

## Hydrogeochemistry and Groundwater Quality Status of Paiko and its Environs, North-Central, Nigeria

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### Abstract

The susceptibility of groundwater within Paiko and its environs to pollution has increased due to increasing population, mining and agricultural activities. Hydrogeochemical studies of the area were carried out to assess the quality status, classify, and determine the hydrogeochemical processes of the groundwater in the area. Groundwater physical characteristics were analysed in the field with a hatch kit while the cations and anions were analysed in the laboratory with Micro-Plasma Atomic Emission Spectroscopy and Ion Chromatography respectively. 39% of the groundwater within the studied area was acidic, 11% of EC and, 10% of Total Dissolved Solid (TDS) were above the acceptable limits. The most abundant cations and anions were  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  respectively.  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^+$ , and  $\text{Hg}^{2+}$  values were higher than the acceptable limits in all samples while  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$ , and  $\text{SO}_4^{2-}$  values were higher than acceptable limits in some samples. The presence of these parameters above the acceptable limits in the groundwater of the area was attributed to geogenic and anthropogenic activities. Other parameters were within the acceptable limits except for  $\text{Co}^{2+}$ , and  $\text{V}^{3+}$  which have no base for comparison. The groundwater within the area can be classified as fresh with TDS values. Four hydrochemical water types (such as Mixed (Ca-Mg- $\text{SO}_4$ -Cl), Ca-Cl, Na-Cl and Mg- $\text{HCO}_3$ ) were identified by this study. Silicate weathering and reverse ion exchange are the major processes that control the hydrogeochemistry of the groundwater in the area. Treatment of groundwater in the area with some local materials has been suggested.

**Keywords:** Hydrogeochemistry, water quality, classification, geogenic, anthropogenic, Paiko

### INTRODUCTION

Freshwater accounts for approximately three percent of the world's water resources with two-thirds of this existing as ice that cannot be accessed easily (Olugboye, 2008). Groundwater however constitutes about 60% of the remaining one-third. The attributes that make groundwater very important

include its abundance, good quality (most of the time), low cost of development compared with surface water, availability in most areas, and the renewability of the resource (Nwankwoala, 2015). Hence, its importance for domestic, agricultural, and industrial purposes cannot be over-emphasized. However, it is faced with the threat of some natural processes (such as

oxidation and reduction reaction, dissolution of minerals in the aquifer and the media through which it moves) and anthropogenic activities (pollutants from activities such as agriculture, domestic, industries etc.) which could have negative effects on the quality and could reduce its usage. Improper waste management increases the pollution load in groundwater (Iqbal and Gupta, 2009). Agricultural activities could also result in the degradation of groundwater resources with organic and inorganic pollutants according to the Food and Agricultural Organization (FAO, 1992). Nitrate and phosphate are common pollutants from agricultural activities (Galadima et al., 2011; Sunitha et al., 2012). Solid waste and effluent when indiscriminately dumped into the environment could pollute the groundwater through infiltration or leaching, and these activities are considered the worst threat to groundwater quality (Bilal et al., 2014; Iqbal, 2016). Mining is a major source of metals to the environment causing pollution of air, soil, vegetation, surface, and groundwater resulting in various health problems for plants and animals including human beings (Aremua et al., 2010; Ameh and Akpah 2011; Ezeh and Chukwu, 2012; Lucky and Temitayo, 2017; Baba et al., 2018). Groundwater quality in Nigeria is affected by natural processes (I.e., geology, geochemistry, saltwater intrusion, and seasonal variation) and anthropogenic activities such as urbanization, domestic waste, industrial waste, Mining waste, and agricultural waste (Edet et al., 2011; Nwankwoala, 2011; Taiwo 2012; Ocheri et al., 2014; Omole et al., 2017). Areas within Paiko and its environs are experiencing a surge in population because it provides cheaper alternative inhabitation for those working within the cities of Abuja (the

Federal Capital Territory of Nigeria). Another reason for the increase in population in the area is the presence of some economic minerals within some localities and fertile land for agriculture. Increasing human activities arising from the increase in population will increase waste generation that could contaminate both surface and groundwater. Domestic, agricultural, mining and other industrial waste could negatively affect the physical and chemical characteristics of groundwater. Abnormal values of lead, potassium, and magnesium have been reported from surface water around the marble mining site around Kwakuti in the Northeastern part of the area (Ako et al., 2015). pH, conductivity, iron, zinc, and copper have been found in elevated quantities in groundwater from hand-dug wells within Lapai in the southwestern part of the area (Oladipo *et al.*, 2011; Amadi et al., 2017). The emergence of waterborne diseases makes the quality of groundwater a source of concern. Consuming contaminated water could result in irreversible damage. Some years back, Nigeria experienced various degrees of casualty arising from water-related diseases. The most notable was the lead poisoning within some villages in Zamfara (neighbouring state) and Rafi in Niger state, Nigeria where over 400 deaths were recorded in the former in the year 2010 while over 20 deaths were recorded in the latter in the year 2015 (MedicalXpress, 2015). These incidences were due to improper gangue disposal leading to the pollution of soil and water resources of the areas. Similar activities (especially gold mining) to those that have resulted in the casualties mentioned above are common in some localities such as Baban Tsauni, Dadabiri, Essan, Takuti, Buyi, Kwakuti,

Aninigi, Fiche Kuchi, Takalafia, Bakajeba, Zolegi, Ebbah, Pago, Butu, and Saminaka in the studied area. Lead-zinc mining is also active in the Baban Tsauni area and the mining of Marble is going on around Kwakuti within the area. These miners dump their gangue into the environment indiscriminately with little to no care for safe environmental practices. These wastes could either be eroded into surface water which could also contaminate groundwater if it is an influent stream or leached into groundwater directly. Some gold miners process their run-off mines in streams and rivers leaving behind gangue. Although some hydrogeochemical studies have been carried out, these studies were restricted to a few locations. The Nigerian Industrial Standard recommended on page 200 of the standard for drinking water quality that the quality status of groundwater should be reviewed at least once every three years according to the Nigeria Industrial Standard for Drinking Water Quality (NSDWQ) in 2007. Therefore, the study aimed to carry out hydrogeochemical classification, hydrogeochemical processes and quality status of groundwater for drinking purposes in Paiko, and its environs, and to also serve as a base for future research in the area. This could aid in the proper management and protection of groundwater resources, and by extension, the protection of public health (NSDWQ, 2007).

### **The Study Area**

The study area, Paiko, and its environs are located on latitude 9°00' to 9°30' and longitude 6°30' to 7°00' covering a total area of about 3080.25 km<sup>2</sup> (Figure 1). Accessibility is by main roads, secondary roads, main paths, and minor paths. The relief of the area has a minimum of 130

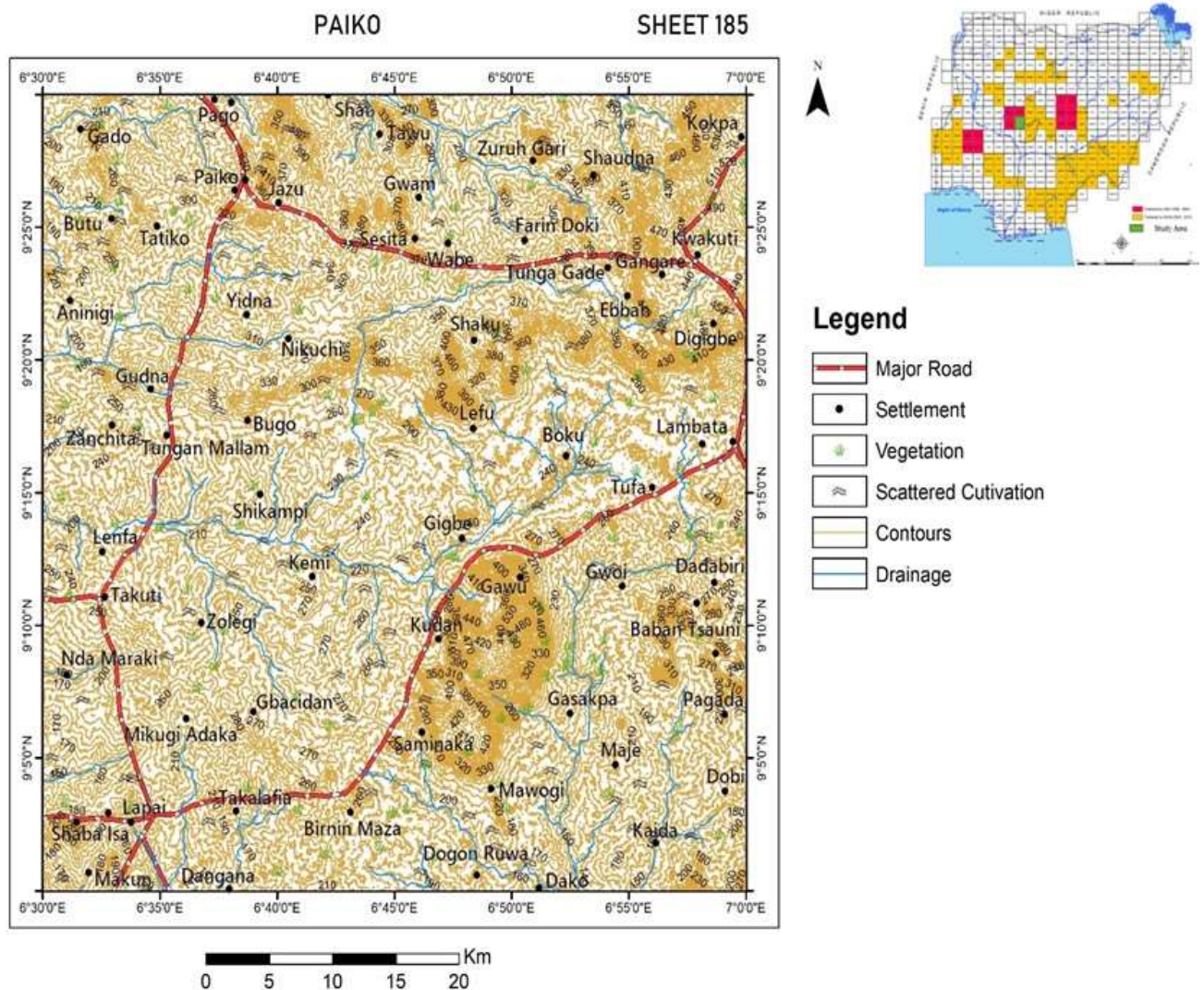
meters above sea level and a maximum of 600 meters above sea level. The area has mainly the dendritic type of drainage with streams and rivers that are either indirect or direct tributaries of River Niger. River Gurara which empties its content into River Niger directly is the largest drainage within the area. The area has a guinea savannah type of vegetation and is characterized by two (the wet season and the dry season) distinct climatic conditions (Njeze, 2011). The area is underlain by basement complex rocks amounting to about 85% and sedimentary rocks of approximately 15% (Figure 2). Lithologically, the area comprises Alluvium; Lateritic capped sandstone; Coarse-grained porphyritic Granite, Medium grained porphyritic Granite, Medium-coarse grained Tonalite, Amphibolite, Migmatitic in part; Migmatitic Gneiss and foliated granite, Marble, Phyllite, Schist interlayered with amphibolite; talc-tremolite-actinolite Schist rock and Migmatite according to the Nigerian Geological Survey Agency, NGSA (2009). Hydrogeological studies show that the fracture pattern within part of Paiko Town was distinct, localized, and noncontinuous (Amadi et al., 2013) and the average depth to the aquifer in part of Lapai was 36.75m (Tsepav et al., 2014). The yield of shallow sedimentary aquifers was between 1.4 to 2.8 l/s while those within granite/gneiss/migmatite ranged between 0.8 to 1.8 l/s (Idris-Nda et al., 2015). The accumulation and flow of groundwater in the area are largely controlled by rock types, fractures, and slopes (Ejepu et al., 2017).

### **Materials and Methods**

A random sampling technique was used to collect 59 groundwater samples each for both dry and wet seasons. Sampling points

are represented by the settlements in Figure 1. Sampling was done by groundwater sampling operating procedures developed for the United States Environmental Protection Agency (Jonathan 2013). The dry season sampling was done between March and April of 2021 while that of the wet season was done in October of 2021. The physical characteristics determined include groundwater pH, total dissolved solid (TDS), Electrical conductivity (EC), and temperature (T) with a hatch kit

containing the necessary tools for the measurements in the field. Samples were stored, transported, and analyzed following the groundwater sampling operating procedure manual (Jackson, 2000). Water chemistry was analyzed with Microwave Plasma Atomic Emission Spectroscopy (for cations) and Ion Chromatography (for anions) at the Centre for Dry Land Agriculture, Bayero University Kano, Nigeria.



**Fig. 1** Location map of Paiko and environs (inset is the map of Nigeria showing the studied area in green)

Rockwork 15 was used to plot Piper's Diagram and Durov's Diagram. Piper diagram was used to classify groundwater into hydrochemical facies using a geochemical interpretation of water analyses by Piper (1953); and Back (1966). Classification of groundwater according to the hydrochemical processes that have influenced the groundwater chemical composition with Durov's diagram was done using Lloyd and Heathcote (1985). Gibbs' plot (Gibbs, 1970) was used to establish the relationship between water composition and aquifer characteristics to show the effects of some factors such as rock-water interaction, rainfall dominance and evaporation dominance on groundwater chemistry. TDS of samples versus Equations 1 and 2 (Gibbs ratio I and II) was plotted to determine the influence of rocks, rainfall and evaporation on the chemistry of groundwater.

$$\text{Gibbs ratio - I} = \frac{\text{Cl}}{\text{Cl} + \text{HCO}_3}$$

Equation 1

$$\text{Gibbs ratio - II} = \frac{\text{Na} + \text{K}}{\text{Na} + \text{K} + \text{Ca}}$$

Equation 2

Ionic concentration ratios are also an important parameter that is useful in

understanding hydrogeochemical processes in groundwater (Lalumbe and Kanyerere, 2022). Therefore, ionic concentration ratios, such as  $\text{Na}^+/\text{Cl}^-$  vs. EC, Ca vs  $\text{HCO}_3$ , Ca vs  $\text{SO}_4$ , Ca + Mg vs Na, Ca + Mg vs  $\text{HCO}_3 + \text{SO}_4$ ,  $\text{Na}^+$  vs.  $\text{Cl}^-$ , Cl vs Na and  $\text{NO}_3$  vs K, were plotted on scattered plots to understand hydrogeochemical processes of the area. Chloroalkaline indices of Schoeller (1965) were also used to understand the geochemical processes that have affected the groundwater in the area concerning the interaction between the groundwater and the host rocks as in equations 3 and 4 below.

$$\text{CAI - I} = \frac{\text{Cl} - (\text{Na} + \text{K})}{\text{Cl}}$$

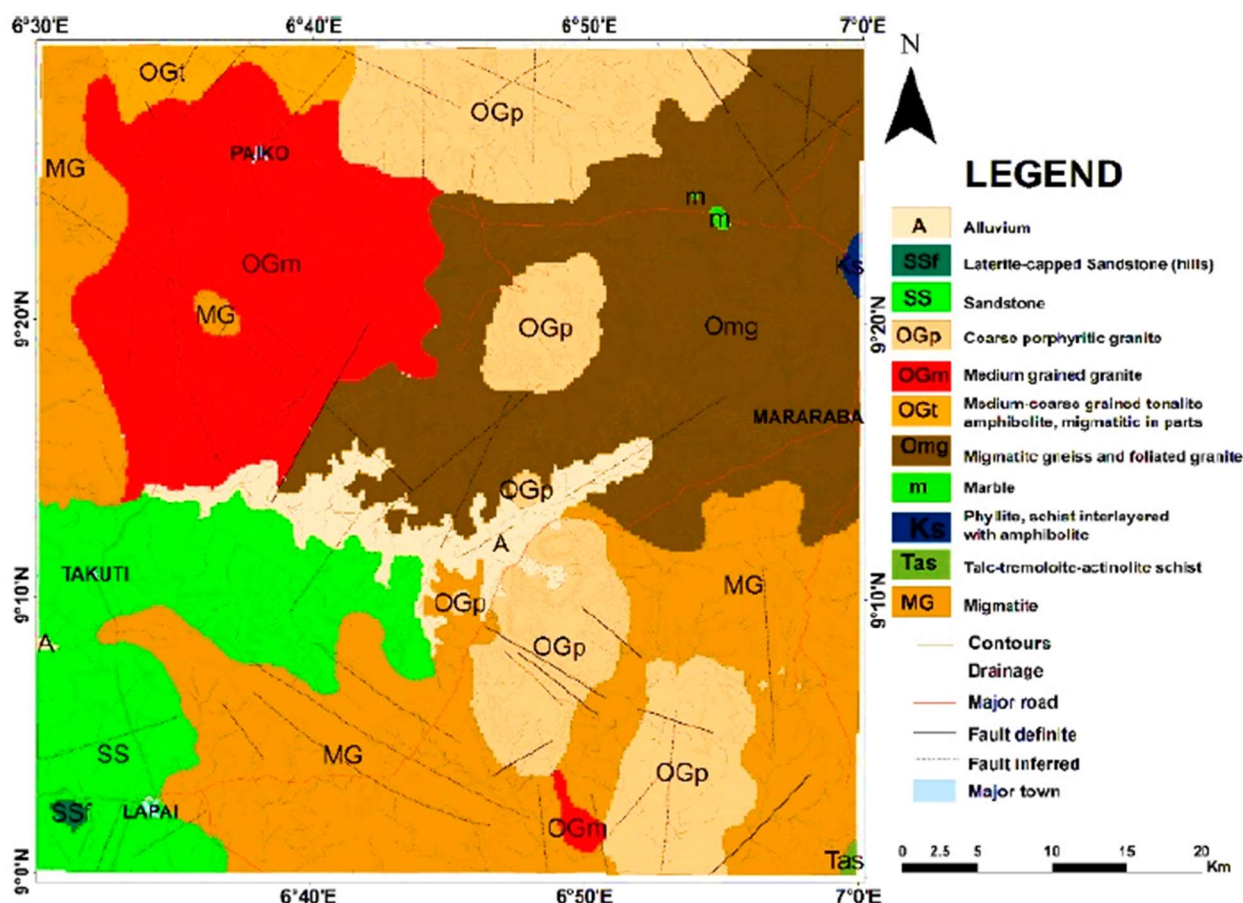
Equation 3

$$\text{CAI - II} = \frac{\text{Cl} - (\text{Na} + \text{K})}{\text{SO}_4 + \text{HCO}_3 + \text{NO}_3}$$

Equation 4

Physico-chemical results were compared with the known standards for drinking water quality such as the Nigerian Standard for Drinking Water Quality (NSDWQ), the World Health Organization (WHO), and the United States Environmental Protection Agency (USEPA) (NSDWQ, 2007; WHO, 2021; USEPA, 2000). The Pollution Index (PI) was calculated and classified groundwater in the area based on Nemerow and Sumitomo (1970).





**Fig. 2** Geological map of Paiko Sheet 185 (NGSA 2009)

## RESULTS AND DISCUSSION

### Hydrogeochemical Classification

The results of the physical and chemical parameters of groundwater samples from the area for both seasons are summarized in Table 1. The result was compared with the standards for drinking water quality to determine the percentage of parameters that are within and those that are outside the standards. The groundwater chemistry result shows that the mean order of abundance of cations is  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{As}^+ > \text{Al}^{3+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+} > \text{V}^{3+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+}$  while that of the anions is  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^{2-} > \text{CO}_3^{2-} > \text{F}^- > \text{NO}_2^-$ . All

anions were within the standards of NSDWQ 2007; WHO (2021); USEPA (2000) except  $\text{SO}_4$  which exceeded the standards of NSDWQ (2007) and USEPA (2000) in just one location (Lambata 2). Cations such as  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^+$ , and  $\text{Hg}^{2+}$  were higher than the standards of NSDWQ (2007); WHO (2021); USEPA (2000) in all samples. Others such as  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mn}^{2+}$  were higher than the standards of NSDWQ (2007); WHO (2021); and USEPA (2000) by 71%, 41%, 19%, 23%, and 15% respectively.

The remaining cations such as  $\text{Na}^+$  and  $\text{Zn}^{2+}$  were within the standards of NSDWQ (2007); WHO (2021); USEPA (2000). Cations such as  $\text{Co}^{2+}$ , and  $\text{V}^{3+}$  had no bases

for comparison with the standards of NSDWQ, NSDWQ (2007); WHO (2021); and USEPA (2000). The mean values of pH fall within the range of the standards of NSDWQ (2007); and WHO (2021) for dry season samples while it falls outside the range for wet season samples. Approximately 39% of groundwater was acidic and the southern half of the area had higher pH values than the northern half. TDS and EC had values that were within the standards of NSDWQ (2007) except in 10% and 11% of samples respectively. The classification of groundwater was done following the table of water classification with TDS values by Gorrell (1958). The

result shows that groundwater within the area can be classified as freshwater because all TDS values were less than 1000 mg/l for both seasons. This is an indication that the groundwater in the area has not been affected by saline water intrusion while short residence time (Singhal and Gupta, 2010) is also a factor that has kept the concentration of TDS within the freshwater range. Percolation of solids from channel water, agricultural water, industrial sewage and dissolution of host rocks are sources of TDS (Selvakumara et al., 2017) but the effects are still minimal in the groundwater of the area.

Table 1: Summary of chemical and physical parameters results of groundwater samples from Paiko and its environs for dry and wet seasons.

| Parameters       | Dry Season           |                       | Wet Season           |                       | Mean                              |                                       | Standards (S)      |                    |                  |
|------------------|----------------------|-----------------------|----------------------|-----------------------|-----------------------------------|---------------------------------------|--------------------|--------------------|------------------|
|                  | % of sample within S | % of sample outside S | % of sample within S | % of sample outside S | % Within dry and wet seasons of S | % Outside of dry and wet seasons of S | NSDWQ (2007), mg/L | USEPA (2015), mg/L | WHO (2012), mg/L |
| Cl               | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 250                | 250                | 250              |
| CO <sub>3</sub>  | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 100                | 250                | 450              |
| SO <sub>4</sub>  | 98                   | 2                     | 98                   | 2                     | 98                                | 2                                     | -                  | -                  | 150              |
| HCO <sub>3</sub> | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | -                  | -                  | 150              |
| F                | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 1.5                | 0.5                | 2                |
| NO <sub>2</sub>  | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 0.2                | 1                  | 0.2              |
| NO <sub>3</sub>  | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 50                 | 10                 | 50               |
| Na               | 100                  | 0                     | 100                  | 0                     | 100                               | 0                                     | 200                | -                  | 200              |
| K                | NA                   | NA                    | NA                   | NA                    | NA                                | NA                                    | -                  | -                  | 200              |

|     |     |     |     |     |     |     |         |          |        |
|-----|-----|-----|-----|-----|-----|-----|---------|----------|--------|
| Ca  | 100 | 0   | 100 | 0   | 100 | 0   | -       | -        | 75-200 |
| Mg  | 0   | 100 | 97  | 3   | 49  | 51  | 0.2     | -        | 100    |
| Al  | 0   | 100 | 0   | 100 | 0   | 100 | 0.2     | 0.05-0.2 | 0.2    |
| Zn  | 100 | 0   | 100 | 0   | 100 | 0   | 5       | 5        | 3      |
| Cd  | 0   | 100 | 100 | 0   | 50  | 50  | 0.003   | 0.005    | 0.003  |
| V   | NA  | NA  | NA  | NA  | NA  | NA  | -       | -        | -      |
| Fe  | 81  | 19  | 82  | 18  | 81  | 19  | 0.3     | 0.3      | 0.3    |
| Cu  | 100 | 0   | 100 | 0   | 100 | 0   | 1       | 1        | 1.5    |
| Ni  | 100 | 0   | 100 | 0   | 100 | 0   | 0.02    | -        | 0.02   |
| As  | 0   | 100 | 0   | 100 | 0   | 100 | 0.01    | 0.05     | 0.05   |
| Co  | NA  | NA  | NA  | NA  | NA  | NA  | -       | -        | -      |
| Hg  | 0   | 100 | 0   | 100 | 0   | 100 | 0.001   | 0.002    | 0.001  |
| Pb  | 49  | 51  | 92  | 8   | 75  | 25  | 0.01    | 0.15     | 0.01   |
| Cr  | 100 | 0   | 100 | 0   | 100 | 0   | 0.05    | 0.1      | 0.05   |
| Mn  | 86  | 14  | 93  | 7   | 89  | 11  | 0.2     | 0.05     | 0.1    |
| EC  | 88  | 12  | 90  | 10  | 89  | 11  | 1000    | -        | -      |
| pH  | 61  | 39  | 73  | 27  |     |     | 6.5-8.5 | 6.5-8.5  | -      |
| TDS | 89  | 11  | 92  | 8   |     |     | 500     | 500      | -      |

### Classification of water with Piper Diagram

A Piper diagram showing the plot of major ions is presented in Figure 3. The results of both seasons show that 53% of samples belong to the no dominant type, 30% belong to the Calcium type, 12% belong to the sodium and potassium type and 5%

belong to the magnesium type in the cations' equilateral triangle. 64% belong to the no dominant type, 24% belong to the sulphate type, 9% belong to the bicarbonate type and 3% belong to the chloride type in the equilateral triangle of anions in the Piper diagram. Diamond-shaped part of the Piper diagram also shows the point of the intersection of cations and anions.



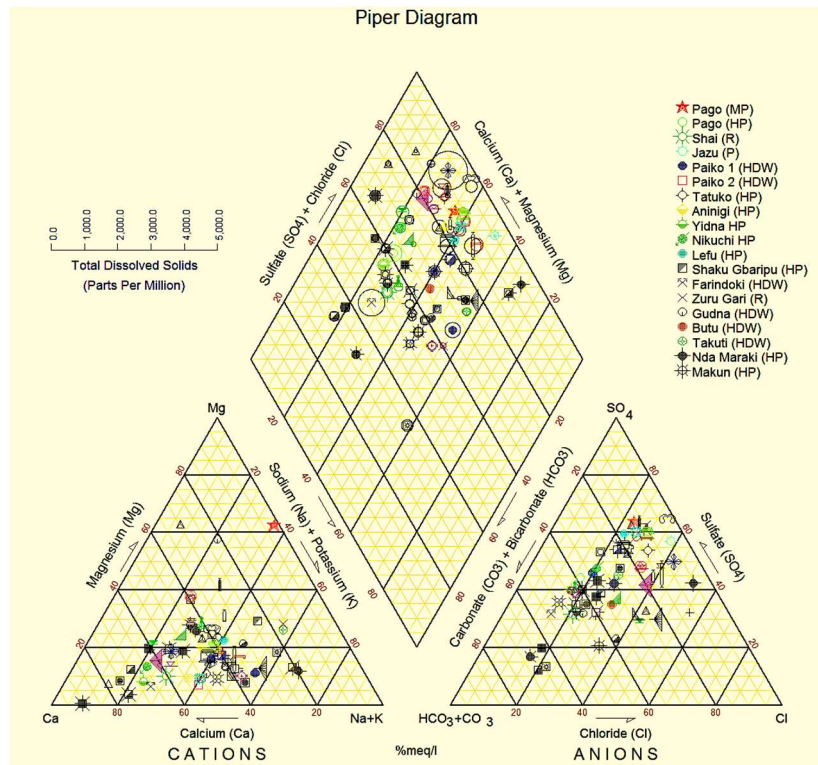


Figure 3: Piper diagram displaying water types for water samples from Paiko and its environs.

Most of the groundwater samples (about 92%) plotted within the region where strong acid exceeded weak acid in the central diamond-shaped diagram (Figure 3) while only 8% plotted in the region where weak acid exceeds strong acid. Approximately 57% of samples belong to the mixed water type (Ca-Mg-SO<sub>4</sub>-Cl), 24% belong to the calcium-chloride (Ca-Cl) water type, 13% belong to the sodium-chloride (Na-Cl) type and 6% belong to the magnesium-bicarbonate (Mg-HCO<sub>3</sub>) type. Ca-Cl water type results from mineral dissolution, rock-water interaction and recharge (Mondal and Singh, 2012). Chloride is a major anion that occurs naturally in all-natural water and constitutes a minor contaminant of groundwater (Kelly et al., 2012). The sources of chloride in groundwater include natural sources (such as the dissolution of chloride-rich minerals) and anthropogenic

sources such as urban runoff, saline intrusion, sewage and industrial effluents (WHO, 1993). Clays, feldspars, evaporites, and industrial waste are the common sources of sodium in groundwater (Singhal and Gupta, 2010). Sources of bicarbonate include soil and atmospheric CO<sub>2</sub>, and carbonates (Singhal and Gupta, 2010) while the dissolution of minerals rich in olivine, pyroxene and amphiboles are the common sources of magnesium in groundwater (Singhal and Gupta, 2010).

### Hydrogeochemical Processes

Durov's diagram (Figure 4) shows that approximately 80% and 88% of groundwater samples of dry and wet seasons plotted within field 5 respectively implied that there are no dominant anions and cations. Water samples without dominant anions and cations usually result

from simple dissolution or mixing hydrochemical processes according to Lloyd and Heathcote (1985). 7% and 10% of water samples plotted in field 6 of Lloyd and Heathcote (1985) meaning that  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  are the dominant ions which is a rare water type that may have occurred as a

result of mixing influence. 6% of water samples of respective dry and wet seasons plotted in field 4 of Lloyd and Heathcote (1985) with  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  as the dominant ions indicating either mixed water, or simple mixing for the dry season only.

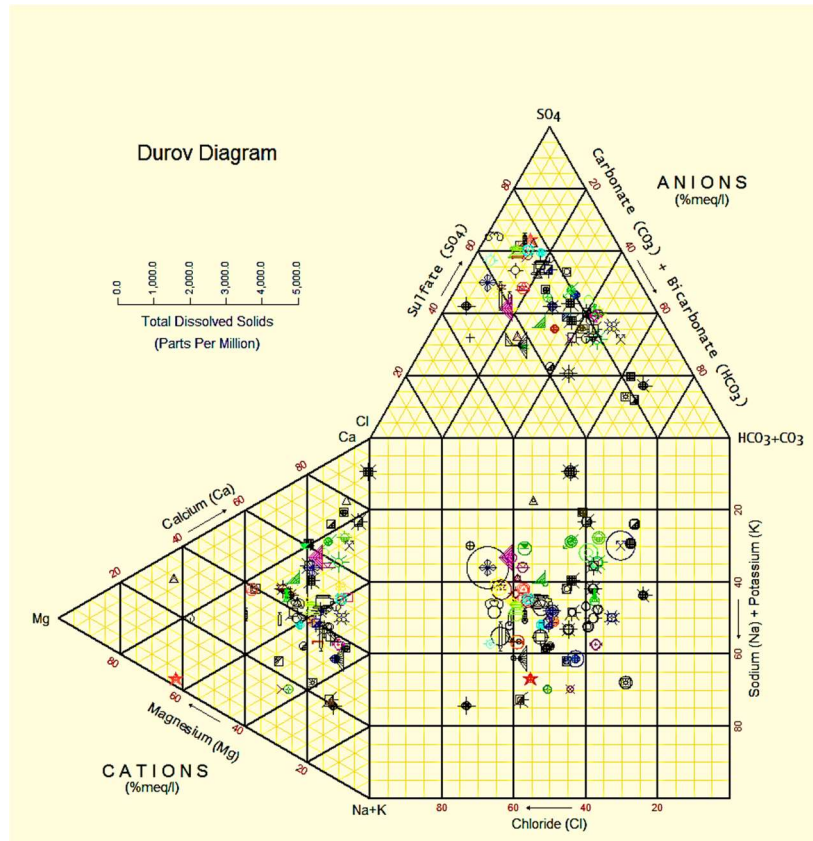


Figure 4: Durov's diagram displaying water types and hydrochemical processes for the water samples from Paiko and its environs.

However, simple mixing is suspected for samples plotted in field 4 of Lloyd and Heathcote (1985) as no evidence of lava was found in the area. 3% and 2% of samples plotted in field 9 of (Lloyd and Heathcote, 1985) meaning that  $\text{Cl}^-$  and  $\text{Na}^+$  are dominant and this frequently indicates endpoint waters for both seasons (Lloyd and Heathcote, 1985). Also, 3% of water samples plotted in field 8, and had  $\text{Cl}^-$  and  $\text{Na}^+$  dominance indicating that reverse ion exchange must have taken place for only the dry season (Lloyd and Heathcote, 1985).

1% of dry season water samples plotted within field 2 meaning that calcium and bicarbonate are the dominant ions signifying ion exchange process must have taken place and another 1% of water samples plotted within field 1 signifying that  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  are dominant, frequently indicating recharging water in limestone, sandstones, and other aquifers for only dry season (Lloyd and Heathcote, 1985).

Figures 5a and 5b show groundwater plots on a graph of TDS against Equations 1 and 2 respectively. Figures 5a and 5b show that all groundwater samples plotted within the rock dominance region which is an indication that weathering of host rocks and aquifer minerals are the main process that has affected the groundwater chemistry of the area.

The scattered plot of Na/Cl versus EC (Figure 6a) shows that 70% of the samples plotted above the broken line and in the region of silicate weathering or forward ion exchange. 24% of samples plotted below and in the region of Na reduction or reverse ion exchange while 6% of samples plotted in the transitional region (i.e., plotted on the

broken line). This suggests silicate weathering and forward ion exchange has the highest effect on the groundwater geochemistry of the area followed by the Na reduction or reverse ion exchange while a mixture of forward ion exchange and reverse ion exchange have the least effect. The scattered plot of Ca versus  $\text{HCO}_3^+$  (Figure 6b) shows 5% of the samples plotted above 1:1 (45° line) indicating carbonate weathering process. 87% of samples plotted below 1:1 (45° line) indicating carbonic acid (silicate) weathering while 8% of samples plotted in the transitional region (i.e., plotted on the 45° line) indicating mixed effects of both carbonate weathering and carbonic acid weathering.

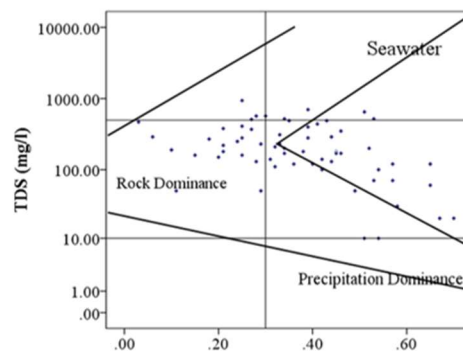
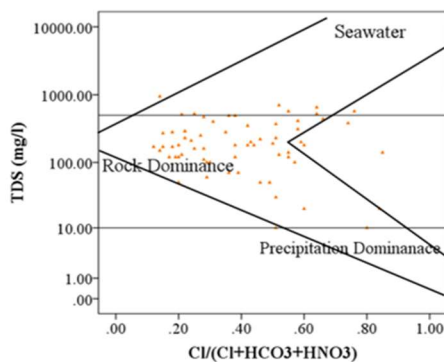


Figure 5a: Gibbs plot of TDS vs  $\text{Cl}/(\text{Cl}+\text{HCO}_3+\text{HNO}_3)$       Figure 5b: Gibbs plot of TDS vs  $\text{Na}+\text{K}/(\text{Na}+\text{Mg}+\text{Ca})$

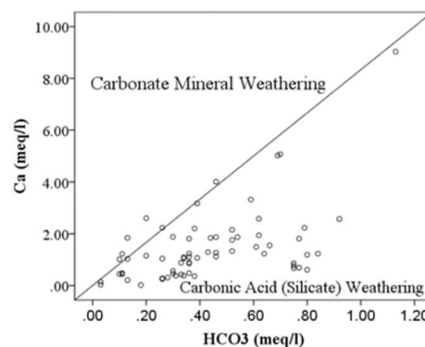
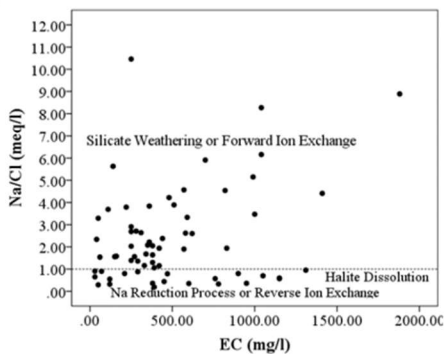


Figure 6a: Scattered plot of Na/Cl vs EC

Figure 6b: Scattered plot of Ca vs  $\text{HCO}_3$

The scattered plot of Ca versus SO<sub>4</sub> (Figure 6c) shows 19% of the samples plotted above the 1:1 line showing silicate weathering or reverse cation exchange as the geochemical process. 73% of samples plotted below the 1:1 line indicating a sulphide oxidation process while 8% of samples plotted on the 1:1 (45° line) showed the dissolution of calcite. The scattered plot of Ca + Mg versus Na (Figure 6d) shows 23% of the samples plotted

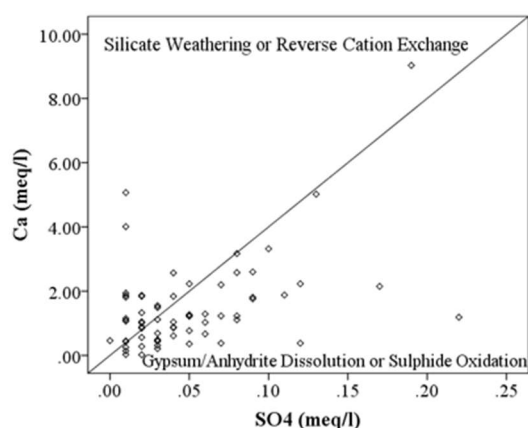


Figure 6c: Scattered plot of Ca vs SO<sub>4</sub>.

The scattered plot of Ca + Mg versus HCO<sub>3</sub> + SO<sub>4</sub> (Figure 6e) shows 18% of the samples plotted above the 1:1 line indicating carbonate weathering. 80% of samples plotted below the 1:1 line indicating the silicate weathering process while 2% of samples were in the transitional region (i.e., plotted on the 45° line) indicating that they have been affected by both carbonate and silicate weathering processes. The scattered plot of Na versus Cl (Figure 6f) shows that 3% of samples

above the 1:1 line indicating a reverse ion exchange geochemical process. The process that allows Ca and Mg to be released into groundwater (Reddy, 2013). 69% of samples plotted below the 1:1 line indicated a forward ion exchange process that allows Na to be released into groundwater (Reddy, 2013). 8% of samples were in transitional regions (i.e., plotted on the 45° line) which shows the effects of reverse ion exchange and forward ion exchange processes.

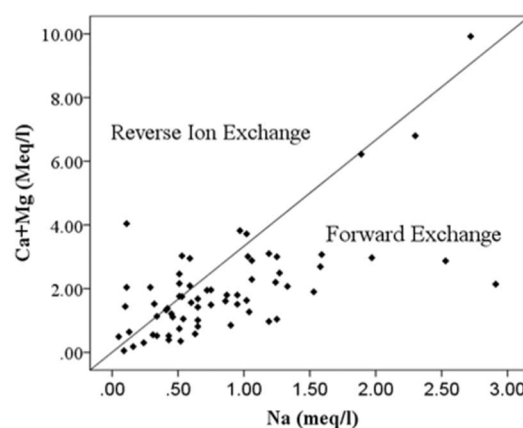


Figure 6d: Scattered plot of Ca + Mg vs Na.

plotted on the (1:1) 45° line while 97% of samples plotted outside the 1:1 (45° line). The samples plotted on 45° line 1:1 indicate that halite dissolution is the source of Na in groundwater while samples plotted outside 45° line indicate ion exchange and silicate weathering as the source of Na in groundwater (Egbueri, 2019). This implies that 3% of the sample of groundwater in the area has been affected by halite dissolution and 97% of the samples have been affected by the ion exchange and silicate weathering geochemical process.

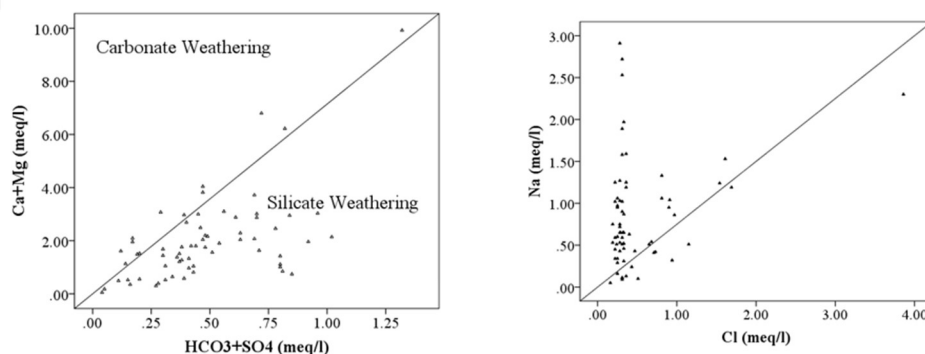


Figure 6e: Scattered plot of Ca + Mg vs  $\text{HCO}_3 + \text{SO}_4$ . Figure 6f: Scattered plot of Na vs Cl.

The scattered plot of Cl versus Na (Figure 6g) shows that 17% of samples have been influenced by anthropogenic activities while 83% of samples have been influenced by ion exchange or silicate weathering. The scattered plot of  $\text{NO}_3$  versus K (Figure 6h)

suggests the usage of fertilizer as the main source of  $\text{NO}_3$  in about 52% of the samples. CAI-I and CAI-II show that 26% of samples have positive values indicating a forward ion exchange while 74% of samples have negative values indicating a reverse ion exchange.

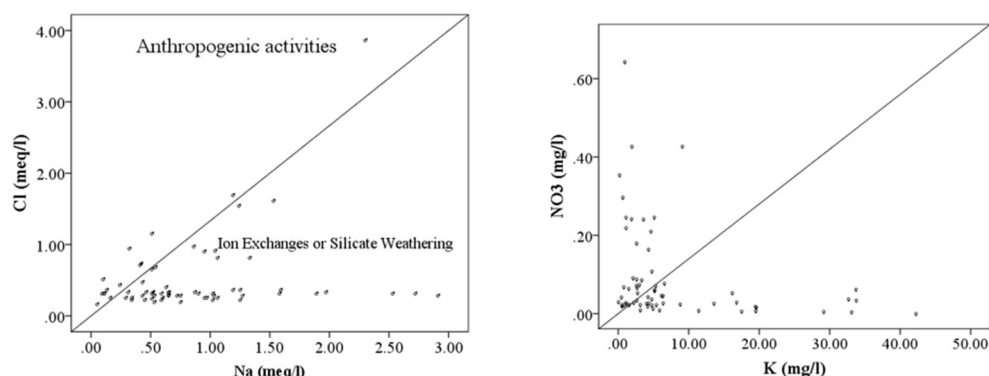


Figure 6g: Scattered plot of Cl vs Na.

Figure 6h: Scattered plot of  $\text{NO}_3$  vs K

## Pollution Index

The pollution index (PI) values of dry season and wet season groundwater samples are presented in Table 2. The classification of the pollution index was done according to Sargaonkar and Deshpande, (2003) who classified the pollution index into Excellent ( $C_1$ ), Acceptable ( $C_2$ ), Slightly polluted ( $C_3$ ), polluted ( $C_4$ ), and heavily polluted ( $C_5$ ). Water with PI of  $C_1$  and  $C_2$  can be consumed without treatment, those with PI

of  $C_3$  can be consumed with minimal treatment while those with  $C_4$  and  $C_5$  require serious treatment before it can be consumed.

Some parameters (such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{As}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and TDS) have higher pollution index (PI) values in dry season while others (such as  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cr}^{2+}$  and pH) have higher values in the wet season (Table 2). Table 2 also shows that  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,

$\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{2+}$ , EC, pH, and TDS in the dry season groundwater samples from the area were classified as excellent.  $\text{SO}_4^{2-}$  and  $\text{Mn}^{2+}$  in groundwater within the area were classified as acceptable.

There was pollution of groundwater by  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  in the dry season groundwater samples. The PI results (Table 2) also show that parameters such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{2+}$ , EC, pH, and TDS in wet season groundwater samples were classified as excellent. The groundwater within the area contains acceptable levels of  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  and is polluted by  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$  for wet season samples. There was pollution by  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{As}^+$ , and  $\text{Hg}^{2+}$  ions in wet season samples. These results imply that groundwater samples from the area are polluted with some heavy metals ( $\text{Hg}^{2+}$ ,  $\text{As}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{2+}$ ), K,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$ .

### Groundwater Drinking Water Quality

Table 1 shows that the groundwater of the area cannot be consumed directly without treatment as elevated amounts of some parameters such as  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^+$ , and  $\text{Hg}^{2+}$  were found in all the samples analyzed.  $\text{K}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$  were also found in an elevated amount in some of the samples analyzed. These parameters could have negative health effects on consumers. The high concentration of sulfate in the groundwater of Lambata HP could be attributed to geogenic sources such as the oxidation of Sulphur-rich minerals. Mining of Sulphide-rich minerals is going on within the neighbourhood (BabanTsauni) of Lambata.

Anthropogenic sources from pesticide and fertilizer application (Schwartz and Zhang, 2003) are the most likely reason for the elevated amount of sulfate in groundwater around Lambata HP as lead ore deposit around Baban Tsauni that could have contributed is many kilometres away from this location. Geogenic activity such as the dissolution of rocks and minerals rich in these pollutants as suggested by Singhal and Gupta (2010) is the main source of Fe, Pb, Mn, Ni, As, Hg, Al, and Mg in the groundwater of the area. Anthropogenic activities such as agriculture and mining as suggested by Brian et al. (2008); Singhal and Gupta (2010); and Fetter et al. (2018) also contribute to the metals (such as Pb, Mn, Ni, As, and Hg) load in the groundwater of the area.

The physical parameter results also show that about 39% of the samples analyzed were acidic. This is generally common in the southern part of the area. All locations with low pH are not associated with mining activities except in Ebbah and Butu Paiko where gold mining activity is active. Higher temperature (T) recorded in some samples is an indication that the groundwater has higher residence time (Fetter, 2001); higher EC observed in some samples is an indication of high ionic concentration and higher TDS indicates higher mineral dissolution (Singhal and Gupta, 2010) and residence time (Screaton et al., 2004). Groundwater interaction with granitic rocks or its equivalent metamorphic rocks (Singhal and Gupta, 2010) and clay (Alshammari et al., 2021) was responsible for the low pH or acidity observed in some samples especially samples from the southwestern part of the area.



Table 2: Pollution index values of dry season and wet season

| Parameters       | PI (Dry Season) | PI (Wet Season) | PI (Dry and Wet Season Average) | Class index score | Class          | Classification |
|------------------|-----------------|-----------------|---------------------------------|-------------------|----------------|----------------|
| Cl               | 0.27            | 0.17            | 0.2                             | 0-1               | C <sub>1</sub> | Excellent      |
| CO <sub>3</sub>  | 1.09            | 0.17            | 0.6                             | 1-2               | C <sub>2</sub> | Excellent      |
| SO <sub>4</sub>  | 0.32            | 0.26            | 0.3                             | 0-1               | C <sub>1</sub> | Excellent      |
| HCO <sub>3</sub> | 0               | 0               | 0.0                             | 0-1               | C <sub>1</sub> | Excellent      |
| F                | 0.006           | 0.89            | 0.4                             | 0-1               | C <sub>1</sub> | Excellent      |
| NO <sub>2</sub>  | 0.17            | 0.26            | 0.2                             | 0-1               | C <sub>1</sub> | Excellent      |
| NO <sub>3</sub>  | 0.14            | 0.066           | 0.1                             | 0-1               | C <sub>1</sub> | Excellent      |
| / P              | 0.45            | 0.097           | 0.3                             | 0-1               | C <sub>1</sub> | Excellent      |
| Na               | 6.53            | 4.55            | 5.4                             | 4-8               | C <sub>5</sub> | Polluted       |
| K                | 3.58            | 6.53            | 5.06                            | 4-8               | C <sub>5</sub> | Polluted       |
| Ca               | 0.47            | 0.032           | 0.3                             | 0-1               | C <sub>1</sub> | Excellent      |
| Mg               | 15              | 1.67            | 6.84                            | 4-8               | C <sub>5</sub> | Polluted       |
| Al               | 4.88            | 6.067           | 5.5                             | 4-8               | C <sub>4</sub> | polluted       |
| Zn               | 0.025           | 0.016           | 0.0                             | 0-1               | C <sub>1</sub> | Excellent      |
| Cd               | 7.25            | 1               | 4.1                             | 4-8               | C <sub>4</sub> | polluted       |
| V                | 7.21            | 6.12            | 6.67                            | 4-8               | C <sub>5</sub> | Polluted       |
| Fe               | 7.05            | 6.02            | 6.54                            | 4-8               | C <sub>5</sub> | Polluted       |
| Cu               | 9.5             | 4.36            | 6.93                            | 4-8               | C <sub>5</sub> | Polluted       |
| Ni               | 0               | 0.14            | 0.1                             | 0-1               | C <sub>1</sub> | Excellent      |
| As               | 1.35            | 1.25            | 1.3                             | 1-2               | C <sub>2</sub> | Acceptable     |
| Hg               | 8.05            | 6.72            | 7.39                            | 4-8               | C <sub>5</sub> | Polluted       |
| Pb               | 10.5            | 4.36            | 7.43                            | 4-8               | C <sub>5</sub> | Polluted       |
| Cr               | 0               | 0.14            | 0.07                            | 0-1               | C <sub>1</sub> | Excellent      |
| Mn               | 1.35            | 1.25            | 0.8                             | 0-1               | C <sub>1</sub> | Excellent      |
| EC               | 0.94            | 0.7             | 0.8                             | 0-1               | C <sub>1</sub> | Excellent      |
| pH               | 0.59            | 0.62            | 0.6                             | 0-1               | C <sub>1</sub> | Excellent      |
| TDS              | 0.94            | 0.61            | 0.8                             | 0-1               | C <sub>1</sub> | Excellent      |

## Remediation Measures

Treatment of water using modern techniques can be capital intensive, especially considering the studied area is dominated by rural communities. Some water projects exist because of individual and/or communal efforts. Therefore, it will be difficult for the inhabitants to address this issue with modern treatment facilities. There are however inexpensive agricultural waste materials such as rice husk, maize cub, neem bark, black gram, Turkish coffee, walnut shell, and grape stalk waste that are readily available in the area and can effectively remove heavy metals from water using guidelines described by El-Said et al. (2012); Tripathi and Ranjan (2015); Muhammad et al. (2020); Yang et al. (2020); Magaji and Saleh (2021). A composite of silica and activated charcoal is also capable of removing heavy metals such as Cd, Pb, As, and Cr from water using guidelines described by Kelly et al. (2012). These readily available local materials can be used to reduce the metal load in the groundwater of the area to reduce the potential for negative consequences on the consumers. Low pH or acidity in water can be neutralized with limestone and slaked lime in line with the procedure described by Bertills and Sundlöf (1995), limestone by Philip et al. (2006), laterite, concrete waste, and limestone by Turingan et al. (2022).

## Conclusion

The order of abundance of cations is  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{As}^+ > \text{Al}^{3+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Hg}^{2+} > \text{Zn}^{2+} > \text{V}^{3+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+}$  while that of the anions is  $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^{2-} >$

$\text{CO}_3^{2-} > \text{F}^- > \text{NO}_2$ . Some chemical parameters such as  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^+$ , and  $\text{Hg}^{2+}$  were higher than the acceptable limit in all samples while  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$ , and  $\text{SO}_4^{2-}$  were higher than the acceptable limits in some samples.  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{F}^-$ , and  $\text{NO}_2$  were within the acceptable limit in all samples.  $\text{Co}^{2+}$ , and  $\text{V}^{3+}$  had no bases for comparison. About 39% of groundwater was acidic while 11% and 10% of EC and TDS were above the acceptable limits respectively. The groundwater was classified as freshwater based on TDS values. Mixed water type is the dominant water type while calcium-chloride water type, sodium-chloride type and magnesium-bicarbonate types are other water type existing in the area. Simple dissolution was the dominant hydrochemical process that affected the quality of groundwater within the studied area. Other hydrochemical processes that have influenced the groundwater of the area include recharging water in sandstones and other aquifers, reverse ion exchange, and mixed water. Medium to high ionic concentration was common in locations that were closer to mining sites. Gibbs plots show that the weathering of host rocks and minerals is the source of ions in the groundwater of the area.

The geochemical processes that have influenced the presence of major ions in the groundwater of the area are silicate weathering and forward ion exchange for Na and K, and silicate weathering and reverse ion exchange for Ca and Mg. Carbonic acid (silicate) weathering is the source of  $\text{HCO}_3^-$  while  $\text{SO}_4^{2-}$  result from the sulphide oxidation process. The source of  $\text{Cl}^-$  is ion exchange and silicate weathering. CAI-I and CAI-II results

show that the effect of reverse ion exchange is about three times greater than that of forward ion exchange on the geochemical evolution of the groundwater in the area. Thus, silicate weathering (reverse ion exchange) is the dominant geochemical process in the area. The groundwater of the area was polluted by  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{Pb}^{2+}$  as shown by the pollution index result. The presence of these pollutants in the groundwater of the area is attributed to geogenic and anthropogenic activities. The groundwater from the area cannot be consumed without treatment. Purification with materials such as rice husk, maize cobs, and a composite of silica and activated charcoal is recommended for use to reduce the metal load of the

groundwater. A periodic review of the groundwater quality of the area is also recommended.

## Abbreviations

FAO, Food and Agricultural Organization; TDS, total dissolved solids; EC, Electrical conductivity; T, temperature; CAI, Chloroalkine Index; PI, Pollution Index; NSDWQ, Nigerian Standard for Drinking Water Quality; WHO, World Health Organization; USEPA, United State Environmental Protection Agency.

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