Review Article

Origin and residence time of shallow groundwater resources in Lagos coastal basin, south-west Nigeria: An isotopic approach

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Abstract

Knowledge of the source of water in the Lagos coastal basin (LCB) groundwater system was to be found vital to the future development and management of the system. Stable and radioactive isotopic measurements have been employed to unravel the source of recharge and residence time of the shallow groundwater system, based on the sampling conducted in 2016 and 2017 on groundwater, surface water and rainfall. The concentration of tritium in the groundwater samples were very low and ranged from less than 1 to 2.8 TU, while measured 14C contents ranged from 59.1 to 88 pMC. The δ18O values of groundwater samples ranged from 4.81 and 3.98 ‰, while the δ2H values ranged from -24.75 and -19.70 ‰ for the wet and dry seasons, respectively. The obtained results indicated non-existence of paleo recharge; rather all groundwater in the basin were found to be essentially of meteoric origin with intermittent surface water contributions. Moreover, shallow groundwater and surface water have
considerable variations in isotopic compositions, reflecting evaporation and preservation of seasonal fluctuation. Though there was an observed generally low tritium content, however, it proved useful in the identification of recent active recharge taking place across the basin. The deduced radiocarbon age reflected the presence of “modern water” and thus supports the presence of present recharge to the groundwater system. Therefore, the source of the shallow groundwater recharge was actively renewable particularly during the wet season and thus water exploitation is potentially sustainable in the basin.

Keywords: Hydrology, Environmental science, Earth sciences, Geology, Geophysics

1. Introduction

Surface water and groundwater interaction studies are vital to implementing effective management of water resources (Winter, 1999; Sophocleous, 2002; Abiye, 2013). It is a known fact that well-managed water resources are vital for sustainable socio-economic development (Abiye, 2013). Groundwater plays a vital role in determining the social and economic growth of Lagos and acts as the major source of potable water supply to a vast majority of the coastal city inhabitants (Akoteyan and Soladoye, 2011; NERC, 2003). Hence, it is imperative to understand the hydrogeological environment (topography, geology, and climate) in order to investigate groundwater-surface water interactions (Sophocleous, 2002; Abiye, 2013). Lagos is located within the southwest of Nigeria coastal domain (6° 34’ 50” North and 3° 19’ 59” East) comprising dominantly of lagoons and coastal creeks developed by a barrier of beaches and situated on series of stratified sedimentary rocks consisting of silts, clay, peats or coal associated with coastal plants (Oyedele and Momoh, 2009). The Lagos metropolis was until 1991 the Federal Capital of Nigeria and still is a commercial epicenter, despite the movement of the seat of power to Abuja. The rate of population growth is about 300,000 persons per annum with an average density of 20,000/km² (Adelana et al., 2008; Atakpo et al., 2011). The coastal city with a total land area of about 3600km² and with an annual growth rate of 4% it was one of the world’s five megacities in 2015 (UN, 2011). The exponential population growth as well as the rapid industrial expansion in the metropolis, consequently, demanded an increase in water supply for domestic and industrial purposes. In Lagos, there is a pressure on groundwater resources, further worsened by anthropogenic pollution. A large number of private wells (boreholes and hand-dug) were sunk without recourse to the source and amount of replenishment to the aquifer (Oyeyemi et al., 2015). However, the roles of sustainable development of the groundwater require an understanding of their origin and renewability (Acheampong and Hess, 2000; Chen et al., 2006; Abiye, 2011).
The study area (Fig. 1) falls within the southern coastal belt of Lagos, which is an integral component of 1000km stretch of Nigeria Atlantic coastline extending from Accra to Lagos within the Dahomey basin (Oyeyemi et al., 2015). This area constitutes vulnerable ecosystem subject to severe anthropogenic and natural hazards, such as sea level rise, land subsidence, flooding and coastal erosion and salinization of groundwater (Bear et al., 1999; Adelana and MacDonald, 2008; Akoteyan and Balogun, 2012). A coastal aquifer is particularly damaged by enhanced pumping for water supply, as this leads, as the case may be, to lowering of water table, increase of land subsidence and intrusion of saline water into fresh aquifers (Barlow, 2003; Kumar et al., 2007). Thus, a major problem in drinking water quality and management of domestic water supply in this coastal strip is the saltwater intrusion in hand-dug wells and boreholes (Olado et al., 2014). Many wells have not been completed, while several existing hand-dug wells and boreholes are abandoned or decommissioned due to saltwater intrusion overtime (Oyeyemi et al., 2015). In order to enhance our understanding of the hydrodynamical nature of the shallow aquifers in this basin for sustainable management, two questions are pertinent to the sustainability of groundwater resources:

How old is the rechargeable water supply? In other words, when did recharge happen?

What is the source of recharge for shallow groundwater? Are we ‘mining’ groundwater or otherwise?

Fig. 1. Location Map of the study area.
The most common approach used to solve this problem is to adopt environmental isotopes technique; an important tool in hydrogeological studies that is specifically not known to the Lagos coastal basin (LCB) prior to this research. The stable isotopes of $^2$H and $^{18}$O occur naturally in precipitation and provide a seasonal meteoric signal in temperate, continental systems that are often attenuated in shallow groundwater (Clark and Fritz, 1997; Abiye, 2013). Environmental isotopes, (stable and radiogenic) as a tool for hydrogeological studies are gaining popularity in recent times and have been used to gain some insight into the subsurface flow and recharge condition (Abiye, 2011). Naturally occurring stable ($^2$H, $^{18}$O) and radiogenic ($^3$H and $^{14}$C) isotopes of water have been widely used over the past 40 years to solve problems related to groundwater recharge and its residence time (Fontes, 1980; Gonfiantini, 1986; Clark and Fritz, 1997; Chen et al., 2006). Isotopes in combination with other hydrochemical and geophysical studies have a wide range of applicability. This includes but not limited to the determination of the age and origin of different groundwaters, delineation of flow systems, quantification of mass-balance relationships, interaction between surface and groundwater, occurrence of groundwater; localize and delimit groundwater catchment areas (Fontes, 1980; Gonfiantini, 1986; Siegel, 1991; Gat, 1996; Clark and Fritz, 1997; Rozanski et al., 1997). We herein present the results of a pioneering attempt at using environmental isotopes to investigate and improve our understanding of the shallow groundwater system in Lagos coastal basin (LCB) of Nigeria specifically with respect to the age and source of recharge and, a possible interaction between surface and groundwaters (Fig. 1).

2. Main text

2.1. Geological and hydrogeological setting

The study area is situated in the coastal strip of Dahomey basin, western Nigeria (Fig. 2). It is an extensive sedimentary basin in the Gulf of Guinea. It extends from southeastern Ghana (Keta basin) in the west, through southern Togo and the southern Benin Republic to thin out at Okitipupa ridge in Nigeria in the east (Billman, 1976). The basin was initiated during the Mesozoic in response to the separation of the African-South American land masses (Gondwanaland) and the subsequent opening of the Atlantic Ocean (Burke et al., 1971; Whiteman, 1982). Deposition began in fault-associated depressions developed in the crystalline basement complex as a result of the rift-generated basement subsidence during the Early Cretaceous (Neocomian). The subsidence gave rise to the deposition of a very thick sequence of various types of sedimentary rocks over the entire basin (Lehner and De Ruiter, 1977). Over 1,400 meters of these sediments are preserved in coastal areas in Nigeria and offshore in Benin republic (Billman, 1976; Omatsola and Adegoke, 1981). In the Santonian, both the basement rocks and the sediments in the basin
were tilted and block-faulted and subsequently forming a series of horsts and grabens during the Maastrichtian. The basin became quiescent during this period and experienced only gentle subsidence (Omatosola and Adegoke, 1981). The coastal zone of Lagos is made up of creeks and lagoons developed by barrier beaches associated with sand deposition in the geologic past. The western limit of the basin is marked by faults while it is bounded to the east by the Benin hinge line demarcating the western limit of the Niger Delta. The basin geology is composed of sedimentary rocks and surficial alluvial deposits. These are essentially composed of loose and light grey sand with varying proportion of vegetation matter content on the lowland, while the reddish and brown loamy soil characterize the upland (Olowofela et al., 2012). The geology is essentially underlain by interbedded sands, gravelly sands, silts, and clays (Akoteyon et al., 2011). The subsurface geology reveals two basic lithologies viz; an alternating sequence of clay and sand deposits (Akoteyon et al., 2011; Olowofela et al., 2012). These deposits are intercalated in places with sandy clay or clayey sand and occasionally with vegetable remains and peat (Ayolabi and Peters, 2005).

Hydro-geologically, the water-bearing strata of Lagos consists of sand, gravel, or a mixture, which range from fine through medium to coarse sand and gravel (Adeleye, 1975). The four major aquiferous units in the Lagos metropolis includes Abeokuta group, Ewekoro formation, coastal plain sands (CPS) and recent sediments (Jones and Hockey, 1964). There is a general decrease in the aquifer thickness from the north towards the coast in the south and also well noticed is the variation in the percentage composition of sand from north to south (Longe et al., 1987). The aquifers vary from unconfined, semi-confined to confined occurrence with depth. The CPS is the most productive and most exploited aquifer in the Lagos state. However, there is
different aquifers’ depth estimation by various authors. The first aquifer extends from ground level to about 12 m below the subsurface. This aquifer is definitely prone to various forms of pollutions due to its limited depth. The second aquifer exists between the 20 m and 100 m below sea level. The third aquifer was intercepted in the central part of Lagos between the depths ranging from 130 m to 160 m below the sea level. The fourth aquifer can be accessed at 450 m depth below sea level and only a few boreholes tap from this aquifer (Jones and Hockey, 1964). This account, however, differs from Onwuka’s (1990) observations. He classified the hydrogeologic units of the Dahomey basin groundwater into three main hydro-stratigraphic units viz: The upper aquifer (Alluvium and Coastal plain sand); Middle aquifer (Ilaro and Ewekoro Formations) and Lower aquifer (Abeokuta Formation) and it is considered most protected aquifer from pollution.

2.2. Materials and methods

Our sampling sites comprised of shallow groundwater wells mostly hand-dug and surface water located around and across the study area. The choice and number of sampling sites were constrained by both availability and accessibility to dug wells. Thirty-shallow groundwater, five-surface water, and one-rain water were sampled for environmental isotope analyses between September–October 2016 and in February 2017, hydrological years. The records of well completion were not available to us or were non-existent. In most cases, we were able to sample groundwater directly from boreholes, while we were compelled to take samples via household taps in places. However, the surface water samples were taken at least 250m away from the onshore, to ensure even mixing and adequate representation. The sampled waters were collected unfiltered and stored unpreserved in tightly sealed plastic bottles. To ensure groundwater samples taken were aquifer representation at any particular location and depth, the wells were thoroughly mixed and pumped as the case may be prior to sampling. The water level depth was taken with the aid of TLC meter. A total of 30-samples for stable isotopes of $^2$H and $^{18}$O, 21-samples for radioactive tritium and 9-samples for $^{14}$C and $^{13}$C isotopes were collected and analyzed. Samples for $^{18}$O and $^2$H were collected in 10ml glass bottles with airtight caps. The samples for tritium analysis were collected in sealed 1L plastic bottles. The samples for carbon isotope determination were collected by precipitating BaCO$_3$ by adding BaCl$_2$ to 50L of water, previously brought to pH $\geq$ 12 by addition of NaOH. The stable isotope of deuterium and oxygen were analyzed at hydrogeology laboratory at the school of geoscience, using the Liquid Water Isotope Analyzer-model 45-EP at the University of the Witwatersrand, South Africa, while tritium, $^{14}$C, and $^{13}$C analyses were carried out at the i-Themba laboratory, Gauteng, South Africa. All samples were replicated. Results are represented in the conventional V-SMOW normalization. The precision obtained was 0.05% and 1% for $^{18}$O and $^2$H respectively.
The stable isotopic composition of a water sample is reported in δ notation as given by Eq. (i):

$$\delta = \left( \frac{R_{\text{sam}} - R_{\text{std}}}{R_{\text{std}}} \right) \cdot 1000$$

Where \( R = \text{D/H or } ^{18}\text{O}/^{16}\text{O or } ^{13}\text{O}/^{12}\text{C} \) and all values are reported in per mil in reference to V-SMOW Vienna Standard mean ocean water (Gonfiantini, 1978). A positive and negative value connotes enrichment and depletion in the heavy isotope respectively relative to the standard. Also, precipitation originated from higher altitude is more isotopically depleted in 2H and 18O than precipitation at lower altitudes. Therefore, these stable isotopic ratios are useful in evaluating the precipitation source areas of recharge to an aquifer (Mazor, 1991). Tritium was determined on electrolytically enriched water samples by low-level proportional counting. The results were reported in tritium unit (TU) with a typical error of ±1TU (Echinger, 1980), while 14C of dissolved inorganic carbon (DIC) was radio metrically determined by liquid scintillation counting after conversion to benzene (Fontes, 1971). The 14C is between 0.7-1.0 pMC. The δ13C was determined spectrometrically and expressed as δ-values related to the V-PDB (Vienna Pee Dee Belemnite) standard. Precision for δ13C is ±0.5. Radioactive isotopes of tritium (3H) and Carbon (14C) do occur in natural waters in low but detectable amounts (Loehnert, 1988). Tritium’s short half-life (12.4 years) allows it to be used for relatively young waters <50 years ago, while the longer half-life of carbon-14 (5730 years) enables it to be used for old hydrological systems. Information about stable isotope contents in precipitation from Benin republic was obtained from the online GNIP database (IAEA).

2.3. Results and discussion

Detailed physical parameters measured in-situ on the field were contained in (Tables 1 and 2), while analytical isotope results were presented in (Tables, 3, 4 and 5) represents a summary of the isotopic data set for both dry and wet seasons. It should be noted that 13C, 14C, and 3H analysis only represent the wet season, as the result for the dry season is not available at the time of writing this paper.

2.3.1. Deuterium (2H) and oxygen-18

The isotope composition (oxygen and hydrogen) of groundwater, surface water from Lagoon, creek, and seawater from the Atlantic Ocean are shown in (Tables 3 and 4). The graphical relationship between 2H and 18O are shown in Figs. 3 and 4. The 2H and 18O values of precipitation and infiltrating water are controlled by many factors such as latitude and altitude effects, intensity, and duration of rainfall, temperature, evaporation, and condensation in recharge and drainage areas (Dansgarrd, 1964;
Table 1. In-situ physical parameters measured for wet season samples in the Lagos coastal basin.

| Sample no | Loc. Name      | Date           | Long.(E) | Lat.(N) | Well-Depth(m) | Water Level(m) | pH  | TDS (ppm) | Ec (µs/cm) | Tritium (T.U) | Carbon-14 (pMC) | Uncorrected ¹⁴C Age (year) | Carbon-13 (%o) |
|-----------|----------------|----------------|----------|---------|---------------|----------------|-----|-----------|------------|----------------|----------------|-------------------------------|----------------|
| Shallow groundwater | | | | | | | | | | | | | |
| GW1       | Coconut/App    | 11/10/2016     | 0626.520' | 00319.876' | 4.5          | 1.2            | 7.5 | 772       | 1563      | 7.8            | 1950 ± 10                 | -17.86                      |
| GW2       | Coconut/App    | 11/10/2016     | 0626.631' | 00319.775' | 7            | 0.7            | 7.7 | 399       | 736       | 1.7            | 78.8                | 1950 ± 10                 | -12.79                      |
| GW4       | Ijora/App      | 11/10/2016     | 0628.163' | 00321.560' | 7.2          | 3.6            | 6.7 | 589       | 1133      | 2.8            | 78.4                | 1950 ± 10                 | -22.95                      |
| GW5       | Badia/App      | 11/10/2016     | 0627.899' | 00321.561' | 3.87         | 1.85           | 7.7 | 670       | 760       | 2.8            | 78.4                | 1950 ± 10                 | -22.95                      |
| GW6       | Wharf/App      | 12/10/2016     | 0626.555' | 00322.017' | 6            | 1.3            | 7.4 | 2172      | 1.7       | 78.4            | 1950 ± 10                 | -12.79                      |
| GW7       | Kirikiri Rd/App| 12/10/2016     | 0626.899' | 00319.837' | 11.2         | 2.2            | 6.8 | 650       | 1232      | 1.1            | 78.9                | 1950 ± 10                 | -22.95                      |
| GW8       | Marina park/Isl| 13/10/2016     | 0627.196' | 00323.052' | 6.5          | 3.04           | 8.2 | 499       | 3387      | 1.3            | 66.8                | 3350 ± 10                 | -22.95                      |
| GW9       | Obalende/Iky   | 13/10/2016     | 0626.908' | 00324.627' | 7.12         | 2.27           | 7.3 | 546       | 1076      | 1.8            | 78.4                | 1950 ± 10                 | -22.95                      |
| GW10      | Adeniji/Isl    | 13/10/2016     | 0627.483' | 00323.925' | 4.25         | 1.7            | 7.8 | 602       | 1200      | 2.2            | 78.4                | 1950 ± 10                 | -22.95                      |
| GW12      | Isale Eko/Isl  | 13/10/2016     | 0627.815' | 00323.259' | 7.1          | 2.7            | 7.9 | 419       | 779       | 1.7            | 78.4                | 1950 ± 10                 | -22.95                      |
| GW13      | Oloowogbowo/Isl| 13/10/2016     | 0627.464' | 00322.938' | 12           | 4.25           | 7.5 | 704       | 1393      | 0.2            | 59.1                | 4350 ± 10                 | -15.32                      |
| GW14      | Abdu Smith/VI  | 14/10/2016     | 0625.891' | 00324.590' | 3.75         | 1.3            | 7.6 | 203       | 342       | -12.99          | 72.7                | 2650 ± 10                 | -12.99                      |
| GW15      | Ribadu Rd/Iky  | 14/10/2016     | 0626.629' | 00325.243' | 5.6          | 2.62           | 7.7 | 380       | 715       | 1.7            | 78.4                | 1950 ± 10                 | -12.99                      |
| GW16      | Awo.Rd/Iky     | 14/10/2016     | 0626.648' | 00324.640' | 5            | 1.3            | 7.8 | 252       | 442       | 1.7            | 78.4                | 1950 ± 10                 | -12.99                      |
| GW17      | Aboyade/Vi     | 14/10/2016     | 0626.213' | 00324.317' | 3.8          | 0.8            | 8.6 | 70        | 112       | 1.7            | 72.7                | 2650 ± 10                 | -12.99                      |
| GW18      | LekkiPhase1    | 17/10/2016     | 0626.341' | 00328.077' | 3.2          | 1.6            | 7.5 | 329       | 594       | 1.5            | 74.5                | 2450 ± 10                 | -12.56                      |
| GW19      | Igboefon/Aj    | 17/10/2016     | 0626.268' | 00331.209' | 3.45         | 0.71           | 7.7 | 288       | 512       | 1.7            | 72.7                | 2650 ± 10                 | -12.99                      |
| GW20      | Lafiaji/Eto    | 17/10/2016     | 0625.884' | 00332.618' | 9.5          | 0.71           | 6.2 | 160       | 251       | 1.7            | 72.7                | 2650 ± 10                 | -12.99                      |
| GW21      | Oke iranla/Eto | 17/10/2016     | 0629.328' | 00334.864' | 9            | 2.7            | 6.8 | 385       | 862       | 1.7            | 72.7                | 2650 ± 10                 | -12.99                      |
| GW22      | Ado/Eto        | 17/10/2016     | 0630.124' | 00336.007' | 7.2          | 0.4            | 7   | 401       | 751       | 0.9            | 81.6                | 1700 ± 10                 | -20.51                      |
| GW23      | Badore/Eto     | 18/10/2016     | 0627.820' | 00340.300' | 6.3          | 1.72           | 7   | 139       | 232       | 1.4            | 78.4                | 1950 ± 10                 | -12.99                      |
| GW24      | Abijo/Ibl      | 18/10/2016     | 0628.139' | 00342.195' | 6.12         | 1.13           | 5.4 | 64        | 83        | 1.2            | 78.4                | 1950 ± 10                 | -12.99                      |
| GW25      | Awoyaya/Ibl    | 18/10/2016     | 0628.427' | 00348.325' | 7.4          | 0.8            | 6.8 | 69        | 111       | 1.7            | 78.4                | 1950 ± 10                 | -12.99                      |
| Sample no | Loc. Name     | Date       | Long.(E)       | Lat.(N)       | Well-Depth(m) | Water Level(m) | pH | TDS (ppm) | Ec (μS/cm) | Tritium (T.U) | Carbon-14 (pMC) | Uncorrected $^{14}$C Age (year) | Carbon-13 (%) |
|-----------|---------------|------------|----------------|---------------|---------------|----------------|----|-----------|-------------|----------------|-----------------|----------------------------------|--------------|
| GW30      | Igando/Ibl    | 18/10/2016 | 0629.103’      | 00353.303’    | 5.85          | 0.2            | 7  | 151       | 254         | 1.8            | 83.4            | 1500 ± 10                      |              |
| GW32      | Sangotedo/Eto | 19/10/2016 | 0628.415’      | 00338.133’    | 7.6           | 3.7            | 6.1 | 380       | 701         | 1.2            | 380             | 1050 ± 10                      |              |
| GW33      | Ajah/Eto      | 19/10/2016 | 0628.466’      | 00334.616’    | 13.2          | 1.3            | 6.3 | 175       | 300         | 1.1            | 300             | 1050 ± 10                      |              |
| GW36      | Ajah markt/Eto| 19/10/2016 | 0628.121’      | 00333.873’    | 7.45          | 3.25           | 7.3 | 192       | 310         | 88             | 701             | 1050 ± 10                      |              |
| GW37      | Idado/Eto     | 19/10/2016 | 0626.380’      | 00331.305’    | 8.2           | 1             | 7.2 | 291       | 514         | 0.1            | 514             | 1050 ± 10                      |              |
| GW40      | Ikota/Eto     | 19/10/2016 | 0626.959’      | 00332.928’    | 4.35          | 2.12           | 7.1 | 112       | 183         | 1.7            | 183             | 1050 ± 10                      |              |
| RW1       | Lagos Island  | 22/10/2016 | 0627.673’      | 00323.666’    | -             | -              | -  | -        | -           | -              | -               | -                  |              |
| SW1       | Lagos Lagoon  | 14/10/2016 | 0629.673’      | 00325.666’    | -             | ND             | 8.6 | -        | -           | 1.7            | -               | -                  | 1            |
| SW3       | Ajah Lagoon   | 19/10/2016 | 0631.541’      | 00334.756’    | -             | ND             | 8.5 | -        | -           | 2              | -               | -                  | 2            |
| SW2       | Oniru beach   | 14/10/2016 | 0623.349’      | 00326.525’    | -             | ND             | 8.6 | -        | -           | 1              | -               | -                  | 1            |

ND = not detected.
Table 2. In-situ physical parameters measured for dry season samples in the Lagos coastal basin.

| Sample No. | Loc. Name     | Date       | Long.(E)   | Lat.(N)   | Well-Depth(m) | Water Level(m) | pH   | TDS (ppm) | Ec (µs/cm) |
|------------|---------------|------------|------------|-----------|---------------|----------------|------|-----------|------------|
| GW1        | Coconut/App   | 14/02/2017 | 0626.520'  | 00319.876' | 4.5           | 3.26           | 7.5  | 785       | 1542       |
| GW2        | Coconut/App   | 14/02/2017 | 0626.631'  | 00319.775' | 7             | 2.29           | 7.4  | 536       | 949        |
| GW4        | Ijora/App     | 14/02/2017 | 0628.163'  | 00321.560' | 7.2           | 5.14           | 5.1  | 20        | 1912       |
| GW5        | Badia/App     | 14/02/2017 | 0627.899'  | 00321.561' | 3.87          | 2.44           | 7.3  | 1034      | 5336       |
| GW6        | Wharf/App     | 14/02/2017 | 0626.555'  | 00322.017' | 6             | 1.72           | 7.6  | 405       | 3089       |
| GW7        | Kirikiri Rd/App| 14/02/2017 | 0626.899'  | 00319.837' | 11.2          | 6.16           | 7    | 728       | 1360       |
| GW8        | Marina park/Isl | 15/02/2017 | 0627.196'  | 00323.052' | 6.5           | 3.67           | 8.5  | 713       | 3832       |
| GW9        | Obalende/Iky  | 15/02/2017 | 0626.908'  | 00324.627' | 7.12          | 3.35           | 7.2  | 558       | 1023       |
| GW10       | Adeniji/Iky   | 15/02/2017 | 0627.483'  | 00323.925' | 4.25          | 1.46           | 7.6  | 862       | 1681       |
| GW12       | Isale Eko/Isl | 15/02/2017 | 0627.815'  | 00323.259' | 7.1           | 2.71           | 7.6  | 641       | 1150       |
| GW13       | Olowogbowo/Isl| 15/02/2017 | 0627.464'  | 00322.938' | 12            | 5              | 7.6  | 685       | 1250       |
| GW14       | Abdu Smith/VI | 16/02/2017 | 0625.891'  | 00324.590' | 3.75          | 2.44           | 7.6  | 537       | 982        |
| GW15       | Ribadu Rd/Iky | 16/02/2017 | 0626.629'  | 00325.243' | 5.6           | 2.54           | 7.6  | 387       | 643        |
| GW17       | Aboyade/Vi    | 16/02/2017 | 0626.213'  | 00324.317' | 3.8           | 1.79           | 7.6  | 263       | 418        |
| GW18       | LekkiPhase1   | 16/02/2017 | 0626.341'  | 00328.077' | 3.2           | 2.71           | 7.7  | 505       | 809        |
| GW20       | Igboefon/Aj   | 17/02/2017 | 0626.268'  | 00331.209' | 4.2           | 1.77           | 8.3  | 375       | 620        |
| GW21       | Lafiaji/Eto   | 18/02/2017 | 0625.884'  | 00332.618' | 3.45          | 2.36           | 8.7  | 114       | 275        |
| GW22       | Ajive/Eto     | 17/02/2017 | 0628.161'  | 00334.789' | 9.5           | 3.46           | 7.5  | 121       | 179        |
| GW23       | Oke iranla/Eto| 18/02/2017 | 0629.328'  | 00334.864' | 9             | AD             | 8.6  | 412       | 693        |
| GW24       | Ado/Eto       | 18/02/2017 | 0629.861'  | 00335.154' | 7.2           | 2.22           | 7    | 528       | 908        |
| GW25       | Badore/Eto    | 18/02/2017 | 0630.124'  | 00336.007' | 6.3           | 2.4            | 6.5  | 368       | 588        |
| GW27       | Abijo/Ibl     | 17/02/2017 | 0627.820'  | 00340.300' | 6.12          | 3.82           | 7.6  | 123       | 142        |
| GW28       | Awoyaya/Ibl   | 21/02/2017 | 0628.139'  | 00342.195' | 7.4           | 2.85           | 7.2  | 35        | 48         |
| GW29       | Igando/Ibl    | 21/02/2017 | 0628.427'  | 00348.325' | 5.85          | 1.89           | 7.3  | 107       | 155        |
| GW32       | Sangotedo/Eto | 21/02/2017 | 0628.415'  | 00338.133' | 7.6           | 4.61           | 5.6  | 314       | 553        |

(continued on next page)
| Sample No. | Loc. Name           | Date          | Long.(E)    | Lat.(N)    | Well-Depth(m) | Water Level(m) | pH | TDS (ppm) | Ec (µs/cm) |
|------------|---------------------|---------------|-------------|------------|---------------|---------------|----|-----------|-------------|
| GW33       | Ajah/Eto            | 17/02/2017    | 0628.466'   | 00334.616' | 13.2          | 3.13           | 6.7 | 225       | 340         |
| GW36       | Ajah market/Eto     | 18/02/2017    | 0628.121'   | 00333.873' | 7.45          | 5.3            | 7.3 | 345       | 555         |
| GW37       | Idado/Eto           | 16/02/2017    | 0626.380'   | 00331.305' | 8.2           | 2.1            | 7.4 | 323       | 530         |
| GW40       | Ikota/Eto           | 18/02/2017    | 0626.959'   | 00332.928' | 4.35          | 3.62           | 7.3 | 75        | 102         |
| GW41       | Ogombo/Eto          | 17/02/2017    | 0626°58.6'' | 00636°45.2'' | 2.41         | 1.92           | 7.5 | 278       | 447         |
| GW42       | Ibeju Lekki         | 21/02/2017    | 0629°21.1'' | 00353°46.2'' | 5.2          | 3.23           | 8.6 | 270       | 357         |
| GW43       | Eleko town          | 21/02/2017    | 0626°26.0'' | 00351°21.6'' | 6.38         | 4.25           | 7.1 | 247       | 388         |
| GW44       | Lakowe              | 21/02/2017    | 0628°27.3'' | 00343°49.2'' | 3.48         | 1.97           | 6.8 | 507       | 845         |
| GW45       | Awoyaya/Ibl         | 21/02/2017    | 0628°40.7'' | 00342°40.9'' | 4.20         | 3.1            | 6.9 | 348       | 477         |
| Surface water |                     |               |             |            |               |                |     |           |             |
| SW1        | Lagos Lagoon        | 15/02/2017    | 0629.673'   | 00325.666' | -             | ND             | 8.6 | 16388     | 24100       |
| SW2        | Oniru beach         | 16/02/2017    | 0623.349'   | 00326.525' | -             | ND             | 8.6 | 19312     | 28400       |
| SW3        | Ajah Lagoon         | 18/02/2017    | 0631.541'   | 00334.756' | -             | ND             | 8.6 | 5835      | 8582        |
| SW4        | Okun Ajah/Sea       | 18/02/2017    | 0624° 08.2'' | 00335° 20.6'' | -            | ND             | 8.7 | 19652     | 28900       |
| SW5        | Apapa Creek         | 22/02/2017    | 0624° 54.1'' | 00321°56.1'' | -            | ND             | 7.1 | 11560     | 17000       |
On a global average, the general meteoric relationship between $^{18}$O and $^2$H was found to be linear for natural water and has been defined by the global meteoric water line (GMWL) with the following equation for fresh water Eq. (ii):

$$\delta^2 H = 8 \ast \delta^{18} O + 10 \%$$ \quad (Craig, 1961) \tag{ii}

The concept of the deuterium excess (d-excess) is given by Eq. (iii):

$$d = \delta^2 H - 8 \ast \delta^{18} O \quad (Dansgaard, 1964) \tag{iii}$$

The location of the data on the (GMWL) indicates the source of air moisture. A local meteoric water line (LMWL) defined by Eq. (iv) was established by Loehnert (1988) in Ore Agbabu, Southwestern Nigeria.

$$\delta^2 H = 7.2 \ast \delta^{18} O + 9.4 \%$$ \quad (iv)

Whereas, local meteoric water line LMWL for Cotonou GNIP station, an extension of the Lagos coastal basin LCB and her immediate neighbor country, between the years 2005–2015 is defined by Eq. (v):

$$\delta^2 H = 7.1 \ast \delta^{18} O + 9.1 \%$$ \quad (v)

This study, however, adopts the Cotonou LMWL for the purpose of this research due to the common features shared by both basins and reliability of the GNIP data. The LMWL show low vapor humidity relative to the GMWL resulting from its lower slope value. A slope is a function of humidity, temperature and other factors (Gat and Gonfiantini, 1981; Rozanski et al., 1997) of a particular groundwater territory. The plots in Figs. 3 and 4 reveal that the groundwater samples were plotted around and along the LMWL, indicating that the groundwaters in the coastal aquifer are of meteoric origin and that a large proportion is subject to evaporation effects. Furthermore, the samples that plotted above the LMWL indicate rapid infiltration of recharge water before evaporation, while samples that plotted below the LMWL are essentially subjected to evaporation prior to recharge. Moreover, the isotopic compositions of the groundwater in the dry season are generally enriched in $^{18}$O and $^2$H resulting in a shift towards the meteoric line indicating higher evaporation relative to the wet season. The seasonal variations can be attributed to amount effect as noted by Dansgaard (1964) that at any given location, the heavier rainfall is more isotopically depleted in composition than the light intensity rainfall during the dry season as the air moisture is subjected to less Raleigh condensation process. These results remain in perfect agreement with several observations for low latitude marine sites of the IAEA monitoring stations (IAEA, 1992).
recharge events and evaporation from unsaturated zones indicate seasonal fluctuations are preserved in the shallow groundwater aquifer. In the groundwater samples the median δ²H and δ¹⁸O of -10.30 and -2.58 ‰, and -12.26 and -3.05 ‰ were observed for wet and dry seasons respectively, reflects the peculiar feature of shallow groundwater. This deduction corresponds with many well-known phenomena documented in most stable isotopes of O and H textbooks. The diagrams of δ²H and δ¹⁸O (Figs. 3 and 4) also reveal most of the samples fall on an evaporation line or mixing line represented by a regression line defined by Eqs. (vi) and (vii) for both wet and dry seasons.

\[
\begin{align*}
\delta^2H &= 3.48 \times \delta^{18}O - 2.8 \text{ ‰ } \quad R^2 = 0.49 \text{ (Wet Season)} \\
\delta^2H &= 3.89 \times \delta^{18}O - 0.87 \text{ ‰ } \quad R^2 = 0.59 \text{ (Dry Season)}
\end{align*}
\]

The point at which the regression line intersects the LMWL (δ¹⁸O = -2.8; δ²H = -12) is attributed to the average stable isotopic composition of the parent rainfall. The low slopes of 3.48 and 3.89 exhibited by both wet and dry seasons are also suggestive of the evaporation process. According to Gat and Gonfiantini (1981) and Sheppard (1986) evaporation from a freshwater surface commonly results in evaporation line with a lower slope of 3.5–6 in a normal range of relative atmosphere humidities of 75–10. The position of rainwater above the LMWL could be related to the condensation effect which is controlled by regional air circulation from South Atlantic Ocean. According to Clarks and Fritz (1997) and Abiye (2013), this occurrence could be due to low humidity in the vapor.

Generally, surface waters are highly enriched with respect to ¹⁸O and ²H with the higher values recorded in the seawater relative to the Lagoon water (Fig. 3, Table 3). Specifically, the seawater samples collected in both seasons (wet and dry) close to the seashore south of the study area have an isotopic composition value that is higher than 0 ‰ for both isotopes as reported for modern oceanic seawater. In the dry season, however, surface water samples collected close to the sea, at the Apapa creek (Sw5) and the Lagos lagoon (Sw1) exhibit both marine and evaporation influence on the isotopic composition with positive stable isotopes values. Contrarily, Ajah lagoon (Sw3) at a greater distance from the sea has isotopic compositions that are only reflective of strong evaporation (Table 5 and Fig. 4). Whereas, in the wet season, both the Lagos and Ajah lagoons (Sw1 and Sw3) have similar depleted values as ground waters with respect to ²H and ¹⁸O and were plotted above the LMWL, but in the same region with parts of the groundwater on LMWL (Fig. 3, Table 3). According to Fritz and Clark (1997), it was rare to find surface and groundwater plotted above the GMWL but in low humidity regions, re-evaporation of precipitation from local surface waters created vapor masses with isotopic content that plot above the local meteoric water line. The shift above the LMWL indicates the
| Sample no | Loc. Name       | Date         | Long.(E) | Lat.(N)             | $\delta^{2}H$ ($\%_{oo}$) | $\delta^{18}O$ ($\%_{oo}$) | d-excess ($\%_{oo}$) | Tritium (T.U) | Carbon-14 (pMC) | Uncorrected 14C Age (year) | Carbon-13 ($\%_{oo}$) |
|-----------|-----------------|--------------|----------|---------------------|---------------------------|----------------------------|---------------------|----------------|-----------------|-----------------------------|---------------------|
| GW1       | Coconut/App     | 11/10/2016   | 0626.520' | 00319.876'          | -0.92                     | -0.08                      | -0.33               |                |                 |                             |                     |
| GW2       | Coconut/App     | 11/10/2016   | 0626.631' | 00319.775'          | -18.18                    | -2.58                      | 0.12                | 1.7            | 78.8            | 1950 ± 10                  | -17.86              |
| GW4       | Ijora/App       | 11/10/2016   | 0628.163' | 00321.560'          | -8.53                     | -0.88                      | -2.29               |                |                 |                             |                     |
| GW5       | Badia/App       | 11/10/2016   | 0627.899' | 00321.561'          | -24.75                    | -4.26                      | 5.49                | 2.8            |                 |                             |                     |
| GW6       | Wharf/App       | 12/10/2016   | 0626.555' | 00322.017'          | -5.57                     | -1.19                      | 2.85                | 1.7            |                 |                             |                     |
| GW7       | Kirikiri Rd/App | 12/10/2016   | 0626.899' | 00319.837'          | -8.26                     | -3.11                      | 13.80               | 1.1            | 78.9            | 1950 ± 10                  | -12.79              |
| GW8       | Marina park/Isl | 13/10/2016   | 0627.196' | 00323.052'          | -6.46                     | -2.39                      | 10.51               | 1.3            | 66.8            | 3350 ± 10                  | -22.95              |
| GW9       | Obalende/Iky    | 13/10/2016   | 0626.908' | 00324.627'          | -7.87                     | -2.41                      | 9.26                | 1.8            |                 |                             |                     |
| GW10      | Adeni/Isl       | 13/10/2016   | 0627.483' | 00323.925'          | -6.72                     | -2.34                      | 9.89                | 2.2            |                 |                             |                     |
| GW12      | Isale Eko/Isl   | 13/10/2016   | 0627.815' | 00323.259'          | -3.00                     | -0.63                      | 1.51                |                |                 |                             |                     |
| GW13      | Olowogbowo/Isl  | 13/10/2016   | 0627.464' | 00322.938'          | -8.03                     | -2.77                      | 11.62               | 0.2            | 59.1            | 4350 ± 10                  | -15.32              |
| GW14      | Abdu Smith/VI   | 14/10/2016   | 0625.891' | 00324.590'          | -14.43                    | -3.89                      | 13.18               |                |                 |                             |                     |
| GW15      | Ribadu Rd/Iky   | 14/10/2016   | 0626.629' | 00325.243'          | -11.37                    | -3.13                      | 10.86               |                |                 |                             |                     |
| GW16      | Awo.Rd/Iky      | 14/10/2016   | 0626.648' | 00324.640'          | -14.95                    | -3.30                      | 8.50                |                |                 |                             |                     |

(continued on next page)
Table 3. (Continued)

| Sample no | Loc. Name     | Date     | Long.(E) | Lat.(N) | δ²H (‰) | δ¹⁸O (‰) | d-excess (‰) | Tritium (T.U) | Carbon-14 (pMC) | Uncorrected ¹⁴C Age (year) | Carbon-13 (‰) |
|-----------|---------------|----------|----------|---------|---------|----------|-------------|---------------|----------------|--------------------------|---------------|
| GW17      | Aboyade/Vi    | 14/10/2016 | 0626.213’ | 00324.317’ | -20.19  | -4.81    | 13.94       | 1.7           | 72.7          | 2650 ± 10                | -12.99        |
| GW18      | LekkiPhase1   | 17/10/2016 | 0626.341’ | 00328.077’ | -11.61  | -3.48    | 13.13       | 1.5           | 74.5          | 2450 ± 10                | -12.56        |
| GW20      | Igboefon/Aj   | 17/10/2016 | 0626.268’ | 00331.209’ | -16.81  | -2.07    | -2.13       |               |              |                          |               |
| GW21      | Lafiaji/Eto   | 17/10/2016 | 0625.884’ | 00332.618’ | -7.89   | -0.83    | -2.00       |               |              |                          |               |
| GW23      | Oke iranla/Eto| 17/10/2016 | 0629.328’ | 00334.864’ | -8.17   | -1.99    | 5.99        |               |              |                          |               |
| GW25      | Ado/Eto       | 17/10/2016 | 0630.124’ | 00336.007’ | -7.93   | -3.06    | 13.79       | 0.9           | 81.6          | 1700 ± 10                | -20.51        |
| GW27      | Badore/Eto    | 18/10/2016 | 0627.820’ | 00340.300’ | -13.47  | -2.13    | 1.65        | 1.4           |              |                          |               |
| GW28      | Abijo/Ibl     | 18/10/2016 | 0628.139’ | 00342.195’ | -13.42  | -2.83    | 6.66        | 1.2           |              |                          |               |
| GW29      | Awoyaya/Ibl   | 18/10/2016 | 0628.427’ | 00348.325’ | -19.83  | -2.64    | -1.10       |               |              |                          |               |
| GW30      | Igando/Ibl    | 18/10/2016 | 0629.103’ | 00353.303’ | -17.36  | -2.52    | 0.50        | 1.8           | 83.4          | 1500 ± 10                |               |
| GW32      | Sangotedo/Eto | 19/10/2016 | 0628.415’ | 00338.133’ | -8.62   | -2.81    | 11.32       | 1.2           |              |                          |               |
| GW33      | Ajah/Eto      | 19/10/2016 | 0628.466’ | 00334.616’ | -10.30  | -1.71    | 1.83        | 1.1           | 88            | 1050 ± 10                |               |
| GW36      | Ajah markt/Eto| 19/10/2016 | 0628.121’ | 00333.873’ | -18.06  | -3.97    | 10.11       |               |              |                          |               |
| GW37      | Idado/Eto     | 19/10/2016 | 0626.380’ | 00331.305’ | -9.44   | -1.79    | 3.25        | 0.1           |              |                          |               |
| GW40      | Ikota/Eto     | 19/10/2016 | 0626.959’ | 00332.928’ | -14.16  | -3.70    | 12.13       | 1.7           |              |                          |               |

(continued on next page)
| Sample no | Loc. Name      | Date       | Long.(E) | Lat.(N) | $\delta^{2}$H ($\permil$) | $\delta^{18}$O ($\permil$) | d- excess ($\permil$) | Tritium (T.U) | Carbon-14 (pMC) | Uncorrected $^{14}$C Age (year) | Carbon-13 ($\permil$) |
|-----------|----------------|------------|----------|---------|---------------------------|----------------------------|----------------------|----------------|----------------|---------------------------------|---------------------|
| Rain water|                |            |          |         |                           |                            |                      |                |                |                                 |                     |
| RW1       | Lagos Island   | 22/10/2016 |          |         | 3.35                      | -1.65                      | 15.05                | 2.2            |                |                                 |                     |
| Surface water|              |            |          |         |                           |                            |                      |                |                |                                 |                     |
| SW1       | Lagos Lagoon   | 14/10/2016 | 0629.673’| 00325.666’ | -11.44                    | -3.17                      | 11.05                | 1.7            |                |                                 |                     |
| SW3       | Ajah Lagoon    | 19/10/2016 | 0631.541’| 00334.756’ | -13.71                    | -3.47                      | 10.93                | 2              |                |                                 |                     |
| SW2       | Oniru beach    | 14/10/2016 | 0623.349’| 00326.525’ | 2.67                       | 0.11                       | 1.89                 | 1              |                |                                 |                     |
Table 4. Analytical results for dry season water samples in the Lagos coastal basin.

| Sample No. | Loc. Name          | Date       | Long.(E) | Lat.(N)   | δ²H (%) | δ¹⁸O (%) | d = excess (%) |
|------------|--------------------|------------|----------|-----------|---------|----------|---------------|
| GW1        | Coconut/App        | 14/02/2017 | 0626.520' | 00319.876' | -9.8    | -2.90    | 10.76         |
| GW2        | Coconut/App        | 14/02/2017 | 0626.631' | 00319.775' | -12.9   | -3.33    | 10.75         |
| GW4        | Ijora/App          | 14/02/2017 | 0628.163' | 00321.560' | -12.5   | -3.29    | 10.89         |
| GW5        | Badia/App          | 14/02/2017 | 0627.899' | 00321.561' | -10.3   | -2.89    | 10.22         |
| GW6        | Wharf/App          | 14/02/2017 | 0626.555' | 00322.017' | -7.6    | -2.29    | 8.72          |
| GW7        | Kirikiri Rd/App    | 14/02/2017 | 0626.899' | 00319.837' | -3.6    | -0.73    | 1.54          |
| GW8        | Marina park/Isi    | 15/02/2017 | 0627.196' | 00323.052' | -11.6   | -2.72    | 7.73          |
| GW9        | Obalende/Iky       | 15/02/2017 | 0626.908' | 00324.627' | -11.8   | -3.29    | 11.59         |
| GW10       | Adeniji/Isi        | 15/02/2017 | 0627.483' | 00323.925' | -10.8   | -2.79    | 9.03          |
| GW12       | Isale Eko/Isi      | 15/02/2017 | 0627.815' | 00323.259' | -10.0   | -2.70    | 9.18          |
| GW13       | Olowogbogbo/Isl    | 15/02/2017 | 0627.464' | 00322.938' | -9.4    | -3.20    | 13.29         |
| GW14       | Abdu Smith/VI      | 16/02/2017 | 0625.891' | 00324.590' | -8.9    | -3.13    | 13.38         |
| GW15       | Ribadu Rd/Iky      | 16/02/2017 | 0626.629' | 00325.243' | -11.2   | -3.36    | 12.62         |
| GW17       | Aboyade/Vi         | 16/02/2017 | 0626.213' | 00324.317' | -13.6   | -3.38    | 10.35         |
| GW18       | LekkiPhaseI        | 16/02/2017 | 0626.341' | 00328.077' | -11.6   | -3.22    | 11.28         |
| GW20       | Igboefon/Aj        | 17/02/2017 | 0626.268' | 00331.209' | -15.3   | -3.71    | 11.08         |
| GW21       | Lafiaji/Eto        | 18/02/2017 | 0625.884' | 00332.618' | -13.0   | -3.12    | 9.17          |
| GW22       | Ajiwe/Eto          | 17/02/2017 | 0628.161' | 00334.789' | -15.5   | -3.35    | 8.31          |
| GW23       | Oke iranla/Eto     | 18/02/2017 | 0629.328' | 00334.864' | -12.9   | -3.06    | 8.88          |
| GW24       | Ado/Eto            | 18/02/2017 | 0629.861' | 00335.154' | -15.4   | -3.37    | 8.52          |
| GW25       | Badore/Eto         | 18/02/2017 | 0630.124' | 00336.007' | -12.0   | -2.93    | 8.74          |
| GW27       | Abijo/Ibl          | 17/02/2017 | 0627.820' | 00340.300' | -16.8   | -3.77    | 9.94          |
| GW28       | Awoyaya/Ibl        | 21/02/2017 | 0628.139' | 00342.195' | -19.7   | -3.98    | 8.59          |
| GW29       | Igando/Ibl         | 21/02/2017 | 0628.427' | 00348.325' | -8.6    | -1.71    | 3.51          |
| GW32       | Sangotedo/Eto      | 21/02/2017 | 0628.415' | 00338.133' | -13.1   | -2.74    | 6.29          |
| GW33       | Ajah/Eto           | 17/02/2017 | 0628.466' | 00334.616' | -13.0   | -2.52    | 4.86          |
| GW36       | Ajah markt/Eto     | 18/02/2017 | 0628.121' | 00333.873' | -16.4   | -3.26    | 6.70          |
| GW37       | Iddao/Eto          | 16/02/2017 | 0626.380' | 00331.305' | -11.1   | -2.60    | 7.34          |
| GW40       | Ikota/Eto          | 18/02/2017 | 0626.959' | 00332.928' | -15.6   | -3.45    | 8.87          |
| GW41       | Ogombo/Eto         | 17/02/2017 | 0626'58.6'' | 00636'45.2'' | -12.5   | -2.48    | 5.04          |
| GW42       | Ilheju Lekki       | 21/02/2017 | 0629'21.1'' | 00353'46.2'' | -11.5   | -2.54    | 6.54          |
| GW43       | Eleko town         | 21/02/2017 | 0626'26.0''' | 00351'21.6''' | -16.9   | -3.04    | 4.70          |
| GW44       | Lakowe             | 21/02/2017 | 0628'27.3''' | 00343'49.2''' | -11.2   | -2.38    | 5.71          |

(continued on next page)
### Table 4. (Continued)

| Sample No. | Loc. Name     | Date          | Lon.(E)     | Lat.(N)      | $\delta^{2}H$ (%) | $\delta^{18}O$ (%) | d-excess (%) |
|------------|---------------|---------------|-------------|--------------|-------------------|-------------------|--------------|
| GW45       | Awoyaya/Ibl  | 21/02/2017    | 0628'40.7'' | 00342'40.9'' | -13.2             | -2.78            | 6.50         |
| Surface water |               |               |             |              |                   |                   |              |
| SW1        | Lagos Lagoon | 15/02/2017    | 0629.673'   | 00325.666'   | 2.5               | 0.36             | -0.02        |
| SW2        | Oniru beach  | 16/02/2017    | 0623.349'   | 00326.525'   | 2.3               | 0.79             | -3.26        |
| SW3        | Ajah Lagoon  | 18/02/2017    | 0631.541'   | 00334.756'   | -1.9              | -0.26            | -0.06        |
| SW4        | Okun Ajah/Sea| 18/02/2017    | 0624'08.2'  | 00335'20.6'' | 1.9               | 0.82             | -3.97        |
| SW5        | Apapa Creek  | 22/02/2017    | 0624 54.1'' | 00321'56.1'' | 2.0               | 0.55             | -1.85        |

### Table 5. Summary of Isotopic Composition in the basin Sub-surface Aquifer.

| Tracers      | Groundwater | Surfacewater |
|--------------|-------------|--------------|
|              | Wet Season  | Dry Season   | Wet Season | Dry Season |
| $^{14}$C (pMC) | 59.1--88    | -            | -          | -          |
| $\delta^{18}$O (%) | -4.81 to -0.08 | -3.98 to -0.73 | -3.47 to 0.11 | -0.26 to 0.82 |
| $\delta^{2}$H (%) | -24.75 to -0.92 | -19.7 to -3.6 | -13.71 to 2.67 | -1.9 to 2.5 |
| $^3$H (TU)   | 0.1 to 2.8  | -            | 1 to 2     | -          |
| $\delta^{13}$C (%) | -22.95 to -12.56 | -            | -          | -          |
| d-excess (%) | -2.29 to 13.94 | 1.45 to 13.38 | 1.89 to 11.05 | -3.97 to -0.02 |

![Fig. 3. Plot of $\delta^{2}$H versus $\delta^{18}$O (%) for wet season waters in Lagos Coastal Basin.](https://doi.org/10.1016/j.heliyon.2018.e00932)
impact of rainwater on the surface water bodies and may also suggest that the vapor evaporated from the hydrologically closed basin. Furthermore, deuterium excess (d-excess = $\delta^2$H - 8 $\delta^{18}$O) interpretation was undertaken in order to ascertain the possible source of precipitation of the area which gives rise to recharge to the shallow aquifer. The $\delta^{18}$O value was plotted against d-excess (Figs. 5 and 6) and the distribution has a range of variations from -2.29‰ to 13.94‰ and 1.45‰ to 13.38‰ for wet and dry seasons respectively. These ranges of values reflect the influence of both local and regional moisture circulation indicating highly enriched humidity in the area of study. The occurrence of lower d-excess values at higher oxygen values ($\delta^{18}$O) connotes evaporative enrichment from regional circulation. On a global scale, the average d-excess value is known to be about 10‰ but differs with variations in humidity, wind speed, and sea surface temperature during evaporation, accordingly, the low d-excess values reflect high humidity during formation of vapor mass (Clarks and Fritz, 1997; Abiye, 2013). The groundwater isotope contents of the LCB in the south are isotopically enriched relative to the isotope compositions of groundwater studied in the northern parts of Nigeria (Kehinde, 1993; Goni and Edmunds, 2001; Adelana et al., 2003), but are similar in isotopic compositions to groundwaters from basement and sedimentary basin of southwestern Nigeria (Loehnart, 1988) and to those reported from other West Africa countries e.g. Ghana (Acheampong and Hess, 2000; Jorgensen and Banoeng-Yakubo, 2001).
The observed south-north depletion of stable isotope compositions in groundwaters may be attributed to both altitude and continental effect of the incident rain.

Tritium has been reliably employed to distinguish groundwater recharge during the pre-bomb time from younger water (Clark and Fritz, 1997). Its variation provides an insight into local recharge and circulation mechanisms. Sequel to early sixties thermonuclear test that injects $^3$H into the atmosphere, the tritium content in precipitation increased to 1000-folds, especially in the northern hemisphere. Since 1963, the peak tritium concentration has decreased to natural values in winter and about double natural in summer. This event consequently affected the groundwater tritium content as aquifers are being recharged. Therefore, $^3$H content can often be used to determine dates ante quem and post quem. For example, water with $^3$H < 5TU must have a residence time of more than 40 years, while waters having $^3$H > 20TU must date after 1961 (Clark and Fritz, 1997). The tritium values of shallow unconfined aquifer ranged from 0.1 to 2.8TU, 1.7 to 2.0 TU for surface water and 2.2 TU for a single rainwater sample (Tables 3 and 5). Rainwater of this composition when dominating a recharge would be considered as derived from the pre-bomb period (Loehnert, 1988). Shallow groundwater and surface waters, however, appear a proper mixture of infiltrated rainwater with tritium contents close to the precipitation. Likewise, the closeness in tritium values exhibited between Lagoon (Sw1 and SW3) and groundwater demonstrates intense and reiterating interaction of the water bodies. Similarly, Loehnert (1998) reported tritium value of 2 TU for rainwater during August break in parts of southwestern Nigeria. The groundwater data, however, apparently reveals clustering into two distinct groups, consisting of a group of relatively young immature shallow groundwater having tritium values >1 TU, and an older group of more mature or admixture of old and recent recharge groundwater with values of <1 TU. Based on groundwater residence time proposed by Clark and Fritz (1997), two distinguished recharges were discernible viz: sub-modern recharged prior to 1952 with tritium value of < 0.8 TU, and a mixture of submodern and recent recharge having tritium value range between 0.8 to 4 TU. For all the samples, the tritium values for both groundwater and surface waters show significant contribution equal to or less than found in precipitation exception being samples (Gw13and Gw37) with extremely low tritium values. This implies recent contributions or an ongoing recharge to the aquifer system and thus short transit time through the unsaturated zone. This assertion is supported by the plot of tritium-$^{14}$C content of the groundwater samples as shown in Fig. 7. Also, sample Gw5 is worth elaborating with tritium value higher than the rainwater content. This could either be attributed to highly enriched tritiated rainwater preserved in less permeable layers or contaminated by wastes being an open abandoned well. However, the observed background values of tritium in these groundwater samples connote recharge under modern climatic conditions. The tritium concentration >1 TU with corresponding high $^{14}$C characterizing the entire study area except for location
Fig. 5. Plot of d-excess versus 18O for the rainy season water samples within the study area.

Fig. 6. Plot of d-Excess Versus 18O for the dry season water samples within the study area.
(Gw13) is an indication that these waters are quite recent. In addition, the aquifer good permeability in the study area also enhances short residence times for the tritiated water, while varying tritium concentration may either depict variable residence times or infiltration with variable tritium content into the aquifer (Kehinde, 1993). However, the anomalous occurrence of poorly tritiated shallow groundwater (Gw13 and Gw37) regarded as sub-recent water may suggest any of the following: probable mixture of young and old water (low tritium) or at least contain an admixture of a certain amount of recent water; or due to the presence of relatively impermeable sediments, which increases residence times and enables disintegration of the tritium content; and an additional possibility to the above is that the aquifer was recharged by younger but poorly tritiated rainwater (Kehinde, 1993). Groundwater samples with zero (near zero) tritium value according to Abiye (2013), have been in circulation for a long time (>50 years) and are not derived from present-day rainfall. In addition, most of the groundwater samples are characterized by low total mineralization with total dissolved solids (TDS) values <500 ppm and electrical conductance (EC) values <750 μs/cm. These values are within the recommended standard of (WHO, 2006) for potable water and equally indicates recently recharged fresh-groundwater to the unconfined shallow aquifer in the basin (Tables 1 and 2). However, a few of them exhibit higher values.

2.3.2. Carbon-14 and δ13C

The carbon isotopes of 13C and 12C are essential and vital tools to quantify the interaction between water and rock in the case of 14C age determination of groundwater. The carbon isotopes were carried out in the study area to establish an input function for dating groundwater and unraveling the source of carbon in the basin (Table 3). The increment in the natural concentrations of both carbon-14 and tritium in waters resulted from the thermonuclear testing in the early 1960s and therefore, elevated concentration of 3H and 14C in groundwater indicates recent recharge. The carbon-14 content, however, decreases in old waters by radioactive decay hence, making it a useful age determination tool while Carbon-13 determinations are useful in the identification of the origin of carbon in groundwater (Loehnart, 1988). The 13C content in the groundwater varies from -22.95 to -12.56 ‰. These values indicate biogenic origin and dominance of shallow water-soil interaction. The notable carbon-13 values for some plant material range from -23 to 3 ‰ while that for carbonate minerals is between -2 to 0 ‰ (Faure, 1986; Mazor, 1991; Ferronsky and Polyakov, 1982). In addition, the depletion of 13C values connotes little or no marine carbonate rock with enriched 13C value was available for dissolution in the subsurface. However, in the present study, the 14C activity was found to vary from 59.1 to 88 pMC for groundwater from the shallow interstitial aquifer. In the recently recharged water, the 14C content is expected to be close to or above 100% because 14C is derived from the soil CO2 and it is likely to contain bomb 14C. The relatively
high activity of $^{14}$C observed in the basin groundwater is indicative of young, shallow and locally recharge source of water. According to Dorr et al. (1987), the $^{14}$C content of shallow groundwater ranges from 90 pMC to about 50 pMC depending on the local condition of the carbonate dissolution. Whereas, adoption of Murray et al. (2015) submission, identified two groups of water for the study area: the first is shallow and recently recharged groundwater with $^{14}$C values between 74 to 94 pMC, comprising of Gw2, Gw7, Gw17, Gw18, Gw25, Gw30, and Gw33 while the second is the mixed group identified with intermediate $^{14}$C values varying from 50 to 70 pMC, entailing Gw8 and Gw13 samples. The calculated mean residence time of recharge based on $^{14}$C activity shows age range between 1050 $^{10}C_{\pm}$ and 4050 $^{10}C_{\pm}$. This estimation is in good agreement with previous work on shallow unconfined groundwater at Illumenden Basin, surmising that aquifer’s recharge occurred between the last humid period (about 4000 years ago) and the present (Le Gal La Salle et al. (2001)). Also, based on carbon-14 and carbon-13 contents, most of the samples lack evidence of mixing; indicating that variation in activity of carbon-14 is essentially due to radioactive decay and represents the true residence time of groundwater. Furthermore, diffusion of CO$_2$ gas from the unsaturated zone to the groundwater could also affect the measured carbon activity in water (Fontes and Edmunds, 1989; Le Gal La Salle et al., 2001). When diffusion occurs, modern CO$_2$ increases carbon-14 activity of groundwater and consequently reduce the estimated groundwater residence time (Le Gal La Salle et al., 2001). Diffusion is known to occur in modern groundwater with high pH where dissolution of CO$_2$ gas is

![Fig. 7. 3H- 14C relation of selected groundwater samples (Wet season) in the coastal basin of Lagos.](https://doi.org/10.1016/j.heliyon.2018.e00932)
enhanced (Fontes and Edmunds, 1989; Stumm and Morgan, 1981). Thus the low pH characterizing the studied area suggests that the diffusion process has no effect on the estimated carbon-14 activity. Similarly, the relative correlations agreement between tritium and carbon-14 (Fig. 7), suggests that carbon-14 signature remain unmodified and still reflect groundwater renewal rate. It can thus be considered herein that diffusion is not important. The residence time (t) of the groundwater, however, provides useful practical implication for water resource management and can be estimated through the below decay equation (Eq. (viii)):

\[ t = -\frac{8267 \ln(a_t^{14C}/a_0^{14C})}{ \text{viii}} \]

where \( a_t^{14C} \) is the measured activity and \( a_0^{14C} \), is the initial activity.

The rock-water interaction enhances dissolution of carbonate and reduces the \( ^{14} \)C activity of groundwater through exchange with dead carbon in the aquifer (Bajjali et al., 1997). The initial carbon \( ^{14} \)C activity (\( a_0^{14C} \)) in the atmosphere is assumed to be 100 percent modern carbon (pMC). This is to be adopted as the \( ^{14} \)C activity of modern CO\(_2\) during recharge. In addition, we can also determine the dilution factor for dating purposes. A dilution (water-rock interaction) factor known as ‘q’ reduces the initial activity of the sample for non-decay \( ^{14} \)C the reduction in \( ^{14} \)C activity through a geochemical reaction in the recharge water may be used to estimate the dissolution factor ‘considering Eq. (ix) below

\[ q^{\text{recharge}} = \frac{14C^{\text{recharge}}}{14C^{\text{atmosphere}}} = \frac{A_{\text{recharge}}}{A_{\text{atmosphere}}} \text{ (ix)} \]

Where the \( A_{\text{recharge}} = \) Average value of \( ^{14} \)C measured in the recharge area and the atmosphere respectively. Generally, due to the dominance of high \( ^{14} \)C activity, groundwater of this region is continuously renewed and can be qualitatively characterized as possessing a relatively high recharge/draft ratio.

2.3.3. Aquifer recharge

The stable isotope of oxygen (\( ^{18} \)O) and hydrogen (\( ^2 \)H) are valued as natural tracers because they neither decay with time nor removed from water during the exchange process of water and rock. They are considered conservative at the LCB since no geothermal effects have been documented in the basin and thus may be used to deduce reliable information on the climatological history of the groundwater in the aquifer. The LCB groundwater has not been defined through any form of long-term isotope monitoring. Consistent, regular and long-term sampling is, however, required in order to quantify the seasonal recharge in the basin without which no detailed interpretation of these fluctuations can be undertaken. However, the groundwater samples in the study area clustered around and along the LMWL on the \( ^{2} \)H- \( ^{18} \)O plot (Figs. 3 and 4) revealed that the groundwater is a mixture of
different episodes of rainfall that occurred during wet and dry seasons. The observed relatively enriched values of ($\delta^2$H $>-24.75\permil$, $\delta^{18}$O $>-4.81\permil$, $\delta^2$H $>-19.7\permil$, $^{18}$O $>-3.98\permil$) exhibited by the groundwaters for both rainy and dry seasons indicate low altitude nature of the basin. In addition, due to the less negative values of stable isotopic composition typifying the basin, it is considered that monsoonal rainfall derived from the south (Atlantic Ocean) was most likely the source of precipitation recharging the LCB. Also, these high values of the $\delta^2$H and $\delta^{18}$O are reflective of the shallowness of and recently recharged groundwater. The groundwater samples are subjected to a various degree of evaporation and as such exhibit some variation in stable isotopic composition and distribution along the LMWL. These variations are attributed to different storms that recharged the aquifers. Considering the size and altitude of the study area the major process that may yield any significant note in the isotopic composition of the rainfall depends on its amount and intensity. Therefore, the mean annual rainfall of about 1800mm in the study area could have produced the relatively depleted isotopic signature preserved in the shallow groundwater. From Figs. 3 and 4, it can be deduced that the groundwater originated essentially from local rainfall and variation in its isotopic composition may be related to the prevailing climatic conditions. This observation may be supported by the groundwater fluctuation plot deduced from the water level data (Fig. 8). It reveals the sensitivity of the aquifer’s quick response to precipitation during the wet season denoted by a sharp rise in water level. In addition, some of the hand-dug wells away from the surface waters’ course, have negligible or absolutely no water content during the dry season indicating precipitation as the main source of recharge to the

Fig. 8. Aquifer response to seasons.
groundwater. Furthermore, in the wet season, the spatial distribution of isotopes (Figs. 3 and 4 and; Tables 3 and 4) in some of the groundwater reflects isotopic signatures similar to that found in the lagoon water samples. This similarity besides the similar d-excess values suggests that the Lagoon also acts as a notable source of recharge to the groundwater. The general conceptual model (Fig. 9) shows the interaction between Surface water and groundwater in the wet season.

The exceptional high TDS values ranging from >500-971ppm and >500—5336ppm and, EC values range between >1200 - 3387 μS/cm and >1200—5338 μS/cm above the drinking water recommended limit of (WHO, 2006) suggests salinity increase and also confirm the surface water-groundwater interaction. This assertion is further supported with salinity increase in both surface and groundwater towards the ocean (Fig. 1 and Table 2). Generally, groundwater salinity decreases away from the saline sources towards the northeast and eastern limit of the study. In the dry season, in contrast, the Lagoon water experiences reduction and exhibits isotopic signatures similar to that of the seawater indicating the significant influence of marine on the Lagoon water that lies next to the shore. This, on the other hand, indicates that probably the surface water does not provide a significant contribution to the recharge of the groundwater system in the dry season (Table 4, Fig. 4). However, most of the groundwater samples are identified as young and modern in age by tritium and carbon-14, while sample Gw 13 represents an exception in Lagos Island and classified as sub-recent water resulting from admixture of old and young waters. This localized zone of mixing could not be delineated.

Fig. 9. General conceptual model for the study area.
with the present paucity of data. In summary, the replenishment to the phreatic aquifer is believed to occur from local rain, flood flows, and surface waters.

3. Conclusions

Radiogenic isotopes ($^{14}$C and $^{3}$H) and stable isotopes ($^{18}$O, $^{2}$H and $^{13}$C) of groundwater in the LCB of Nigeria has provided the basis for better understanding of the shallow unconfined groundwater system in the basin with respect to age and recharge sources. Our findings show that shallow groundwater infiltration across LCB is generally affected by evaporation. The regional and local prevalent climatic conditions are the factors responsible for the observed evaporation effect in the isotopic composition of the groundwater. The relationship of $^{18}$O and $^{2}$H identified that rainfall is the main source of recharge to the basin’s groundwater system. In addition, shreds of evidence from isotopic signature and water level map revealed the mutual interaction between the groundwater and the Lagoons and creeks’ water bodies particularly during the rainy season thus suggesting another source of recharge to the aquifer. The general low concentrations of tritium, relatively equal to its current concentration in rainfall suggest the presence of modern recharge. In other words, the tritium data indicates that the groundwater systems are essentially modern in age, whereas, the apparent age of the groundwater based on $^{14}$C activity reveals older water of over a few units of thousand years. Therefore, the groundwater system in the LCB represents recharge under modern climatic conditions. Thus, the source of groundwater in this region is considered renewable and water exploitation is potentially sustainable. However, groundwater exploitation is considered ‘mining’ especially during the dry season, if groundwater withdrawal rate is higher than recharged. The facts and findings presented in this study do not only reflect meteorological and hydrological characteristics of shallow groundwater in the basin, but also provide the essential and valuable isotopic database from where information can be generated for groundwater resource management and further future study in the basin.

Declarations

Author contribution statement

Mumeen A. Yusuf: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Tamiru A. Abiye: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Michael J. Butler: Analyzed and interpreted the data.

Kehinde O. Ibrahim: Contributed reagents, materials, analysis tools or data.
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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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