relationship between K and Na produced a trend (Figure 3). The relationship between these two parameters is strong ($R^2$= 0.6623). It is important to acknowledge that the level of confidence is not substantial; nonetheless, the examination aids in formulating inferences regarding the correlation of the variables within the designated research region, relying on the accessible data collections (Fatoba et al., 2011).

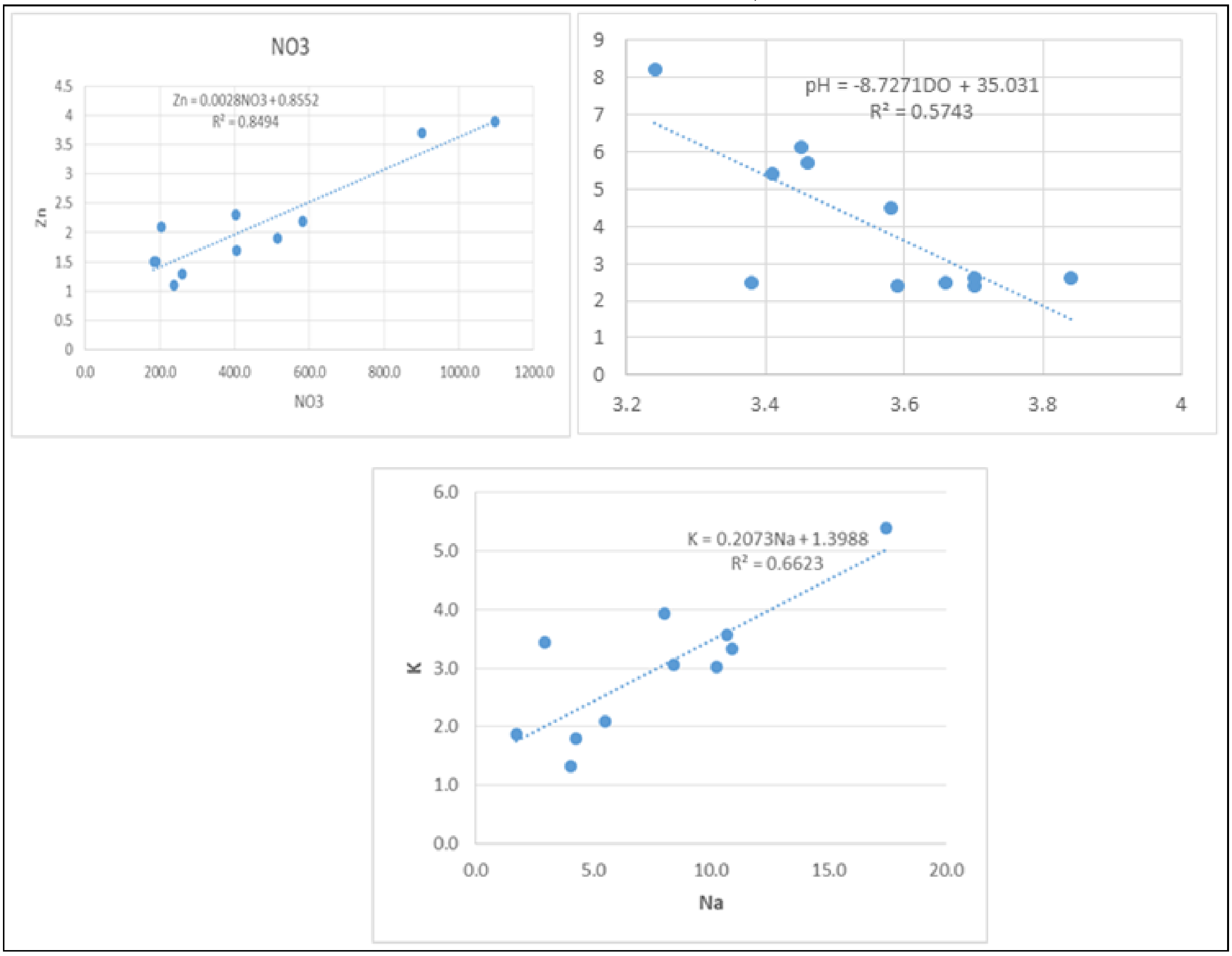


Fig 3 The Regression Plots of Zinc against Nitrate, pH against Dissolve Oxygen, Potassium against Sodium

## VI. CONCLUSION

In other to examine the hydrochemical data from 20 water samples, geostatistical approaches such as correlation and simple regression analysis were utilized to obtain some information that was initially unavailable in the research area to get some information that was not available at first glance. Sixteen parameters encompassing pH, EC, TDS, SO4, Na, Ca, Mg, Fe, Zn, Cu, and Pb were assessed. The average metal concentrations in the groundwater are ordered as follows: Mn>Zn>Co>Ni>Fe>Al>Cr>Cu>Ca>Si>Mg>K>As>Pb>Na. Most ion concentrations abide by the acceptable limits set by the WHO, with a few exceptions at certain locations where some metal concentrations slightly surpass both the desired and allowable thresholds. This could potentially be attributed to mining activities at Odagbo. Correlation analysis conducted within the study area reveals that the relationship between parameters with a high ion character is stronger compared to those with a lower ion character. The varying nature of this relationship emphasizes the intricacy of groundwater quality and the influence of interactions between rock and water. A regression analysis was employed to predict the values of one variable using the information from other variables, for which more extensive data were available.

Therefore, bivariate statistical techniques can be utilized to comprehend intricate water quality datasets and identify the primary factors and mechanisms governing the chemical composition of groundwater in the study area. These findings are crucial for the management of water quality. While bivariate statistical methods alone cannot directly elucidate hydrochemical processes, multivariate analysis can enhance our understanding of groundwater quality in the given area and the factors that drive such processes.

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