Review article

Hydrogeochemical and salinity appraisal of surficial lens of freshwater aquifer along Lagos coastal belt, South West, Nigeria

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ABSTRACT

In order to determine the hydrogeochemical processes and salinity status of the surficial lens of freshwater aquifer in the Lagos coastal basin, physicochemical parameters and hydrogeochemical tools were employed in this study. These tools include existing methods such as Piper diagram, Durov diagram, Gibb's diagram, statistical analysis and geochemical modelling, and the newly proposed cationic contribution evaluation and ionic ratio bivariate plots. The Piper plot revealed that chemical facies is rich in (Ca, Mg, Cl and HCO$_3$) and (Ca and HCO$_3$) for the groundwater in both wet and dry seasons while Mg-Cl and Na-Cl water types characterised the lagoon and the Ocean, respectively. The surficial aquifer is an essentially freshwater in the dry season and partly saline in the wet season due to flash flood, marine aerosol precipitation and infiltration from the surrounding brackish surface waters. The Ca$^{2+}$/Mg$^{2+}$ vs total cation (TZ$^{+}$); HCO$_3$/Ca$^{2+}$/Mg$^{2+}$ and HCO$_3$/Ca$^{2+}$/Na$^{+}$ plots as well as geochemical modelling indicated that carbonate weathering is the dominant chemical process controlling the groundwater chemistry for both seasons. In a descending order, water-rock interaction, ion exchange and evaporation are the geochemical processes controlling the groundwater quality in the area. Besides the natural processes, factor analysis revealed the imminent influence of anthropogenic activities (industrial and domestic) on the groundwater chemistry indicated by the presence of Mn, Fe, Ni, Cd, Pb, Cu and NO$_3$ above the permissible limit of drinking water standard, particularly in the wet season. In addition to the successful application of the proposed ionic plots, the study justifies the importance of multiple tools application in the hydrogeochemical deductions and recommends consistent monitoring of the shallow aquifers in the Lagos coastal basin.

1. Introduction

Groundwater is undoubtedly the most precious and endowed natural resource. It plays a vital role in the water supply, ecology, social and economic development of a particular region (Yusuf et al., 2018). The quality of groundwater is as important as its quantity in order to support and sustain life. Groundwater quality is influenced by natural processes such as the composition of precipitation and geological structure, geochemical processes, the interaction between the groundwater and aquifer matrix, and saline intrusion or modification can occur via anthropogenic activities, such as industrialization, urbanization and land use patterns (Jalali, 2007; Subramani et al., 2010; Avtar et al., 2013). In a typical humid and coastal region, several processes, such as precipitation, evaporation, sea-water intrusion, mineral dissolutions and precipitation of minerals, oxidation-reduction and biological processes, ion-exchange, rock-water interaction could be involved in the groundwater chemistry at the same time (Singh et al., 2011; Ji et al., 2020). The consequent interaction of these factors evolves into various water types and are responsible for the seasonal and spatial variations in groundwater chemistry (Rajmohan and Elango, 2004; Belkhiri and Mouni, 2012).

In Turkey, Guler et al. (2012) found that both anthropogenic activities and natural processes influenced groundwater chemistry in Tarsus Coastal Plain, Turkey. Similarly, the deterioration of surface water quality in Lagos Coastal Basin (LCB) is reportedly caused by anthropogenic activities, such as industrial effluent, sewage disposal, etc (Yusuf et al., 2018). The water requirement of this region has increased in recent times due to population growth, industrialization, accelerated tourism development and urbanization with most of the water demands derived from unconfined or semi-confined aquifer through a number of large shallow wells (Yusuf et al., 2018). The stress on groundwater is further aggravated by incessant discharge of untreated sewage into neighboring lagoon, creeks, streams and canals, and the subsequent leakage of the

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contaminants to the underlying shallow aquifer, thereby causing water pollution. As a consequence of these factors, groundwater contaminants in the present study area may be classified into two, namely: contaminants which migrate as leachates from surface into groundwater and subsurface pollutants in the form of saline water intrusion (Yusuf and Abiye, 2019). Salinization of groundwater is an issue of major concern particularly in the coastal areas of the world and it has become a major threat to the quality of the adjoining freshwater aquifers (Yusuf and Abiye, 2019).

The aim of the current study was to characterise the shallow groundwater chemistry and to evaluate its seasonal variability to gain fresh insight into the evolution and dominant chemical processes controlling water chemistry of Lagos Coastal Basin (LCB). Many authors have developed various methods to assess the hydrogeochemical processes and geochemical evolution on a basin scale. These include the works of Datta and Tyagi (1996), Fisher and Mullican (1997), Adams et al. (2001) and Subramani et al. (2010). An attempt was made to evaluate the groundwater quality of the present study area using geochemical method by Adewuyi et al. (2010), Akoteyon et al. (2011). Later, few samples were studied to assess the mixing proportions of the groundwater in this region by Ayolabi et al. (2013), Oyeyemi et al. (2015) and Yusuf and Abiye (2019). However, detailed hydrogeochemical processes with seasonal variations in this region using ionic processes, saturation indices and statistical method are still lacking; hence, necessitating the present study.

Based on Dalton and Upchurch (1978) conventional methods such as the use of Durov, Schoeller plots and Piper (1944) are limited to assessment of major ions in groundwaters, while minor ions such as NO₃ and trace metals, whose presence in elevated levels portend danger for human health, were excluded (Guler et al., 2002). Meanwhile, it is noteworthy that statistical methods, such as Factor analysis (FA) and Principal Component Analysis (PCA) are capable of analyzing all water parameters in an analytical suite through data reduction and classification (Dalton and Upchurch, 1978; Masindi and Abiye, 2018). Furthermore, due to variations and unique peculiarity of every geographical location across the globe, the current research proposed new ionic ratio(s) formula and bivariate plots besides the use of existing statistical method and geochemical model to evaluate the dominant chemical processes controlling the shallow groundwater chemistry. Hence, it is hoped that the present study will contribute to improved understanding of the hydrogeochemical characteristics of the surficial groundwater in the study area.

2. Main text

2.1. Description of the study area

The port city of Lagos is located in the southwestern part of Nigeria, a zone of coastal creeks and lagoons (Elueze and Nton, 2004). The state is bound in the south by the 180 km long Atlantic coastline, while it is bordered in the northern and eastern ends by Ogun State and sharing a boundary with Benin Republic at the western limit. The coastal city of Lagos has a total landmass of about 3,577 km² out of which approximately 787 km² (22 %) is occupied by water (Odumosu et al., 1999). Lagos, unlike the northern part of the country, is very humid with a relative humidity of above 70 % throughout the year (Ogunde, 2012). The region falls into a tropical climatic region characterised by hot and wet conditions associated with the movement of the Inter-Tropical Convergent Zone (ITCZ) north and south of the equator. The annual average rainfall of about 1,800 mm/a (70 inches) was reported for Lagos by Oke (2015). Eighty percent of the annual rainfall (1,440 mm) falls during the southwest monsoon (April to October) and the remaining twenty percent (360 mm) falls during the northeast monsoon (November to March). The area is characterised by two major seasons; the wet season spans between April and November while the dry season covers the months of December to March. Temperatures peaked in the dry season with the maximum temperature ranging between 29 °C and 34 °C and lowest in the wet season with the minimum temperature ranging between 24 °C and 28 °C (Ogunde, 2012).

The study area is situated within the coastal plain sand (CPS) aquifer of Lagos and lies between longitudes 3014°E to 3053°E and latitudes 6020°N to 6030°N. It is bordered in the east by Ibeju-Lekki, in the west by Apapa, in the north by lagoon, and in the south by the Atlantic Ocean (Figure 1). The study area is a densely populated region comprising industrial and residential in the west, commercial and residential in the central, while the eastern segment (Eti-Osa) is predominantly a residential and tourism domain. It is a typical hydrological complex terrain situated at the discharge zone where all the surface waters such as rivers, streams, canals, and creeks from the upstream are connected to the lagoon that eventually linked them to the Ocean.

The relief of the study area is generally low-lying alluvial plain that it is roughly about 35 m above the sea level. The area is generally characterised with a shallow water table (as shallow as 0.2 m) and depressions were observed in some places along the coastal belt which are prone to flooding, as they are apparently below the surface of the lagoon (Figure 2). Based on the worst flood occurrence in Lagos state in the year 2011, in which the supposed rainfall of 264 mm for one full month was recorded in less than a day (Kalu, 2011), the calculated average threshold of 0.37 mm/h, or 8.8 mm/day maybe proposed as the threshold for the study area beyond which floods will occur. A comparison of this threshold with the average of 15.53 mm/h that it rained in less than a day in 2011 was 42 times more than the proposed threshold value. It is, therefore, not surprising that the National Emergency Management Agency tagged the event as the most devastating flood occurrence in Lagos State.

The geology of Lagos has been described in detail in several research studies conducted on the Lagos metropolis and its environs by (Jones and Hockey 1964; Aisivuaju-Bello and Akanade, 2001). The geology consists essentially of rocks that cover geological records from Precambrian to Recent (Figure 3).

Also, the general stratigraphic setting of the Dahomey basin have been extensively discussed by Omatsola and Adegoke (1981) and Adekeye (2005) among others (Figure 4).

The lithological characteristics of the sedimentary outcrops that are in the southwestern part of Nigeria explain the nature, type and extent of the aquifer system that occurs in the Lagos metropolis. The average water level of 1.6 m and 2.45 m were reported for both wet and dry seasons, respectively (Yusuf, 2020). Contrary to the general N–S groundwater flow direction in cosmopolitan city of Lagos, the study area exhibited multiple groundwater flow directions dictated by surface water with dominant influence draining a particular domain and the subsurface topographical features (Yusuf and Abiye, 2019). According to Adelana et al. (2005) and Yusuf et al. (2018), there are four aquifers that are identified in the Lagos metropolis:

The upper aquifer extends from the ground level to roughly 12 m below the ground. This consists of alternating layers of sand and clay. It is of minor importance and exploited to some extent through the use of shallow hand-dug wells for drinking and domestic purposes. It is also useful as a good source of recharge for the underlying aquifer systems. The second layer aquifer system is of great importance for water supply purposes throughout Lagos State. This aquifer layer occurs between 20 m and 70 m below the sea level (mbsl) in the northern part of Lagos and dips to between 40 mbsl and 100 mbsl near the coast (Adelana et al., 2005). It is estimated that about 75% of the groundwater uses for domestic and industrial purposes in Lagos State are abstracted from this second aquifer. The third layer aquifer underlying the greater part of Lagos is found in the central part of Lagos at elevations ranging from 130 mbsl to 160 mbsl, and dipping towards the coast where it has a range of between 170 mbsl and 210 mbsl with a thickness of between 15 m and 30 m. This aquifer layer also sustains several industrial boreholes in Lagos State. The major aquifer in the state comprises the upper and lower coastal plain sand constituting the second and the third layers aquifer. The fourth layer aquifer is located at elevations of about 450 mbsl. It is
separated from the third aquifer by a rather thick layer of shale of the Ewekoro formation.

2.2. Materials and methods

The phreatic water samples were collected from the shallow groundwater through large diameter wells from 45-dug wells in wet (October, 2016) and dry (February, 2017) seasons, respectively. The surface water samples, however, were taken at least 250 m away from onshore areas and below the surface (>20 cm) to avoid collection of floating debris and ensure even mixing as well as relatively adequate representation. The first step was to locate the sampled points, thus coordinates were taken with the aid of Global Positioning System (GPS). The wells water was thoroughly mixed before the groundwater samples could be taken with the aid of a suspended bucket. The surficial groundwater sampling depths are generally less than 10 m. Waters were sampled for various multi-elements analyses. The analytical details of both groundwater and surface waters samples is presented in Table 1.

The water samples were collected in a pre-cleaned and tightly sealed polyethylene bottle to prevent contamination and evaporation of the water samples. Sampled waters were kept under 4 °C to reduce microbial activities and ensure chemical composition are intact prior to laboratory analyses. Nitric acid was added to the samples for cation analysis in order to reduce the pH of water below two. The water samples pH and
temperature were measured on site with the aid of digital meters; WTW-conductivity meter model L/92 and WTW-pH meter model pH/91 in the dry season, while solinst model 107 TLC meter was used in the wet season to measure temperature, water level and conductivity. Atomic absorption spectrophotometer (AAS) was employed to analyse the trace elements (Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Ag$^+$, and Cr$^{3+}$) and cations in both groundwater and Ocean water (undiluted). The anions were analysed from un-acidified water samples using UV spectrophotometry and volumetric techniques. While nitrate and sulphate were analysed using UV spectrophotometry technique, volumetric analysis method was used to analyse bicarbonate and sulphate. Following the standard procedures, microbial analysis was carried out on the water samples for faecal coliform count under the microscope. Analyses were carried out at the department of Geology, University of Ibadan, Oyo

![Figure 3. (a) An insert map of Nigeria (b) Geological map of Lagos state within the Dahomey Basin (after Yusuf et al., 2018).](image)

![Figure 4. The generalised stratigraphy of Dahomey Basin.](image)
State, Nigeria. The accuracy of the chemical analysis was verified by calculating ion-balance errors (Mandel and Shifrin, 1981) where the errors were generally around ±10%. The analytical results were also subjected to statistical analysis using SPSS software (version 16) to enhance further characterisation of the samples. The principal component analysis was carried out using Kaiser’s Varimax Rotation in order to identify the main natural and anthropogenic processes causing variation in the groundwater chemistry. The main principal component loadings were also presented in simple statistical diagrams relative to PCA 1 for ease of assessment. It is important to state that the outliers were included for statistical consideration in this study because the water chemistry results cannot be regarded as just random numbers but provide crucial information concerning the groundwater chemistry of the area.

In this research, the study area was divided into three segments for ease of identification and clarification. The western segment – jointly known as Apapa and denoted by ‘App’ – included samples GW 1 to GW 7 (Industrial and residential region). The central parts – collectively referred to as Island and denoted by ‘Isl’ – constituted samples GW 8 to GW 19, GW 21, GW 37, GW 38, GW 39 and GW 40 (Commercial and residential area). The eastern parts – generally described as Etiósia and represented by ‘Eti’ – made up the remaining samples from GW 20 to GW 45 (Residential and tourism area). It is worthy to mention that additional data for brackish surface water (P-SW 1, P-SW 2 and P-SW 3) was obtained from a study conducted by Yusuf et al. (2014), only for its physical parameters and major ion content towards deducing the relationship between groundwater and the surrounding surface waters.

### Table 1. Major ions, metals and microbial count analyses and number of samples analysed for groundwater and surface waters.

| Season          | Water media   | Major ions* | Metals** | Microbial count (F. coli) |
|-----------------|---------------|-------------|----------|--------------------------|
| Wet season      | Shallow ground water | 40          | 40       | 40                       |
|                 | Surface water (Ocean) | 1           | 1        | 1                        |
|                 | Surface water (lagoon) | –           | 3        | 2                        |
| Dry season      | Shallow ground water | 42          | –        | –                        |

*Ca, Mg, Na, K, Cl, HCO₃, SO₄, CO₃, NO₃, **Zn, Cu, Pb, Mn, Fe, Ni, Cd, Ag, Cr.

### Table 2. Summary of physicochemical, major ions, microbial population in groundwater obtained for the wet and dry seasons in the study area.

| Parameters                       | Wet season | Dry season |
|----------------------------------|------------|------------|
| **pH**                           | Minimum    | Maximum    | Mean   | Minimum    | Maximum    | Mean   |
| TDS (mg/L)                       | 5.40       | 8.60       | 7.26   | 5.10       | 8.70       | 7.40   |
| EC (μS/cm)                       | 69.00      | 1 642.00   | 458.85 | 114.00     | 1 916.00   | 361.43 |
| Total Hardness as CaCO₃          | 111.00     | 3 284.00   | 885.35 | 142.00     | 3 832.00   | 638.93 |
| Temperature (°C)                 | 26.00      | 29.50      | 27.8   | 27.60      | 30.70      | 28.8   |
| Turbidity (NTU)                  | 0.10       | 0.99       | 0.66   | –          | –          | –      |
| Ca²⁺ (mg/L)                      | 0.05       | 9.37       | 11.11  | 8.20       | 12.80      | 11.1452|
| Mg²⁺ (mg/L)                      | 1.29       | 16.77      | 5.91   | 2.44       | 6.23       | 3.6995 |
| Na⁺ (mg/L)                       | 0.15       | 14.77      | 2.42   | 4.10       | 9.10       | 5.4756 |
| K⁺ (mg/L)                        | 0.14       | 23.77      | 3.04   | 3.89       | 9.10       | 5.7005 |
| Cl⁻ (mg/L)                       | 1.00       | 720.00     | 110.65 | 2.50       | 97.00      | 4.755  |
| HCO₃⁻ (mg/L)                     | 6.10       | 335.51     | 101.68 | 17.00      | 97.00      | 67.39  |
| CO₃²⁻ (mg/L)                     | 3.00       | 210.00     | 51.54  | 0.80       | 6.00       | 3.70   |
| NO₃⁻ (mg/L)                      | <0.001     | 108.70     | 22.33  | <0.001     | 0.06       | 0.025  |
| SO₄²⁻ (mg/L)                     | <0.001     | 88.00      | 36.234 | 0.01       | 0.21       | 0.089  |
| Faecal coliforms/100 ml          | 2.00       | 201.00     | 170.00 | –          | –          | –      |

**WHO (2018)**

### Table 3. Summary of physical, bacteriological and macro-element contents of surface water (lagoon and ocean) obtained in the study area (Previous and present study).

| Parameters | Lagoon Minimum | Maximum Mean | Ocean WHO Minimum | Maximum Mean |
|------------|----------------|--------------|-------------------|--------------|
| pH         | 7.83           | 8.25         | 7.98              | 8.4**        | 7.5–8.5    |
| TDS (mg/L) | 2 000          | 2 000        | 2 000             | 35 040**     |
| EC (μS/cm) | 3 999          | 3 999        | 3 999             | 48 000**     |
| Temperature (°C) | 29.8       | 32          | 31.3              | -            |
| Ca²⁺ (mg/L) | 430           | 1 750       | 1 268.33          | 321.28**     |
| Mg²⁺ (mg/L) | 1313          | 4 850       | 3 479.33          | 5 036.23**   |
| Na⁺ (mg/L) | 1 750         | 7 000       | 5 083.33          | 8 674.52**   |
| K⁺ (mg/L) | 44            | 175         | 127.33            | 294.27**     |
| Cl⁻ (mg/L) | 2 327         | 9 308       | 6 759.33          | 15 582**     |
| HCO₃⁻ (mg/L) | 40            | 80          | 42                | 180**        |
| CO₃²⁻ (mg/L) | 218           | 245         | 231               | 9.6**        |
| SO₄²⁻ (mg/L) | 465           | 1 862       | 3 51.33           | 102**        |
| Faecal coliforms/100 ml          | 34**         | 1 733**     | 883.5**           | 173**        |

** present study.

### 2.3. Results and discussion

#### 2.3.1. General hydrochemistry

#### 2.3.1.1. Physico-chemical and major ions. A statistical summary of the major hydrochemical parameters analysed in this research at different periods is presented in Table 2 and Table 3. The pH values recorded in the analyzed groundwater water samples with a mean value of 7.26 and 7.40 for wet and dry seasons suggests that the groundwater in the area ranged between neutral and slightly alkaline, whereas the average value of 7.98 in the surface water may be reflecting alkaline nature of the surface water. The temperatures of the groundwater at the time of the sample vary slightly with an average of 27.8 °C and 28.8 °C in the wet and dry seasons. The low temperature range may probably be due to the shallow nature of the aquifer. A comparison of the shallow aquifer temperature...
of 48000 μC/m in the study area (Yusuf, 2020). There is an observed general increase in EC and TDS values in the groundwater in wet season relative to dry season, and in the west (App) and central (Isl) relative to the eastern parts (Eti) of the study area (Figure 5). The comparatively higher values of EC and TDS in the wet season were similar to the result of Shaikh and Mandre (2009) conducted on potable water in industrial area of Khed (Lote). This could be indicating higher mineralization in the wet season, possibly from the influence of surface water and/or flash flood or surface runoff during intense rainfall, thereby introducing more particulates to the shallow fresh groundwater (Eduvie and Olaniyan, 2013; Yusuf, 2020). Whereas in surface waters, the expected highest occurrence value of 48000 μS/cm was recorded in the ocean, while the steady value of 3999 μS/cm documented in the lagoon at P-SW 1, P-SW 2 and P-SW 3 might be due to the upper specification limit of the equipment used during field campaign (Table 3). The microbial content is notably higher in the lagoon water than the shallow large diameter wells (Yusuf, 2020). In summary, the substantial reduction in the concentration recorded for both seasons may be indicating essentially dissolution of carbonate rocks and ion exchange process in the wet season. The Mg²⁺ concentration is notably higher in the wet season than the dry season. The observed higher magnesium value (Mg²⁺ > Ca²⁺) exhibited in the wet season with Ca²⁺/Mg²⁺ ratio of <1 in the 75% of groundwater samples with the exception of GW (1–5, 14, 16–18, 30, and 38) (Table 5) maybe suggesting marine influence in parts of the study area. The observed higher concentration values of K⁺ and Na⁺ relative to Mg²⁺ in the dry season may possibly be attributed to the effect of evaporation and ion exchange between the aquifer material (clayey sand) and the solution or anthropogenic contribution (Prasanna et al., 2019; Yusuf, 2020). The order of cationic abundance for both seasons is as follows: Ca²⁺ > K⁺ > Na⁺ > Mg²⁺ and Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ for the respective dry and wet seasons (Figure 6).

Chloride and bicarbonate are the dominant anions with mean values of 110.65 mg/L and 101.68 mg/L for both wet and dry seasons, respectively. Generally, the dominance of anions in the analogue water samples are Cl⁻ > HCO₃⁻ > SO₄²⁻ and HCO₃⁻ > Cl⁻ > SO₄²⁻ for both wet and dry seasons. The dominance of HCO₃⁻ in the dry season is an indicator of carbonate dissolution and decomposition of organic matter (Avtar et al., 2013). It was suggested that the groundwater is in contact with rapidly dissolving carbonate rock which increases the relative concentration of these ions in solution during recharge processes. Likewise, the hardness of the groundwater in the wet season is a function of calcium carbonate. Higher chloride values observed in the wet season could indicate mixture of different water types besides the influence of rainwater and flash floods (Yusuf, 2020). In summary, the substantial reduction in the concentrations of the cations and anions in the aquifer between the two seasons (wet and dry), as observed in Figure 7, may be suggesting

Calcium is the predominant cation found in the groundwater with mean values of 11.11 mg/L and 11.15 mg/L for both wet and dry seasons, respectively (Table 2). Calcium ions are derived also from cation exchange process (Appelo and Postma, 2005). Thus, the variation in Ca²⁺ concentration recorded for both seasons may be indicating essentially dissolution of carbonate rocks and ion exchange process in the wet season. The Mg²⁺ concentration is notably higher in the wet season than the dry season. The observed higher magnesium value (Mg²⁺ > Ca²⁺) exhibited in the wet season with Ca²⁺/Mg²⁺ ratio of <1 in the 75% of groundwater samples with the exception of GW (1–5, 14, 16–18, 30, and 38) (Table 5) maybe suggesting marine influence in parts of the study area. The observed higher concentration values of K⁺ and Na⁺ relative to Mg²⁺ in the dry season may possibly be attributed to the effect of evaporation and ion exchange between the aquifer material (clayey sand) and the solution or anthropogenic contribution (Prasanna et al., 2019; Yusuf, 2020). The order of cationic abundance for both seasons is as follows: Ca²⁺ > K⁺ > Na⁺ > Mg²⁺ and Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ for the respective dry and wet seasons (Figure 6).

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A comparison of the water quality with the WHO (2018) drinking water standard shows that the groundwater is below the guidelines in the dry season for all the major ions. Similarly, the wet season is also within the permissible limit of WHO with the exception of Ca²⁺ at GW 1 and GW 2 (west; App.) and Cl⁻ at GW 5, GW 6, GW 8 and GW 19 (west and central; App/Isl). NO₃ and f. coli were found in higher occurrence than the recommended limit in almost all the groundwater from west to east of the study in the wet season.

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carbonate dissolution (Yusuf, 2020). NO$_3$ was also higher in the wet season relative to the dry season with respective mean concentrations of 22.35 mg/L and 0.0251 mg/L, indicating a higher anthropogenic contribution to the aquifer in the wet season. Similarly, higher concentration of sulphate was also documented for the rainy season (Table 2; Figure 7), although comparatively lower than chloride concentration for both seasons. Earlier, Datta and Tyagi (1996) had suggested that groundwater with high Cl$^-$/C0$^2-$ and low SO$_4$$^{2-}$ probably indicates sulfate reduction. In addition, an increase in sulphate from fossil fuel combustion has been observed in precipitation over the Lagos coastal basin (Aderogba, 2012). Therefore, atmospheric deposition of sulphate through rainfall in such an urbanized and industrial area of study may have caused the aquifer signatures in the wet season.

In surface water, magnesium is the dominant cation in the brackish water, while sodium remains the dominant cation in the Ocean. Chloride, as expected, was the dominant anion in both media (Table 3). In comparison with the WHO standard, the mean values for all the physico-chemical parameters in the surface waters are higher and above the recommended standard for drinking water except NO$_3$ and SO$_4$$^{2-}$ in the Ocean, which may be reflecting the influence of dilution.

**2.3.1.2. Hydrochemical facies.** The Piper Trilinear diagram is a very useful tool in bringing out the groundwater chemical relationship in more concise terms (Walton, 1970). In the present study, hydrochemical data were plotted on the Piper Trilinear diagram (Piper, 1944) to evaluate the groundwater composition in wet and dry seasons. According to Hem (1985), the water in which no cations or anion constitute as much as 50% of the total should be recognised as a ‘mixed type’ and identified by dominant cations and anions. In this study, a 50% minimum benchmark for individual cation or anionic concentrations (meq/L) in their respective totals has been considered in formulating the water type.

The Piper plot shows the groundwater samples for the wet season fall on the Ca-dominant type, Mg-dominant type and non-dominant type; whereas, samples from the dry season fall essentially within the non-dominant type and Ca-type on the cationic triangle. Based on anionic triangle classification, bicarbonate type, chloride type and non-dominant type...
type characterised the wet season, while the dry season are dominantly bicarbonate type. The samples can be grouped into the following major groundwater facies based on their position on the diamond-shaped field of plot. The wet season groundwater samples revealed essentially four distinct hydrochemical types: Ca–Mg–HCO₃, Ca–Mg–Cl–SO₄, mixed Ca–Mg–Cl, and Ca–Cl, and the predominant types were the Ca–Mg–HCO₃, Ca–Mg–Cl–SO₄, constituting about 37.5 % and 32.5 %, respectively, while the dry season was composed of Ca–HCO₃, Ca–Mg–HCO₃, and Ca–Mg–Cl–SO₄ types representing 39.5 % and 37.5 %, respectively (Figure 8). The cation and anion ternary plot revealed that bulk of the water from both seasons have no dominant ions. This could be explained by mixing of water from different sources, cation exchange between Mg–Ca–Na and the replacement of HCO₃ by Cl– (Masindi and Abiye, 2018).

The hydrochemical facies for the supposedly fresh surface water (lagoon) is Mg–Cl type (Figure 8). When seawater intrudes into fresh coastal waters, the water type results in Ca–Cl₂ or Mg–Cl₂ water (Appelo and Postma, 1999). Thus, Mg–Cl type water in the lagoon may be due to the mixing of seawater and the lagoon water being dictated by the tidal influence of the Ocean. Similarly, the Ca–Cl type water (an intermediate facies) observed in parts of the groundwater samples maybe suggesting interaction between the brackish surface water/flash flood and the groundwater. However, as expected, the only seawater sample was Na–Cl water type. Interestingly, no single groundwater sample fall in the class of Na–Cl water type, indicating no direct seawater intrusion within the sampled depths of the surficial shallow aquifer.

### 2.3.1.3. The Heavy Metal Pollution Index

The summary of metal concentrations in waters is presented in Table 4. The degree of contamination resulting from metals in water was evaluated using the Heavy Metal Pollution Index (HPI) method (Odukoya and Abimbola, 2010; Ayolabi et al., 2013). The tolerable level is the elemental concentration in the water considered safe for human consumption (Ayolabi et al., 2013). The HPI was calculated using Eq. (1) below by Mohan et al. (1996):

$$HPI = \frac{M_i / T_i}{N_m}$$

where:

- $M_i$ represents the heavy metal concentration in water;
- $T_i$ = a tolerable level; and,
- $N_m$ = number of heavy metals under consideration.

When the HPI is $> 1$, the water is regarded as being contaminated. More than 50 % of the groundwater in the area is polluted, having an HPI between 1.0 and 2.86. Figure 9a presented the contribution of significant metals to HPI. Mn²⁺ contributed the highest percentage (62 %) to the HPI, followed by Fe²⁺/³⁺ (19 %), and closely followed by Ni²⁺ (8 %), Cu²⁺ (8 %), Cr³⁺ (2 %) and Zn²⁺ (1 %). The plot of the metal concentrations revealed that the elevated metal concentrations occurred in the west (GW 1—GW 7) and central (GW 8 – GW 20) parts of the study area (Figure 9b). This suggests possible influence of anthropogenic activities such as industrial effluent and sewage discharge into the surface water that infiltrates into the surficial groundwater. Moreover, although the trace elements mean concentrations for the groundwater show values below the specified limit of WHO for drinking water; however, Mn²⁺ at GW 6; Fe²⁺ at GW 3, GW 5 and GW 15; Ni²⁺ at GW 1 to GW 5; Cd²⁺ at GW 3 and Cr³⁺ at GW 8, GW 18 and GW 20 are found high and above the permissible limit of drinking water standard.

#### 2.3.1.4. Mechanisms controlling groundwater chemistry

Gibb’s diagram is widely employed to deduce the main mechanisms controlling groundwater chemistry, namely the sources of dissolved chemical constituents, such as precipitation dominance, rock dominance and evaporation/crystallization dominance (Gibbs’ 1970). The present study revealed that most of the groundwater samples from the two seasons (wet and dry) plotted essentially in the rock dominance and partly in the evaporation fields (Figure 10). This implies that chemical weathering of rock-forming minerals is essentially influencing the groundwater quality by dissolution of rocks through which there is circulation. The correlation of the higher TDS value with the corresponding Na⁺/(Na⁺+Ca²⁺) indicates

### Table 4. Summary of metal concentrations in groundwater and surface water.

| Heavy metals | Groundwater range | Mean | Standard deviation | Surface water range | Mean | Standard deviation | WHO (2018) (μg/L) |
|--------------|-------------------|------|-------------------|---------------------|------|-------------------|-------------------|
| Zn²⁺ (μg/L)  | $<0.1$–240        | 8.4  | 37.9              | $<0.1$–19.9         | 6.7  | 11.4              | 3000              |
| Cu²⁺ (μg/L)  | $<0.1$–1330       | 49.3 | 214               | $<0.1$             | $<0.1$ | $<0.1$         | 2000              |
| Mn²⁺ (μg/L)  | $<0.1$–14900      | 382.4| 2,354.4           | 4–10               | 244.9| 347.7            | 400               |
| Fe²⁺/³⁺ (μg/L)| $<0.1$–1,580      | 118  | 266.9             | 104.5–240          | 173.5| 68.2              | 300               |
| Ni²⁺ (μg/L)  | 179–567           | 50.1 | 142.1             | $<0.1$–10          | 8    | 1.4               | 70                |
| Cd²⁺ (μg/L)  | $<0.1$–10         | 0.2  | 0.6               | 21.6–190           | 70.1 | 10.3              | 3                 |
| Ag⁺ (μg/L)   | $<0.1$–40         | 2.7  | 7                 | 24,974.8–24,980    | 16,651.5| 14,420.6 | -                 |
| Pb²⁺ (μg/L)  | $<0.1$–30         | 2.1  | 4.3               | $<0.1$–450         | 151.2| 261.8             | 10                |
| Cr³⁺ (μg/L)  | 3.9–5             | 14.3 | 14.3              | $<0.1$–120         | 65.2 | 63.3              | 50                |

Figure 9. (a) Contribution of significant metals to HPI; (b) Concentration of each metal in the groundwater of the study area.
that cation exchange reactions involving Na\(^+\) and Ca\(^{2+}\) may account for the variability in groundwater chemistry (Li et al., 2013; Sunkari et al., 2019). Besides, the meteoric origin of the groundwater might have been lost due to water–rock interaction, mixture with high charged surface waters and ion exchange reactions. Earlier, Zaidi et al. (2015) reported alteration in the meteoric source of the groundwater in the Arabia coastal basin as a result of rock-water interaction.

Other important mechanism affecting groundwater quality is the evaporation effect, which was elucidated with the use of the correlation between Na\(^+\)/Cl\(^-\) and EC to examine the degree and trend of evaporation in the study area. The plot of Na\(^+\)/Cl\(^-\) versus EC shows the influence of evaporation on the overall groundwater chemistry of an area (Fisher and Mullican, 1997). Occurrence of evaporation is indicated by a constant Na\(^+\)/Cl\(^-\) ratio with increasing EC values and is represented by horizontal line on the Na\(^+\)/Cl\(^-\) versus EC plot (Jankowski and Acworth, 1997). In the present study, the Na\(^+\)/Cl\(^-\) ratio are almost horizontal, particularly in the wet season, suggesting possible evaporation processes (Figure 11). In an evaporation environment, the chloride concentration is expected to remain constant with an increasing EC value (Appelo and Postma, 2005). In the study area, it was proposed that the evaporation signature observed in the wet season may be due to mixture of the surrounding highly evaporated surface water (brackish) with the shallow groundwater through flash flooding, bank infiltration and surface run-off. This finding is consistent with the isotope submission of Yusuf et al. (2018) that showed possible interaction between surface water (lagoon) and the surficial groundwater in the wet season at the LCB. The evaporation was further enhanced by the flat nature of the study area, which tends to hold water at the surface for a longer period prior to infiltration (Yusuf, 2020). Several authors have reported that decrease in Na\(^+\) compared to Cl\(^-\) indicate the influence of other sources such as leaching of salt from the surface or recharge due to evaporated water (Chidambaram et al., 2009; Prasanna et al., 2010), where the latter remain the possible cause for the present study. Whereas, in the dry season, the Na\(^+\)/Cl\(^-\) ratio vs EC scatter diagram showed a trend line that slightly increases in the Na\(^+\)/Cl\(^-\) ratio with an increasing EC (Figure 11), indicating enrichment of Na\(^+\) relative to Cl\(^-\) with increasing salinity. This may be as a result of ion exchange reaction and equally suggesting insignificant effect of the evaporation. In general, the low R\(^2\) value observed for both seasons is a good pointer to the fact that evaporation may not be the dominant geochemical process controlling the groundwater quality in the basin.

Figure 10. Gibb’s diagram showing groundwater evolution in the basin.

![Figure 10](image1.png)

Figure 11. Shows scatter diagram indicating seasonal variation in evaporation.

![Figure 11](image2.png)
2.3.1.5. Geochemical evolution of groundwater. The rock–water interaction and various hydrogeochemical processes, such as precipitation, dissolution, and cation exchange in an aquifer with increasing residence time, are responsible for variation in groundwater composition as it evolves into different water facies from the recharge area through transition to the discharge zone. The dry season water samples are essentially characterised by calcium bicarbonate (Ca–HCO₃ supply) type of water. Chemical weathering is a dominant natural process that consumes atmospheric CO₂ and converts it into alkalinity (HCO₃⁻ and CO₃²⁻) of the water (Millot et al., 2002). The high concentration of HCO₃⁻ and CO₃²⁻ is an indicator of chemical weathering and possible decomposition of organic matter (Yusuf, 2020). The Ca–HCO₃ water type, therefore, is thought to be generally derived from the carbonate dissolution such as calcite, which contributes Ca²⁺ and HCO₃⁻ to the groundwater. It may also occur as cementing material in sedimentary rocks. We therefore proposed that the Tertiary Ewekoro limestone is the major source of carbonate rocks in the basin. Furthermore, the Ca–HCO₃ and Ca–Mg–HCO₃ water types are normally dominated by the earth’s alkaline water and weak acids as observed in the present study (Karanth, 1987). In addition, higher concentration of Ca²⁺ and HCO₃⁻ may also be attributed to base ion exchange, where Na⁺ in groundwater is being replaced by Ca²⁺ and Mg²⁺ at favourable exchange sites (Jankowski and Acworth, 1997). The higher Na⁺/K⁺/Cl⁻ ratio observed in the dry season may suggest cation exchange and reflects concentration of alkalis from sources other than precipitation. Whereas in the wet season, the different types of water that characterised the groundwater is a true reflection of a discharge zone and it ranged from Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻ dominated water types. The different facies types could be explained by:

i. Leaching and dissolution of salts: The high concentration of chloride ion as observed in the wet season is associated with decreasing bicarbonate concentration and enriching of sulphate concentrations. This process clearly defines leaching and dissolution of soluble salts through precipitation and surface run-off during groundwater movement to the Ocean. This consequently resulted in various forms of HCO₃⁻–Cl⁻–SO₄²⁻ water types, depending on the dominant cation. Similar results have been reported by Prasanna et al. (2019) in the geochemical processes of coastal aquifer, south east coast of India.

ii. Simple mixing between brackish water and fresh groundwater through flash floods indicated by the relative enrichment of magnesium and impoverishment of calcium with increasing chloride. When seawater charged with Na⁺ and Cl⁻ as the dominant ions intrudes into or mixes with the fresh coastal water, cation exchange reaction, as written in Eq. (2) according to Martinez and Bocanegra (2002), may occur:

\[ \text{Na}^+ + \frac{1}{2} \text{Ca-X} \rightarrow \text{Na-X} + \frac{1}{2} \text{Ca}^{2+} \]  

(2)

As the exchanger site picks up Na⁺, then Ca²⁺ or Mg²⁺ are released and the hydrochemical water types evolve from Na–Cl water to Ca–Cl or Mg–Cl. Another possible explanation for the decrease in calcium concentration could be when calcium from carbonate rocks is removed and replaced with magnesium from groundwater through an ion exchange reaction (dolomitisation process) (Yusuf, 2020).

2.3.1.6. Hydrogeochemical processes deduction using new ionic ratio methods. The rapid dissolution of soluble rocks (carbonates, gypsum, halite) and gradual dissolution of relatively soluble rock (silicates), resulting from rock–water interaction, are part of the chemical weathering that play a role in mineral enrichment and depletion (Oke, 2015). The measurement in groundwater of these rock components informed the dominant weathering process that characterises a particular aquifer. Several methods have been adopted by various authors across the world to gain insights into the chemical processes that govern water quality (Datta and Tyagi, 1996; Lakshmanan and Kannan, 2016; Al-Ruwaih and Shaﬁullah, 2017). However, the present study has adopted the proposed methods of cationic contribution evaluation [Ca²⁺+Mg²⁺ vs total cation (TZ⁺)] in meq/L and ionic ratio bivariate plots of HCO₃⁻/Ca²⁺ vs Ca²⁺/Mg²⁺ and HCO₃⁻/Ca²⁺ vs Ca²⁺/Na⁺ in meq/L. For the purpose of interpretation, the sum of Ca²⁺+Mg²⁺ ≤ 0.5 TZ⁺ i.e. ≤ 50 % (TZ⁺) identifies dominance of carbonate weathering while the sum of Ca²⁺+Mg²⁺ ≤ 0.5 TZ⁺ i.e. < 50 % (TZ⁺) identifies silicate weathering dominance. Meanwhile, with respect to ionic bivariate plots, the interpretation range on the logarithmic graph was defined by range of values as follows: from 0.01 to 1.0; from 0.1 to 1.0; and > 1 identify evaporate, silicate and carbonate dominant zones, respectively (Yusuf, 2020).

In the present study, the concentration of Ca²⁺+Mg²⁺ relative to the total cations, was 85 % in the wet season and 76 % in the dry season, both of which are far and above the < 50 % TZ⁺ proposed for silicate weathering (Figure 12). Therefore, carbonate weathering is the dominant process that controls the groundwater quality in the study area. The R² values of approximately 0.98 and 0.88 for both seasons further supported the validity of carbonate dissolution as the dominant process.

Moreover, based on the bivariate plots of ionic ratios presented in Figure 13, most of the groundwater samples fall within the proposed carbonate zone, confirming carbonate weathering as the major chemical process characterising the shallow groundwater system in the study area. However, the few samples that plot within the proposed silicate zone maybe attributed to contribution as the groundwater crosses heterogeneous aquifers.

2.3.1.7. Ion exchange processes. Although there are many proposed methods by different authors to assess ion exchange that controls the groundwater chemistry, this study adopts the Ca²⁺+Mg²⁺/HCO₃⁻+SO₄²⁻ ratio by (Cerling et al., 1989) reported in meq/L. The reverse ion exchange is identified by an excess of (Ca²⁺+Mg²⁺) over (HCO₃⁻+SO₄²⁻), while ion exchange is marked by a higher occurrence of (HCO₃⁻+SO₄²⁻) over (Ca²⁺+Mg²⁺) (Cerling et al., 1989; Fisher and Mullican, 1997; Edet et al., 2011). Here, the aquifer matrix picks up the Na⁺ in solution in exchange for its adsorbed/attached Ca²⁺. The hydrochemical composition thus evolves from Na–Cl to Ca–Cl or Mg–Cl.

In the study area, the calculated ionic ratio of Ca²⁺+Mg²⁺/HCO₃⁻+SO₄²⁻ < 1 in 85 % of the samples was in the wet season. Similarly, 84 % of the samples had a ratio of Ca²⁺+Mg²⁺/HCO₃⁻+SO₄²⁻ < 1 in the dry season (Table 5). This suggests the dominance of ion exchange (Fisher and Mullican, 1997). It could also be due to mixing of waters with different hydrochemical properties. However, a few groundwater samples, 15 % and 16 % for both wet and dry seasons, exhibited Ca²⁺+Mg²⁺/HCO₃⁻+SO₄²⁻ > 1 probably as the groundwater tends to flush out brackish water to restore its freshness. It is important to point out here that the Ca²⁺+Mg²⁺/HCO₃⁻+SO₄²⁻ > 1, as observed in the wet season, may be attributed to reverse ion exchange or simple dissolution with no dominant major anion or cation (Yusuf, 2020). However, in the dry season, it does not necessarily imply reverse ion exchange; the higher ionic ratio than unity may be due to high dissolution of rocks or evaporation effects which tend to enrich the soil salinity.

Complementarily, the Durov diagram (1948) (Figure 14) was employed to substantiate the assertion observed about the ion process governing the groundwater in the basin. The prevalent mixed water type in the wet season was supported by data plot in Figure 14; 67.5 % of the samples plotted in Field 5 of the plot along the dissolution or mixing line. Based on the classification of Lloyd and Heathcoat (1985), this trend can be attributed to fresh recharge water exhibiting simple dissolution or mixing with no dominant major anion or cation. In addition, a few samples (15 %) in Field 4 show reverse cation exchange process. The remaining 17.5 % in Field 3 and Field 6 exhibited ion exchange process; whereas in the dry season, samples plotted in Field 6 of the plot along the ion exchange line, showed that the groundwater is related essentially to ion exchange with Ca–HCO₃ water. The remaining 15 % belongs to Field 5 of the plot along the simple dissolution of the rock mixing line without a dominant anion or cation. In general, it is clear from the above that ion
exchange and dissolution of rocks or mixing with other water types essentially contribute to the groundwater chemistry, while rock dissolution and ion exchange were the dominant exchange processes characterising the wet and dry seasons, respectively. The numerous geochemical factors responsible for the hydrogeochemistry of the shallow groundwater, particularly in the wet season, is an attestation to the complexity of the basin hydrological systems as the main recipient of all water types from the upstream of the study area.

2.3.1.8. Marine impact evaluation. Ionic ratios are widely employed worldwide to understand the seawater ingress along the coastal aquifer domain (Batayneh et al., 2014; Sridharan and Nathan, 2017; Masindi and Abiye, 2018). It is well known that no single variable definitively identifies seawater intrusion; however, by considering various analyses, we can ascertain when fresh groundwater mixes with seawater (Werner and Gallagher, 2012). This research made use of ionic plot of Na\(^+\)/Cl\(^-\) to investigate the possible marine influence on the surficial groundwater of the study area. In addition to the existing ratios, this research proposed the use of Ca\(^{2+}\) + Mg\(^{2+}\) vs Cl\(^-\) and Ca\(^{2+}\)/Mg\(^{2+}\) ratios against Cl\(^-\) for the same purpose. The use of chloride is imperative because it is known to be highly conservative in nature. Chloride enters groundwater through wet and dry depositions during precipitation and a rainout effect (Guan et al., 2010; Oke, 2015). Based on Starinsky et al. (1983), the Na\(^+\)/Cl\(^-\) ratio is used to indicate saltwater intrusion where the ratio values are less than unity, and when the ratio is greater than or equal to unity, it connotes fresh meteoric water. In the present study, all the groundwater samples in the wet season exhibited values less than one for all water samples, while the dry season samples have Na\(^+\)/Cl\(^-\) ratio values generally above unity (for 92% of the samples), the exception being the samples GW 22, GW 31 and GW 45 at ‘Eti’ eastern parts of this study. This may indicate simple mixing of groundwater with the brackish water through flash floods or surface run-off as a major process in the wet season, whereas the dry season may indicate cation exchange resulting from water–rock interaction (Yusuf, 2020). The few samples that demonstrated salinity in the dry season may be related to leaching from the soil surface and evaporation. In general, ion of Na\(^+\) correlated

![Figure 12. Plot of Ca\(^{2+}\) + Mg\(^{2+}\) vs total cations showing carbonate dissolution in groundwater (a) Wet season and (b) Dry season.](image)

![Figure 13. Bivariate plot of Ca\(^{2+}\)/Mg\(^{2+}\) vs HCO\(_3\)/Ca\(^{2+}\) and Ca\(^{2+}\)/Na\(^+\) vs HCO\(_3\)/Ca\(^{2+}\) showing dominant of carbonate dissolution in groundwater for wet and dry seasons.](image)
positively with the Cl\textsuperscript{−} in the wet season (Figure 15a and Figure 15b), suggesting possible leaching of secondary salt (Prasanna et al., 2019); however, such ions may be derivatives of mixing water. The low to moderate regression coefficient values (R\textsuperscript{2}) indicated slight mixing with highly diluted brackish water. A slight positive correlation observed for the wet season reflects a signature of slightly saline groundwater. Another possible explanation of the association between these ions is likely to be deposition of marine-derived salts from precipitation (Oke, 2015; Masindi and Abiye, 2018). In contrast, in the dry season, the ions plot does not show any significant correlation but almost horizontal with Cl\textsuperscript{−}/C\textsubscript{0} ions reflecting equilibration in the enrichment of the ions which may be due to evaporation (Jankowski and Acworth, 1997). Lack of intermixing between the brackish surface water and the unconfined groundwater during the dry season was further supported by the insignificant R\textsuperscript{2} values recorded for the period. The plot of Ca\textsuperscript{2+}/Mg\textsuperscript{2+} vs Cl\textsuperscript{−} further reveals a slight correlation in the wet season, whereas in the dry season it does not show any relationship, indicating mixing between fresh floods and surficial groundwater in the wet season (west and central parts of the study) and non-interaction between aquifer and surface water in the dry season (Figure 15c and Figure 15d). However, in the wet season, the ratio of Ca\textsuperscript{2+}/Mg\textsuperscript{2+} vs Cl\textsuperscript{−} revealed a negative correlation (Figure 15e). This reflects enrichment of Mg\textsuperscript{2+} with increasing Cl\textsuperscript{−} in the wet season and maybe suggesting another source for the Mg\textsuperscript{2+}, resulting from intermixing between surface waters (brackish) and groundwater or cation exchange (Yusuf, 2020). It may also be deduced that salinity increases with a more negative correlation, although the R\textsuperscript{2} value might not

| Sample ID | Wet season | Dry season |
|-----------|------------|------------|
|           | Ca/Mg      | Na + K/Cl  | Ca/Ca + SO\textsubscript{4} | Ca + Mg/HCO\textsubscript{3} + SO\textsubscript{4} |
|           |            |            |                             |                             |
| GW1       | 3.60       | 0.25       | 1.00                        | 1.12                        |
| GW2       | 10.59      | 0.88       | 0.80                        | 1.96                        |
| GW3       | 4.67       | 0.39       | 0.61                        | 1.21                        |
| GW4       | 2.98       | 0.26       | 0.63                        | 0.95                        |
| GW5       | 2.57       | 0.11       | 0.80                        | 1.22                        |
| GW6       | 0.48       | 0.01       | 0.86                        | 0.21                        |
| GW7       | 0.73       | 0.03       | 0.20                        | 0.36                        |
| GW8       | 0.48       | 0.01       | 0.24                        | 0.29                        |
| GW9       | 0.47       | 0.03       | 0.15                        | 0.24                        |
| GW10      | 0.87       | 0.02       | 0.29                        | 0.24                        |
| GW11      | 0.48       | 0.02       | 1.00                        | 0.26                        |
| GW12      | 0.73       | 0.04       | 0.21                        | 0.17                        |
| GW13      | 0.75       | 0.02       | 0.28                        | 0.22                        |
| GW14      | 1.67       | 0.04       | 0.58                        | 0.58                        |
| GW15      | 0.78       | 0.04       | 0.38                        | 0.33                        |
| GW16      | 1.47       | 0.03       | 0.36                        | 0.39                        |
| GW17      | 1.06       | 0.03       | 0.61                        | 0.50                        |
| GW18      | 1.34       | 0.05       | 0.44                        | 0.37                        |
| GW19      | 0.03       | 0.01       | 0.03                        | 0.24                        |
| GW20      | 0.65       | 0.15       | 0.41                        | 0.24                        |
| GW21      | 0.01       | 0.02       | 0.01                        | 0.27                        |
| GW22      | 0.45       | 0.11       | 0.12                        | 0.24                        |
| GW23      | 0.14       | 0.04       | 0.09                        | 0.30                        |
| GW24      | 0.30       | 0.03       | 0.12                        | 0.27                        |
| GW25      | 0.49       | 0.02       | 0.21                        | 0.32                        |
| GW26      | 0.48       | 0.01       | 0.33                        | 0.59                        |
| GW27      | 0.20       | 0.09       | 0.16                        | 0.36                        |
| GW28      | 0.04       | 0.08       | 0.01                        | 0.10                        |
| GW29      | 0.50       | 0.37       | 0.15                        | 0.32                        |
| GW30      | 1.07       | 0.11       | 0.14                        | 0.23                        |
| GW31      | 0.67       | 0.35       | 0.93                        | 1.12                        |
| GW32      | 0.26       | 0.02       | 0.82                        | 0.62                        |
| GW33      | 0.22       | 0.73       | 0.98                        | 1.36                        |
| GW34      | 0.44       | 0.02       | 0.91                        | 0.72                        |
| GW35      | 0.31       | 0.01       | 0.15                        | 0.50                        |
| GW36      | 0.28       | 0.05       | 0.15                        | 0.57                        |
| GW37      | 0.56       | 0.04       | 1.00                        | 0.45                        |
| GW38      | 1.21       | 0.03       | 0.23                        | 0.40                        |
| GW39      | 0.25       | 0.02       | 0.07                        | 0.13                        |
| GW40      | 0.50       | 0.10       | 0.12                        | 0.34                        |
| GW41      | -          | -          | -                           | -                           |
| GW42      | -          | -          | -                           | -                           |
| GW43      | -          | -          | -                           | -                           |
| GW44      | -          | -          | -                           | -                           |
| GW45      | -          | -          | -                           | -                           |
be significant, depicting minimal marine influence; however, the negative intercept value (−0.0233) exhibited by Ca^{2+}/Mg^{2+} vs Cl^− in the wet season may suggest simple mixing between the phreatic aquifer and the flash floods or surface run-off. The Ca^{2+}/Mg^{2+} vs Cl^− ratio in the dry season follows a similar pattern of the preceding ions, connoting non-contaminated freshwater (Figure 15f). This provides additional evidence for the assertion that there is no interaction between the phreatic aquifer and surface water during the dry season. However, this is not to negate the fact that seawater intrusion can have a chance at deeper aquifers for both seasons in the study area.

2.4. Statistical analysis

To facilitate further understanding of the different water types, factor analysis was used to evaluate the hydrochemical results. This is because the geostatistical method simplifies and organises large geochemical data sets to enhance the quality of interpretation (Amadi, 2011). The use of factor analysis is to sort out hydrochemical processes and relationships of the analysed groundwater data, and it has been successfully employed over the past couple of years (Lawrence and Upchurch, 1982; Amadi, 2011). The factor analysis involves three main essential steps: extraction of initial factors, rotation of factors and calculation of scores for each factor. In the present study, principal components were used for factor extraction, whereas varimax rotation with Kaiser Normalization was used for orthogonal rotation and results in uncorrelated factors (Usunoff and Guzman, 1989; Amadi et al., 2012). The computed factor scores for each observation expressed the importance of each factor at that observation site (Dalton and Upchurch, 1978; Amadi et al., 2012). Based on the study of Liu et al. (2003) factor loadings may be classified into three, namely strong, medium, and weak, corresponding to >0.75, 0.75–0.50, <0.50 values, respectively.

For this study, a factor loading of >0.5 was chosen as the parameters that influenced the factor. Seven-factor and six-factor components (Eigenvalue >1) emerged, accounting for the wet and dry seasons, respectively (Table 6 and Table 7).

In the wet season the first factor (F1) loading with 24.78% of the total variance showed higher loadings for TDS, EC, Mg^{2+}, Cl^−, HCO_3^−, CO_3^{2−}, pH and Cr^{2+}, depicting a large influence of natural and anthropogenic processes. The high positive loading of these ions with EC and TDS shows that they are the major contributors to mineralization of the groundwater, while association of Cr^{3+} in this factor indicates the mixing of both industrial effluents and domestic wastes with the superficial groundwater.

The high concentration of Cl^−, Mg^{2+}, TDS, and EC is an indication that the groundwater was in contact with water of marine influence and thus, a high possibility of intermixing of surface water run-off, flash floods and superficial groundwater of the study area is suggested (Yusuf, 2020). The high TDS value with a dominance of Mg^{2+}, Cl^−, HCO_3^− and CO_3^{2−} is mainly demonstrating the impact of carbonate dissolution and mixing of water from various sources (Prasanna et al., 2019; Yusuf, 2020). Also, the pH of the water is suspected to have been influenced by calcite dissolution, organic matter, atmospheric precipitation, and anthropogenic activities (Chidambaram et al., 2009; Yusuf, 2020).

The second factor (F2), which accounts for 22.28% of the total variance showed a high positive loading for Na^+, K^+, Ca^{2+}, Zn^{2+}, Ni^{2+} and Ag^+, and may indicate both natural and anthropogenic influence, while the enrichment of Na^+ and K^+ relative to Ca^{2+} may be due to the ion exchange process or derivatives from leaching of clay minerals, since the aquifer are essentially hosted within the clay matrix of sand and clayey
Figure 15. a-f: Ionic plot indicating mixing groundwater (wet season) and non-mixing groundwater (dry season).

Table 6. Factor loading and communalities Factor for groundwater chemistry in the wet season.

| Parameters (mg/L) | F1     | F2     | F3     | F4     | F5     | F6     | F7     | Communality |
|------------------|--------|--------|--------|--------|--------|--------|--------|-------------|
| pH               | 0.556  | -0.044 | 0.138  | 0.175  | -0.355 | -0.148 | 0.518  | 0.777       |
| TDS (mg/L)       | 0.575  | 0.276  | 0.151  | 0.030  | 0.426  | 0.368  | 0.216  | 0.794       |
| EC (μs/cm)       | 0.927  | 0.075  | -0.075 | -0.009 | 0.216  | 0.043  | 0.041  | 0.920       |
| Ca²⁺ (mg/L)      | 0.160  | 0.790  | 0.106  | 0.145  | -0.049 | -0.044 | -0.044 | 0.215       |
| Mg²⁺ (mg/L)      | 0.908  | 0.199  | 0.152  | -0.070 | 0.077  | -0.051 | -0.032 | 0.901       |
| Na⁺ (mg/L)       | 0.112  | 0.891  | 0.243  | 0.338  | -0.017 | -0.023 | 0.071  | 0.986       |
| K⁺ (mg/L)        | 0.134  | 0.934  | 0.018  | 0.294  | -0.011 | -0.012 | 0.083  | 0.984       |
| Cl⁻ (mg/L)       | 0.855  | 0.069  | 0.170  | -0.024 | 0.065  | -0.053 | -0.053 | 0.775       |
| HCO₃⁻ (mg/L)     | 0.903  | 0.097  | 0.013  | -0.070 | 0.126  | 0.249  | 0.004  | 0.908       |
| CO₃²⁻ (mg/L)     | 0.923  | 0.067  | -0.003 | -0.062 | -0.158 | 0.178  | -0.061 | 0.921       |
| NO₃⁻ (mg/L)      | -0.008 | -0.171 | -0.040 | -0.019 | 0.909  | -0.079 | -0.079 | 0.868       |
| SO₄²⁻ (mg/L)     | 0.478  | 0.051  | -0.079 | 0.062  | 0.481  | -0.552 | -0.060 | 0.781       |
| Zn²⁺ (mg/L)      | -0.065 | 0.713  | -0.136 | -0.157 | 0.009  | -0.017 | -0.098 | 0.556       |
| Cu²⁺ (mg/L)      | 0.023  | 0.363  | 0.913  | 0.076  | -0.0050 | -0.011 | 0.013  | 0.974       |
| Mn²⁺ (mg/L)      | 0.302  | -0.079 | -0.033 | -0.011 | -0.010 | 0.858  | 0.028  | 0.837       |
| Fe²⁺/³⁺ (mg/L)   | -0.071 | 0.255  | 0.067  | 0.909  | -0.083 | 0.166  | 0.028  | 0.909       |
| Ni²⁺ (mg/L)      | 0.048  | 0.917  | 0.368  | 0.058  | -0.051 | -0.023 | 0.039  | 0.986       |
| Cd²⁺ (mg/L)      | -0.094 | 0.015  | -0.051 | 0.941  | 0.073  | -0.040 | -0.025 | 0.904       |
| Ag⁺ (mg/L)       | 0.215  | 0.810  | 0.279  | -0.128 | -0.054 | 0.028  | 0.003  | 0.801       |
| Pb²⁺ (mg/L)      | 0.140  | 0.124  | 0.955  | -0.046 | 0.001  | 0.016  | 0.055  | 0.952       |
| Cr³⁺ (mg/L)      | 0.503  | -0.432 | -0.072 | -0.136 | -0.336 | -0.215 | -0.035 | 0.623       |
| Faecal coliforms | -0.127 | 0.160  | 0.023  | -0.043 | 0.135  | 0.089  | 0.889  | 0.860       |
| Eigenvalues      | 5.452  | 4.901  | 2.168  | 2.056  | 1.617  | 1.367  | 1.198  | 1.98        |
| % Of variance    | 24.783 | 22.725 | 9.856  | 9.348  | 7.349  | 6.215  | 5.447  | 1.98        |
| Cumulative %     | 24.783 | 47.059 | 56.915 | 66.262 | 73.611 | 79.826 | 85.273 | 100         |
In the present study, domestic waste is the probable source of NO₃ with respect to K⁺ ion exchange process. However, it has a moderate but negative loading association might indicate gradual leaching of salts from the surface or total variance with a low loading of HCO₃⁻.

Dissolution of ammonium ions (Masindi and Abiye, 2018). Groundwater. However, nitrate could be partially sourced from oxidation of ammonium ions (Masindi and Abiye, 2018).

The fourth factor (F4) was represented by iron and cadmium with 9.35% of the total variance. The strong factor loading of >0.9 associated with both elements suggested common anthropogenic sources. The generated wastes such as industrial effluents, sewage and land fill leachate, galvanised pipes, welding, battery and electroplating are possible sources of these elements into the groundwater (Yusuf, 2020).

The fifth factor (F5) that accounts for 7.35% of the total variance showed a higher loading of nitrate. Nitrate enrichment in groundwater indicates anthropogenic influence on the shallow coastal aquifer such as domestic sewage and/or agricultural impact (Masindi and Abiye, 2018). In the present study, domestic waste is the probable source of NO₃ in the groundwater. However, nitrate could be partially sourced from oxidation of ammonium ions (Masindi and Abiye, 2018).

The sixth factor (F6) associated with manganese constituted 6.22% of the total variance. This suggested anthropogenic sources which may be linked to leachate from domestic waste discharge, deterioration of abandoned electronics, vehicle and machine scrap from their natural occurrence.

The seventh factor (F7), with a higher loading for faecal coliforms, accounted for 5.45% of the total variance. The presence of faecal coliforms in the groundwater indicates contamination by animal and human faeces (wastes). These findings are consistent with that of Ikem et al. (2002) which showed the impact of urbanization and industrialization on the groundwater quality around Lagos metropolis.

In the dry season, the F1 factor showed a higher loading for TDS and EC, constituting 14.57% of the total variance. The linear relationship between these parameters indicates high mineralisation due to weathering. As the TDS increases with more dissolution of minerals, the salinity equally increases and consequently increases the EC of the groundwater.

The F2 factor, enriched with CO₃²⁻ and Cl⁻, constituted 13.51% of the total variance with a low loading of HCO₃⁻, Na⁺ and Mg²⁺. This type of association might indicate gradual leaching of salts from the surface or ion exchange process. However, it has a moderate but negative loading with respect to K⁺. This may indicate a different source for the potassium which is likely to be derived from the sand-filled materials brought from the hinterland or anthropogenic contribution.

Factor F3 is represented by SO₄²⁻, Ca²⁺ and K⁺ with a total data variability of 13.10%. The positive loading of SO₄²⁻ and Ca²⁺, with a negative loading of K⁺, denote their antithetic covariance. The positive loading of Ca²⁺ and SO₄²⁻ may not necessarily indicate dissolution or weathering of sulphate-bearing minerals such as gypsum and anhydrite, since the source of these rocks have not yet known or reported for the study area. Possible sources of sulphate may be anaerobic decomposition of organic wastes and municipality dumps, and dead plants could also release H₂S, which joins the oxic zone and interacts with H₂O and dissolved oxygen to generate SO₄²⁻. Sulphate is also a major constituent in the aerosols which is coming from industries and automobiles (Kumar et al., 2015). In the study area, higher sulphate might have been derived from the atmospheric deposition of industrial and automobile aerosols and, to a lesser extent, decomposition of organic wastes (Yusuf, 2020).

Factor F4, constituting 11.91% of the total variance, was represented by a highly negative loading for NO₃, indicating an anthropogenic impact from a unique source and substantial reduction in NO₃ contribution to the shallow groundwater in the dry season.

Factor F5 showed a higher loading for Ca²⁺ and HCO₃⁻, constituting 11.84% of the total variance. This positive loading between Ca²⁺ and HCO₃⁻ may be indicating chemical weathering. This simply indicates dissolution of carbonate minerals in the presence of soil CO₂ (Yusuf, 2020).

Factor F6, constituting 11.04% of the total variance was enriched in Mg²⁺ with a negative loading for Na⁺, Ca²⁺ and HCO₃⁻, indicating ion exchange processes, leading to enhancement of Mg²⁺.

In the present study, the extracted seven factors and six factors for the wet and dry seasons, respectively (eigenvalues >1) accounted for 82.27% and 75.97% of the total variance, revealing their significant contribution to the variance of the groundwater hydrochemistry in the area. Similarly, the high communalities ranging between 0.556 and 0.984; 0.533 and 0.876 recorded for both seasons, indicated that most of the variance of each variable is explained by the extracted factors.

The plot of the dominant factors was undertaken in order to appreciate and identify the dominant chemical processes and common hydrogeochemical variables based on principal components (Figure 16a-e). Figures 16a and 16b represent the wet season, while the dry season is represented by Figure 16 c-e. The plots also give credence to the fact that geogenic contribution plays a major role in both seasons; however, anthropogenic influence was equally prominent in the groundwater chemistry, particularly in the wet season relative to the dry season.

### 2.5. Geochemical modelling

The state of mineral saturation was calculated from the analytical data. The SI of a mineral indicates the degree of saturation of a particular mineral phase in an aqueous solution from where the trend of precipitation or dissolution of the mineral phases may be deduced. To assess
the dissolution/precipitation of these minerals, their saturation indices were simulated using the thermodynamic software PHREEQC (Parkhurst and Appelo, 1999) and plotted on a graph in (Figure 17).

The PHREEQC results show that water samples from the study area were undersaturated and supersaturated variably for all the examined rock minerals. It was observed that gypsum and halite (evaporate) were dominated by negative saturation indices (Figure 17a and Figure 17b) implying that the groundwater was essentially undersaturated with respect to these minerals for both seasons. This gives further credence to atmospheric deposition of aerosols and/or anaerobic decomposition of organic matter as the possible source of sulphate to the groundwater. In the wet season, the groundwater appeared to be in transition from under-

Figure 16. Loading plot of F2, F3 and F5 on F1 showing (i) geogenic and anthropogenic contributions in the wet season (a, b); (ii) dominance of geogenic influence in the dry season (c-e).

Figure 17. The saturation index of calcite, gypsum and halite minerals for (a) wet season (b) dry season.
saturation to super-saturation state with respect to calcite (Figure 17a). The positive saturation index for calcite in the dry season and the majority of the samples in the wet season (Figure 17b) suggested that those samples are saturated with respect to calcite under present conditions. The supersaturation exhibited by calcite for both seasons in most samples under the present condition suggested longer residence time of the minerals relative to the undersaturated mineral constituents, such as halite and gypsum in groundwater (Ako et al., 2012; Sunkari et al., 2019) and also indicated the dominance of carbonate weathering as the principal factor controlling the groundwater chemistry. In contrast, samples with negative saturation indices (gypsum and halite) as observed for both seasons connoted shorter residence time for these minerals in the groundwater and may have been suddenly precipitated into the water (Sunkari et al., 2019). In addition, the most negative SI values in the groundwater exhibited by halite and gypsum may also imply an insignificant contribution of these minerals to the groundwater chemistry. Furthermore, it was observed that the source of the chloride concentrations are not limited by mineral equilibrium and thus could not originate from brine water. Therefore, Na⁺ and Cl⁻ loading may be attributed to ion exchange resulting from mixed water (Jankowski et al., 1998). In summary, the saturation index result agrees with deductions from various hydrochemical plots (Trilinear, Gibbs and Durov) and scatter diagrams which showed that carbonate weathering and ion exchange are the major processes controlling the groundwater quality in the study area.

3. Conclusion

This study presents fresh insights into the hydrogeochemical processes that govern the shallow groundwater quality of the LCB. A comparison of the physico-chemical parameters of the groundwater with WHO (2018) standard for drinking water are generally found to be within the acceptable limit of WHO for drinking water except TDS, EC, NO₃ and f. coli in some of the samples, particularly during the rainy season. The predominant cations and anions in the groundwater and surface waters are: Ca²⁺ > Mg²⁺ > K⁺ > Na⁺ and Cl⁻ > HCO₃⁻ > SO₄²⁻; Ca²⁺ > K⁺ > Na⁺ > Mg²⁺ and HCO₃⁻ > Cl⁻ > SO₄²⁻ in wet and dry seasons, respectively. These accounted primarily for the dominance of Ca–HCO₃, Ca–Mg–HCO₃, and Ca–Mg–Cl–SO₄ water types in the groundwater of the study area. Meanwhile, the lagoon and Ocean waters are characterised by Mg–Cl and Na–Cl water types, respectively. One of the major findings in this study is that the groundwater chemistry is essentially controlled by both natural and anthropogenic processes. Interpretation from hydrochemical data suggests that water rock interaction, carbonate dissolution, ion exchange, simple mixing and evaporation are the notable geochemical processes controlling the shallow groundwater chemistry in the study area. The anthropogenic activities such as domestic waste discharge, commercial activities, and industrial effluents are possibly significant sources of NO₃, Mn²⁺, Fe²⁺, Cu²⁺, Ni²⁺ and faecal coliform. The saturation index result corroborates the proposed ionic ratios methods, given credence to the dominance of carbonate weathering in the shallow aquifer. Salinity evaluation showed that the surficial aquifer is an essential freshwater, particularly in the dry season across the basin, except being some few samples that exhibited slight marine impact in the west and central parts of the study area during the wet seasons. In summary, despite the relatively limited number of data, the major factors controlling the evolution of the groundwater in the LCB has been deduced. Therefore, it is recommended that the aquifer be consistently monitored for pollution trend across the basin over time and space. Lastly, this study has improved the understanding of hydrogeology through successful application of the newly proposed cationic contribution evaluation and ionic ratio bivariate plots to deduce various hydrochemical processes controlling the groundwater chemistry in the study area, hence may be adopted for use in similar terrains worldwide.

Declarations

Author contribution statement

Yusuf, M.A.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Abraye, T.A.: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Ibrahim, K.O., Abubakar, H.O.: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

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The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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