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ORIGINAL ARTICLE

Stable Isotopic Signatures (^{18}O and ^{2}H) and Hydrochemistry in Assessing Basement Aquifer Recharge and Driving Forces of Groundwater Quality in Parts of Ilorin, Northcentral Nigeria

*[1]Yusuf, Mumeen Adebayo, [2]Abiye, Tamiru Alemayehu, [3]Alao, Joseph Omeiza, [1]Ibrahim, Kehinde Olojoku, [1]Oyeleke, Tolulope Ayobi, [1]Awujo, Emmanuel Daberechukwu, [1]Omotoso, Oladele Ajiboro, [1]Iheme, Kenneth Obinna, [4]Bakare, Ussein Taiwo and [1]Omorinoye, Omolayo Ajoke

[1]Department of Geology and Mineral Sciences, University of Ilorin, Ilorin, Nigeria.
[2] School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa
[3] Department of Physics, Air Force Institute of Technology, Kaduna, Nigeria.
[4] National Centre for Hydropower Research and Development (NACHRED)
*Corresponding author: asiribo.ma@unilorin.edu.ng, ORCID: https://orcid.org/0000-0002- 4849-3508

ABSTRACT - Groundwater resources in parts of Asa Local Government Area in Kwara State, Nigeria are threatened by increasing pressure due to growing population, and agricultural and industrial activities, which necessitates a comprehensive assessment of the groundwater resources to ensure their sustainability and safety for human consumption. Evaluation of groundwater resources in parts of Asa Local Government Area in Kwara State, Nigeria was undertaken using the integration of stable isotope of δ^{18}O and δ^{2}H and hydrogeochemical tools including Water Quality Indexes, Gibbs diagrams, and Chadha diagram towards deciphering the source of groundwater recharge as well as factors controlling its chemistry in the study area. The collected groundwater samples from shallow wells and deep boreholes were subjected to major ions, trace elements, and isotope analyses. Hydrochemical models revealed Ca-Mg-HCO_3, mixed Ca-Na-HCO_3, and Na-HCO_3 water facies suggesting the early transformation stage of the groundwater. The WQI indexes ratings revealed essentially fair to good to excellent water quality for human consumption. The isotope values in groundwater samples vary between -4.12±0.1 ‰ and -2.60±0.1 ‰ and between -15.0±0.2 ‰ and -24.0±0.2 ‰ for δ^{18}O and δ^{2}H, respectively, indicating isotopically relatively enriched groundwater. The plot of δ^{18}O and δ^{2}H in groundwater samples along meteoric lines indicate meteoric origin with little effect of evaporation. Residence time evaluation using Ec and δ^{18}O relationship identified recent recharge and recent recharge but polluted groundwater. In addition, the relation between salinity and δ^{18}O revealed water-rock interaction as the main geochemical process controlling groundwater chemistry.

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INTRODUCTION

Water, the elixir of life is an essential natural resource for the sustenance of both plants and animals on Earth. The water resources (surface and groundwater) in quantity and quality are under perpetual threat due to human influence, population increase, and climate change [1; 2; 3; 4]. Surface water has been the water source for municipalities over the years, but this source of water has been under constant threat from anthropogenic pollution. Likewise, the study area, Laduba is located in Asa local government which hosts one of the largest rivers in the state. However recent studies have shown that the water is plagued with elevated heavy metals from anthropogenic activities (industrial effluents, discharge of wastewater from fish ponds, run-off from agricultural wastes [5]. These in turn impair human health negatively causing life-threatening illnesses such as cancer, heart diseases and teratogenic abnormalities, diarrhea

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*Corresponding Author: Yusuf, Mumeen Adebayo. University of Ilorin (Unilorin), email: asiribo@unilorin.edu.ng

[6; 7]. Surface water and groundwater interaction studies are crucial in effectively managing water resources [8]. It has been established that a properly managed water resource is crucial to the socioeconomic development of any society [4; 8]. In the study area, groundwater has now been a haven. Conversely, groundwater contamination is also becoming prevalent and a serious global issue [9; 10]. In recent times, water quality assessment, sources of contamination, health risk assessment, and related health studies have been the focus of many research studies. For example, [5] carried out a preliminary health risk assessment and some impacts of trace elements in Asa River, Kwara State, Nigeria and they found that the average Carcinogenic Risk (CR) of Cr and Pb for adults and children is higher than the risk limit of 10^{-6} and 10^{-4}.

The stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ are known to be potential markers of water sources. Isotopes have been employed successfully in groundwater investigations around the world. Although the application of the isotope method in groundwater investigation is still limited in Nigeria, before this research, isotope investigation of groundwater was never known to the study area. However, some researchers have adopted isotope techniques in groundwater evaluation in the Southwestern and Northern parts of Nigeria. [11; 12; 13] adopted the use of stable isotopes of oxygen and hydrogen successfully in the southwestern parts of Nigeria, while [14; 15; 16] successfully deployed similar stable isotopes in groundwater in the northern parts of the country. When combined with hydrogeochemistry study, stable isotopes provide a powerful tool to unravel the origin and mechanisms controlling the groundwater characteristics. Therefore, the present study aims to investigate the groundwater resources in the study area using a combination of stable isotopes ^{18}O and ^{2}H and hydrogeochemistry, to identify the recharge source to the aquifer, to determine the groundwater residence time, to assess factors controlling the groundwater quality and evolution, and evaluate the suitability of the groundwater for human consumption, to provide a better understanding of the groundwater system in the study area.

Geological and Hydrogeological Setting

Laduba in Asa Local Government Area is situated in the North-central region of Nigeria, within Kwara State. Its administrative centre is the city of Afon with geographical coordinates of Latitude: 8.8932° N and Longitude: 4.4693° E (Figure 1).

The area of study is sitting on the Crystalline Precambrian Basement complex of Nigeria comprising mainly Migmatite-Gneiss complex rock units, which constitute almost 75% of the rock units occurring within the region [17; 18; 19]. These rock units are thought to have been formed during the Paleo-Protozoic era, between 2500 and 1000 million years ago. The remaining 25% of the rock units in Asa LGA are younger metasedimentary rocks, which are probably from the Paleo-Protozoic era as well. The migmatite-gneiss complex rock units are characterized by their high degree of metamorphism [19].

The outcrops within the area are generally low-lying and are covered by hard lateritic material which shows evidence of complete weathering and laterization processes.

In summary, the area comprised banded gneisses, migmatite gneiss, and granite gneiss with complex and simple pegmatites embodied with garnet mineralization. The detailed geology of the area has been published by [18; 20; 19].

The study area has a complex hydrogeological setting made up of both shallow and deep aquifers. The shallow aquifers in the area are typically unconfined in occurrence within the overburden (weathered rocks) and are recharged by direct rainfall while the deep aquifers are essentially confined within the fractured basement and mostly recharged by lateral flow from the surrounding uplands [21] . The study of well inventory in the study area revealed that the average shallow aquifer depth in the study area is 5.70m and, it is suspected to be a perched aquifer in occurrence due to its response to seasonal variations. The second aquifer that serves the community all year round is being tapped by the deeper wells (boreholes) at an average depth of 120 m within the fractured basement.

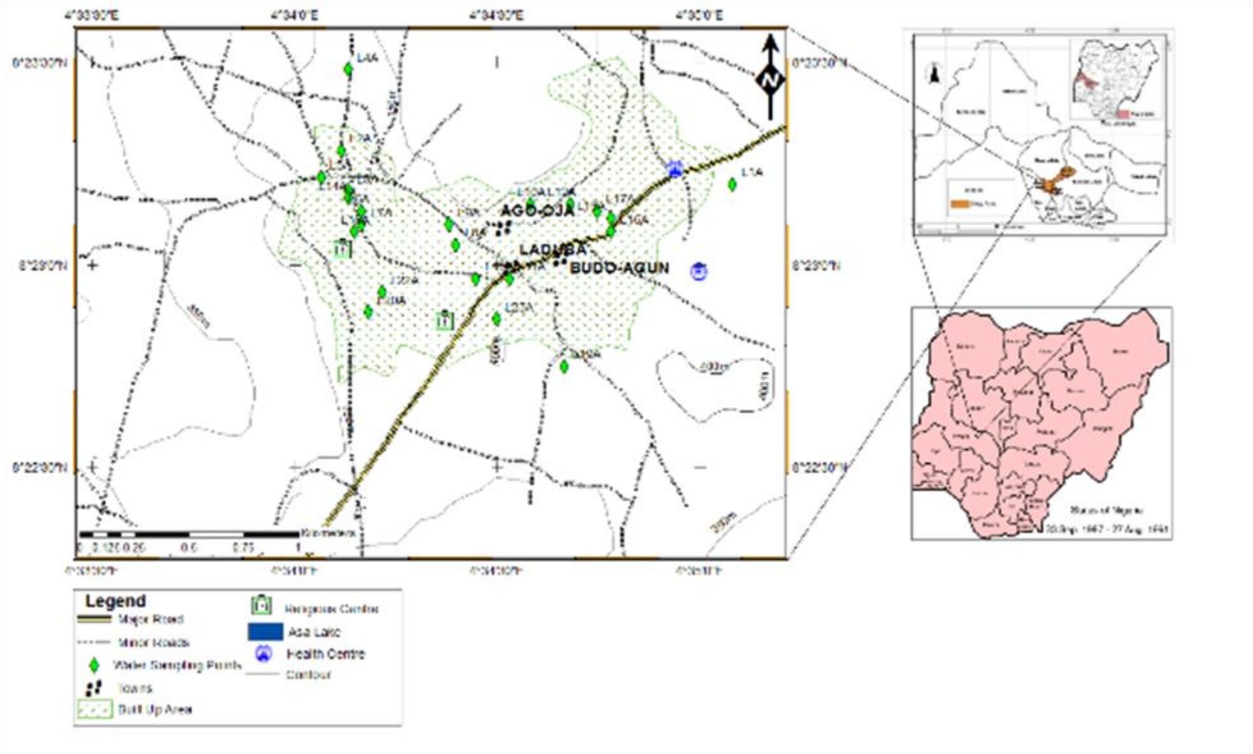

Figure 1. Map of the study area showing the sampling points

MATERIALS AND METHODOLOGY

Fieldwork and Sampling Procedures

The fieldwork was conducted at Asa local government of Kwara state, between the 10th and 15th of February, 2023. Wells and boreholes were selected for sampling at different locations based on availability and accessibility with a total of 24 groundwater samples collected for the area. Location/coordinates reading was achieved with the Global positioning system (GPS). Physical parameters such as pH, temperature, electrical conductivity, salinity, and total dissolved solids were determined in situ on the field using a multipurpose 7 in 1 Hanna portable water testing kit. The wells' total depths and water levels were also measured using a Solinst Model 107 TLC meter. Local plastic fetcher and manual pumping were used for taking out groundwater samples from the shallow wells and the boreholes.

To ensure a true representation of groundwater samples at each location, the wells were thoroughly mixed and boreholes pumped for about five minutes before sampling. The sampled waters were collected unfiltered and stored unpreserved in tightly sealed plastic bottles. The water samples were collected in triplicates; 10 ml, 60 ml, and 500 ml in precleaned sample bottles for various hydrochemical analyses. Each of the 10 ml, 60 ml, and 500 ml bottle samples was meant for Isotope, cation, and anion analyses. The water samples were analyzed for the various cations (major and trace elements) in the Agilent Research laboratory, Lagos State using the ICP/MS method while Major ions were analyzed at the Central Research Laboratory, University of Ilorin, using the AAS method. The stable isotope of deuterium and oxygen were analyzed at the hydrogeology laboratory at the School of Geoscience, using the Liquid Water Isotope Analyzer-model 45-EP at the University of the Witwatersrand, South Africa. The analytical precision is estimated at 0.5‰ and 1.5 ‰ for O and H. The laboratory methods were aimed at determining the major, trace, and rare earth elements in the water samples collected. In addition to the major ions, the analyzed trace elements present are (As, Cr, Cu, Cd, Mn, Ni, K, and Zn).

Samples for ^{18}O and ^{2}H were collected in 10ml glass bottles with airtight caps. The stable isotope of deuterium and oxygen were analyzed at the hydrogeology laboratory at the School of Geoscience, using the Liquid Water Isotope Analyzer-model 45-EP at the University of the Witwatersrand, 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.

Geospatial Analysis

A geostatistical method was employed in this work to better understand the spatial variation of the parameters under study. The Geostatistical analysis was implemented using the kriging method in the Golden software (Surfer 15). The analysis was executed separately for each heavy metal contained in the water samples using kriging interpolation techniques. Kriging models were executed and the surfaces were created using ArcGIS 10.8 from ESRI Desktop.

Water Quality Index (WQI)

Arithmetic Weighted Water Quality Index

The water quality index (WQI) was estimated to determine its suitability for drinking purposes [22]. WQI enables the conversion of many values obtained from the physicochemical assessments into a single value. This value classifies the quality of the water into excellent, good, moderate, poor, and fair water for drinking purposes (Table 1). The calculation was performed as described by [23].

$$Qi = \frac{(Mi - Li)}{(Si - Li)} x\ 100 \tag{1}$$

$$W_i = \frac{K}{S_i} \tag{2}$$

$$WQI = \sum_{i=1}^{n} \frac{W_i Q_i}{\sum_{i=1}^{n} W_i} \tag{3}$$

Table 1. WQI categorization based on CCME and Arithmetic method

S/N	Rank for CCME	Value	Rank for Arithmetic method	Value
1	Poor	CCME WQI values 0-44	Excellent	0 – 25
2	Marginal	CCME WQI values 45-59	Good	26 – 50
3	Fair	CCME WQI values 60-79	Poor	51 – 75
4	Good	CCME WQI values 80-94	Very poor	76 – 100
5	Excellent	CCME WQI values 95-100	Not suitable	>100

where Mi is the monitored value of the parameter, li is the ideal value (ideal value for dissolved oxygen = 14.6 mg/L, pH = 7, and other parameters = 0), Si is the standard value of the ith parameter, Qi is the sub-index of the ith parameter, K is the proportionality constant, n is the number of parameters, and Wi is the unit weightage of the ith parameter.

Canadian Councils of Ministers and Environments (CCME)

The CCME method was adopted in the current research because it is known for its efficiency in assessing the overall quality of groundwater resources, identifying potential water quality issues and areas of improvement, comparing the water quality of different groundwater resources or locations, and informing management and decision-making strategies for maintaining or improving groundwater quality. The CCME water quality index (CWQI) model consists of three measured variances from selected water quality objectives (scope, amplitude, and frequency). These three measures of variance join to produce a value range of 0 and 100 (with one being the least and 100 demonstrating the best water quality (Table 1) representing the overall water quality. Within this range, designations are set to classify water quality as poor, marginal, fair, good, or excellent. These same designations were adopted as the basis of interpretation in this research work.

The detailed formulation of the WQI, as described in the Canadian WQI 1.0–Technical Report is as follows: The measure for scope is F1 (Scope) represents the extent of the water quality guideline. Non-compliance throughout interest

$$F1 = \frac{Number\ of\ Variables}{Total\ Number\ of\ Variables} * 100 \tag{4}$$

The measure for frequency is F2 (Frequency) represents the percentage of individual tests that do not meet objectives (failed tests).

$$F2 = \frac{Number\ of\ failed\ test}{Total\ Number\ of\ Variables} * 100 \tag{5}$$

F3 amplitude

The measure for amplitude is F3 represents the amount by which failed tests do not meet their objectives calculated in three steps: Step 1-Calculation of Excursion. The excursion is the number of times an individual concentration is more significant than (or less than, when the objective is a minimum) the objective.

When the test value must not exceed the objective

$$F3 = \frac{Failed\ test\ value\ I}{Objective} - 1 \tag{6}$$

When the test value must not fall below the objective:

$$F3 = \frac{Objective\ I}{Failed\ test\ valueI} - 1 \tag{7}$$

Step 2-Calculation of Normalized Sum of Excursions. The normalized sum of excursions is the aggregate amount by which individual tests are out of compliance calculated by summing the excursions of individual tests from their objectives and dividing by the total number of tests (both those meeting objectives and those not meeting objectives).

$$nse = \frac{\sum_{N=1}^{I} excursion}{Number\ of\ Tests} \tag{8}$$

Step 3-Calculation of F3. F3 (Amplitude) is calculated by an asymptotic function that scales the normalized sum of the excursions from objectives to yield a range from 0 to 100.

$$F3 = \frac{nse}{0.01nse + 0.01} \qquad (9)$$

$$WQI = 100 - \frac{\sqrt{F12 + F22 + F32}}{1.732} \qquad (10)$$

Geochemical Evaluation

Piper Trilinear Diagram

The hydrochemical evolution of stream water is understood by plotting the major cations and anions in the Piper trilinear diagram [24]. This graphical plot distinctly categorized groundwater's dominant geochemical facies and provided an understanding of the water type. This diagram is comprised of two triangles at the base and one diamond shape at the top to represent the major significant cations and anions responsible for the nature of groundwater. The geochemical evolution can be described from the Piper plot, which has been divided into six subcategories, viz. I (Ca–HCO3 type); II (Na–Cl type); III (mixed Ca-Na-HCO3 type); IV (mixed Ca–Mg–Cl type); V (Ca–Cl type) and VI (Na-HCO3 type). [25] introduced a diagrammatic representation of processes controlling the chemistry of surface water as atmospheric precipitation, rock dominance, or the evaporation process. Precipitation, rock weathering, and evaporation dominance are the major geochemical processes that govern the dissolution of ions into the groundwater [26]. The formula calculates the Gibbs ratio for the cation: $Na^+/ (Na^+ + Ca^{2+})$ meq/L and the Gibbs ratio for the anion is calculated using the formula: $Cl^-/(Cl^- + HCO^-_3)$ meq/L [25].

Chadha Plot

For a better understanding of the hydrochemical process of groundwater, it is worth referring to the Chadha plot which is a modified version of the Piper diagram. Chadha diagram was generated by plotting the difference in milliequivalent percentage between alkaline earth (Ca^{2+}+ Mg^{2+}) and alkali metals (Na^++K^+) expressed as percentage reacting values on the X-axis. The difference in milliequivalent percentage between weak acidic anions (CO^{2-}_3 + HCO_3^-) and strong acidic anions (Cl^- + SO_4^{2-}) is plotted on the Y-axis [31]. Moreover, Chadha classified the groundwater into eight sub-fields, each of which typically represents a water type as follows:

(1): Alkaline earths (Ca^{2+} + Mg^{2+}) exceed alkali metals (Na^+ + K^+).

(2): Alkali metals (Na_+ +K^+) exceed alkaline earths (Ca^{2+} + Mg^{2+}).

(3): Weak acidic anions (CO_3^{2-} + HCO_3^-) exceed strong acidic anions (Cl^- + SO_4^{2-})

(4): Strong acidic anions (Cl^- +SO_4^{2-}) exceed weak acidic anions (CO_3^{2-} + HCO_3^-)

(5): Alkaline earth and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. Ca^{2+}-Mg^{2+}-HCO^3 - type, Ca^{2+}-Mg^{2+} dominant HCO^3 – type, or HCO_3 – dominant Ca^{2+}-Mg^{2+} type waters.

(6): Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. Ca^{2+}-Mg^{2+}-Cl^- type, Ca^{2+}-Mg^{2+} dominant Cl^- type or Cl^- dominant Ca^{2+}-Mg^{2+} type waters.

(7): Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. Na^+-Cl^- type, Na_2SO_4 type, Na^+ dominant Cl^- type, or Cl^- dominant Na+ type water.

(8): Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. Na+-HCO_3^- type, Na^+ dominant HCO_3^- type, or HCO_3^- dominant Na^+ type water.

RESULTS AND DISCUSSION

Physicochemical Parameters

pH measures the oxidization power (electron activity or availability), and pH may be defined as a measure of a solution's hydrogen ion concentration (abundance of protons). The pH value of groundwater samples ranges between 5.8 and 9.14 indicating slightly acidic to slightly basic. The value of electrical conductivity ranges (EC) from 484 to 1130μS/cm, and the total dissolved solids (TDS) ranges from 241.5 to 563.0 mg/l both are within the permissible drinking water limit of WHO except in two samples (L3A and L7A) (Table 2).

The concentration of sulphate ranges from 0.062 to 0.717mg/l with an average value of 0.128mg/l (Tables 1; Figure 2b) is also within the WHO recommended limit and suspected to be of the atmospheric source. Ca^{2+} has a concentration range from 0.31 to 326.32 mg/l with an average value of 146.9 mg/l. K^+ ranges from 213.06 to 290.11 mg/l with an average concentration of 250.25 mg/l while Na^+ and Mg^{2+} have a concentration range from 124.48 mg/l to 363.82 mg/l with a mean value of 243.34 mg/l, and 1.05 to 7.04 mg/l with an average value of 3.15 mg/l, respectively. Comparing the concentrations of major ions with WHO standards, Mg^{2+} has a concentration within the WHO recommended standards (Table 2) [27] while Fe, Ca^{2+}, $Na^{+,}$ and K^+ have 50 % of its samples (L3A, L4A, L6A, 9A, L10A, L14A, L16A, L18A, L19A, L20A, L22A, L24A) within the WHO recommended standard, the remaining 50 % have concentrations above the acceptable set standards (Table 2, Figure 2a). The general order of cationic and anionic abundance is as follows: Ca> K > Na > Mg and HCO_3 > Cl > SO_4. The observed higher concentration values of K^+ and Na^+ relative to Mg^{2+} may be attributed to the effect of evaporation and ion exchange between the aquifer material (clayey sand) and the solution or anthropogenic contribution [12] while the dominance of HCO_3^- may probably be indicating carbonate dissolution and decomposition of organic matter [28].

The mean concentrations (mg/l) of the trace metals in decreasing order are as follows: Fe (38.89 mg/l) > Ni (1.20 mg/l) > Cu (0.57 mg/l) > Mn (0.56 mg/l) > Zn (0.24 mg/l) > Pb (0.14 mg/l) > Co (0.06 mg/l) > Cd (0.04 mg/l) (Table 2). The trace elements concentrations in groundwater are above the WHO recommended level except for Zn which has values lower than the WHO recommended value of 3 mg/l (Table 2, Figures 2c, d). The high level of trace elements is a result of the increasing influence of anthropogenic activities arising from the gradual rise in mining and industrial activities in the study area. The consequent high level of these trace elements in the study area exposes the dwellers to different health challenges like neurological disorders, toxicity to the kidney, cancer, and gastrointestinal disorders [27].

Table 2. Descriptive statistic summary for the water quality parameters

Parameters	N total	Mean	Std. Dev	Sum	Minimum	Median	Maximum	WHO,2017
pH	24	7.561	0.914	181.46	5.8	7.39	9.14	6.5-8.5
EC	24	501.875	298.420	12045	154	484	1130	1000
TDS	24	250.500	148.895	6012	77	241.5	563	500
Temp	24	28.992	1.803	695.8	26.8	28.45	34.7	25 – 50^{o}C
Alkalinity	24	0.019	0.014	0.464	0	0.015	0.05	-
Fe	24	38.885	33.580	933.236	4.413	14.780	97.104	0.30
Ca	24	146.890	148.870	3525.359	0.308	127.863	326.316	250
Na	24	122.996	129.670	2951.907	2.388	63.682	363.816	200
K	24	127.510	126.339	3060.241	2.561	110.310	290.113	12
Mg	24	2.327	1.589	55.850	0.081	2.010	7.038	200
Mn	24	0.565	0.394	13.550	0.147	0.356	1.205	0.05
Cd	24	0.039	0.024	0.929	0.000	0.038	0.104	0.003
Co	24	0.060	0.064	1.438	0.000	0.045	0.240	-
Cr	24	0.102	0.092	2.450	0.006	0.051	0.338	0.05
Cu	24	0.566	1.787	13.582	0.000	0.146	8.915	2
Ni	24	1.202	0.958	28.838	0.206	0.669	3.503	0.07
Zn	24	0.240	0.239	5.764	0.009	0.139	0.926	3
Pb	24	0.135	0.210	3.238	0.000	0.070	0.798	0.01
SO4	24	0.128	0.131	3.070	0.062	0.096	0.717	100
Cl	24	6.417	4.106	154	2	5.5	17	250
CO3	24	32.100	34.634	770.4	4.8	16.8	141.6	-
HCO3	24	103.497	64.532	2483.92	12.2	106.14	219.6	-

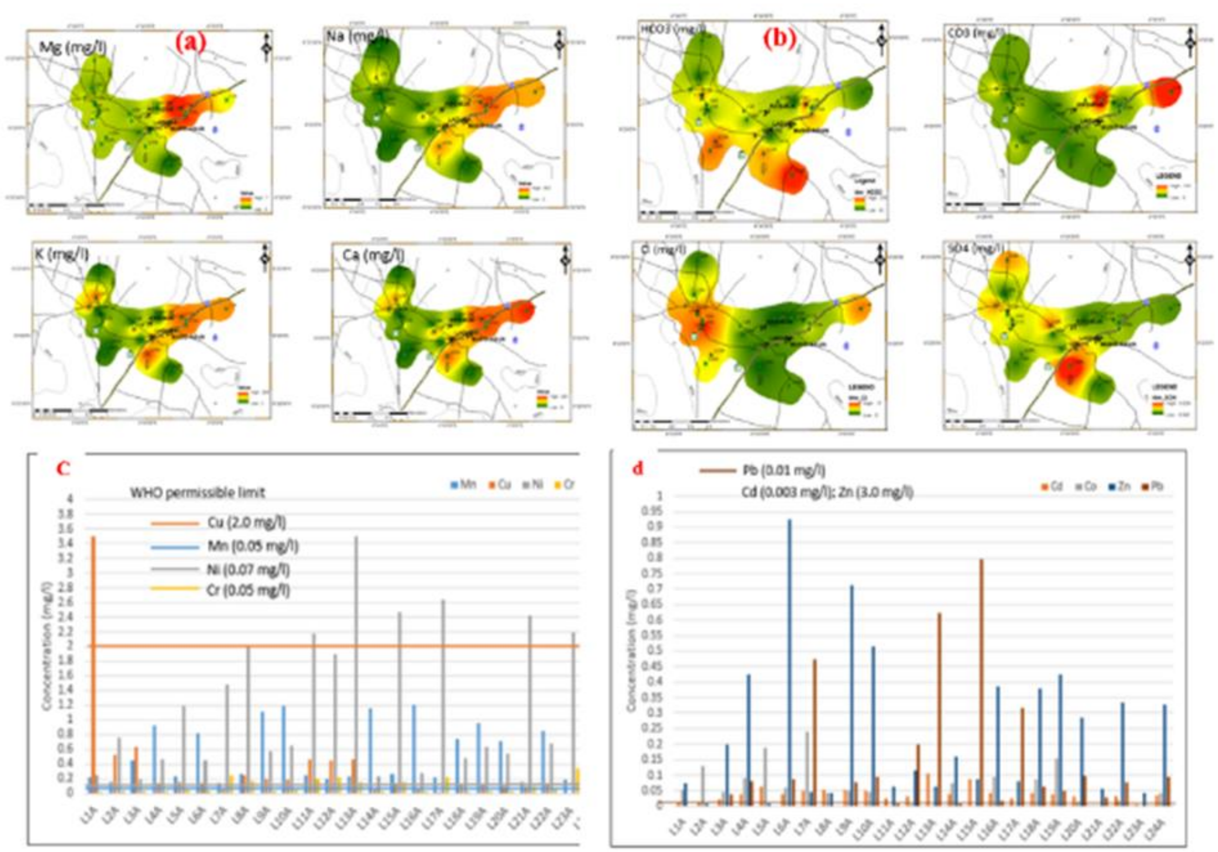

Figure 2. (a and b) show the spatial variations of major ions; (c and d) show column charts for trace metals in the study area

Natural Geochemical Process (Gibb's diagram)

Gibbs diagrams [25] help analyze major natural mechanisms that govern groundwater chemistry [29; 30]. Based on these diagrams, three main natural mechanisms can be found: evaporation dominance, rock dominance, and precipitation dominance [9; 25; 30]. As shown in Figures 3a and b, the groundwater samples of the study area fell in the zone of rock dominance, which suggests that rock weathering, dissolution, leaching, and precipitation of minerals are major processes affecting groundwater chemistry [30]. This is primarily due to the interaction between the groundwater and the geologic materials in the study area, rather than atmospheric or anthropogenic factors.

Hydrogeochemical Characteristics of Groundwater

Piper Tri-linear Diagram

The major ions obtained for the groundwater samples are plotted on the Hill-Piper Trilinear diagram to classify the water according to the hydrochemical facies [24]. In the study area, the water samples were observed to have Ca-Mg-HCO_3 water type, mixed Ca-Na-HCO_3, and Na-HCO_3 water type (Figure 3c). The dominance of these water types indicates that the groundwater in the study area is primarily influenced by carbonate and silicate weathering reactions. This suggests that the water is likely to be hard to moderately hard, with neutral to slightly alkaline pH as indicated in Table 2. The presence of Ca-Mg-HCO_3 and mixed

Ca-Na-HCO_3 indicates that the groundwater is interacting with carbonate rocks, in contrast, the Na-HCO_3 water type suggests there may be some influence from silicate weathering or ion exchange processes. The variation in water types across the study area may indicate differences in groundwater flow paths, recharge areas, or aquifer properties.

Chadha Plot

Based on the above, the major hydrochemical facies of the water samples as shown in (Figure 3d) revealed that 50 % of the samples fall in category 3 while the other 50% fall into category 8.

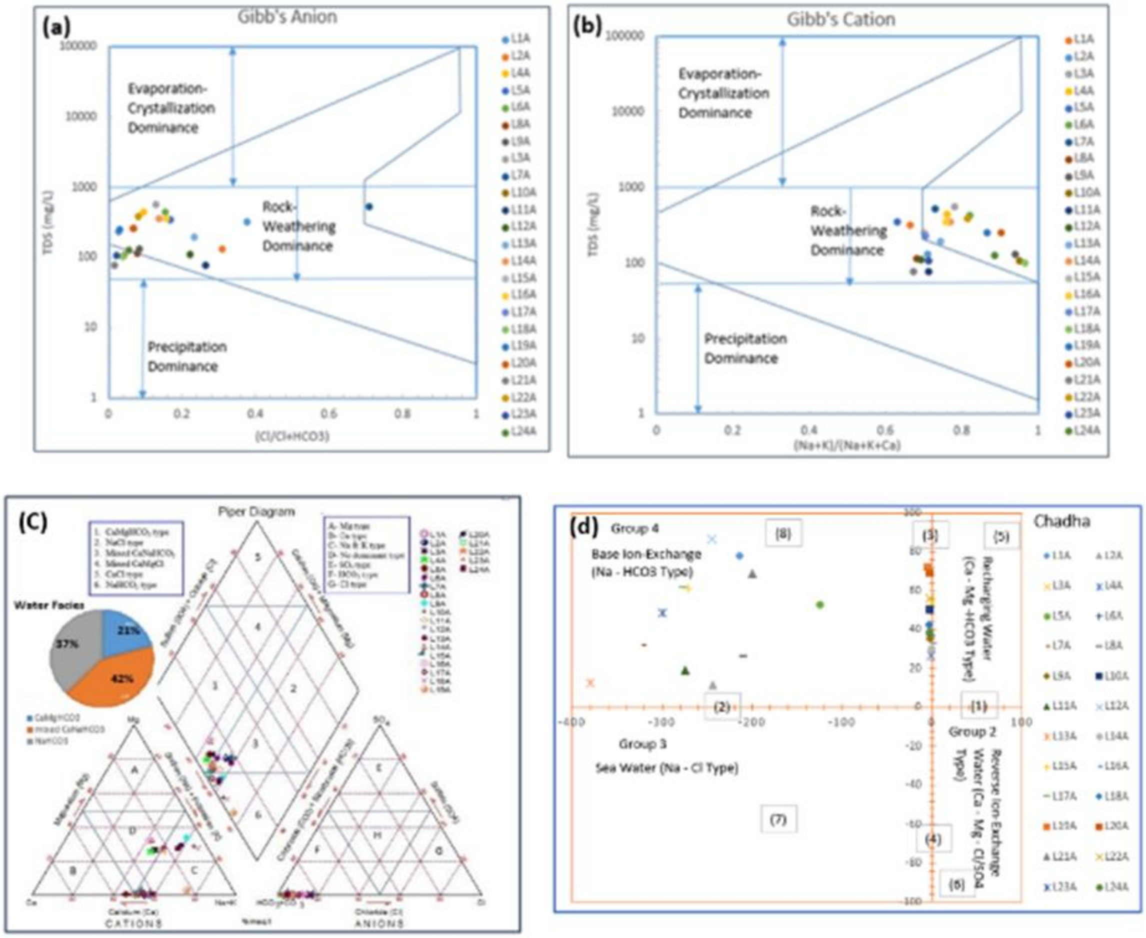

Figure 3. Gibbs diagrams indicating the groundwater natural evolution mechanisms (a): TDS vs. Cl/(Cl+ HCO_3); (b) TDS vs. Na/(Na+ Ca); (c) Piper tri-linear diagram showing hydrochemical facies (d) Chadha's plot showing the evolution of the groundwater

This implies samples in the study area constitute groundwater in which alkali metals exceed alkaline earth and weak acidic anions exceed strong acidic anions.

Category 3 which implies weak acidic anions (CO32− + HCO3−) exceed strong acidic anions (Cl− + SO42−) suggests that the groundwater in these samples is dominated by bicarbonate and carbonate ions, typical of groundwater interacting with carbonate rocks. Category 8 depicts Alkali metals exceeding alkaline earths and weak acidic anions exceeding strong acidic anions. Na^+-HCO_3^- type, Na^+ dominant HCO_3^- type, or HCO_3^- dominant Na^+ type water. This suggests that the groundwater is characterized by high sodium and potassium ion concentrations, indicating a possible influence from silicate weathering or ion exchange processes. This finding is in tandem with the deductions by trilinear diagram.

Water Quality Indices

The water quality index (WQI) maps were produced using ArcGIS 10.8 from ESRI based on the selectively chosen quality parameters to decipher the various quality classes viz. excellent, good, poor, very poor, and unsuitable at each sampling point for drinking purposes (Table 3 Figure 4). The WQI Map for CCME of the study area indicates that 50% of the samples have good quality while the remaining 50% have fair quality. 50% of the samples with good quality, indicating that they meet most of the WHO guidelines and are suitable for drinking with minimal treatment, while 50% that have fair quality imply meeting some of the WHO guidelines and may require treatment before consumption. For the Arithmetic WQI, 12% of the water samples have poor quality ratings, indicating that they do not meet most of the WHO guidelines and are unsuitable for drinking without extensive treatment. 50% have good quality, connoting minimal treatment before consumption according to the WHO guidelines. The remaining 38% have excellent quality ratings indicating that they meet all the WHO guidelines and are suitable for drinking without any treatment (Table 3; Figure 4). The map indicates that groundwater in Laduba and its environs comprises poor to excellent water quality. The two WQI methods adopted in this work showed a high degree of similarity. The two methods produced the same amount of good quality (50% each) just as they both rated the groundwater to be of good quality in the northern, western, and southern parts of the study area. The WQI maps have significant implications for groundwater management in the study area and therefore, can serve as a baseline for monitoring and evaluating the effectiveness of water management strategies and interventions.

Table 3. Results of the water quality indices for the water samples

Sample station	CCME WQI	Remark	WQI	Remark
L1A	65.62	Fair	46.36	Good
L2A	74.22	Fair	55.19	Poor
L3A	87.11	Good	10.67	Excellent
L4A	87.1	Good	25.91	Good
L5A	74.21	Fair	48.83	Good
L6A	87.11	Good	25.64	Good
L7A	61.32	Fair	49.02	Good
L8A	61.32	Fair	50.22	Good
L9A	87.11	Good	31.35	Good
L10A	82.81	Good	31.63	Good
L11A	69.92	Fair	47.58	Good
L12A	65.62	Fair	21.8	Excellent
L13A	65.62	Fair	56.81	Poor
L14A	91.4	Good	20.36	Excellent
L15A	69.92	Fair	67.42	Poor
L16A	87.11	Good	23.69	Excellent
L17A	65.62	Fair	37.7	Good
L18A	91.4	Good	25.45	Excellent
L19A	91.4	Good	24.31	Excellent
L20A	91.4	Good	25.37	Excellent

L21A	69.92	Fair	38.66	Good
L22A	82.81	Good	23.45	Excellent
L23A	69.92	Fair	16.4	Excellent
L24A	82.81	Good	26.08	Good

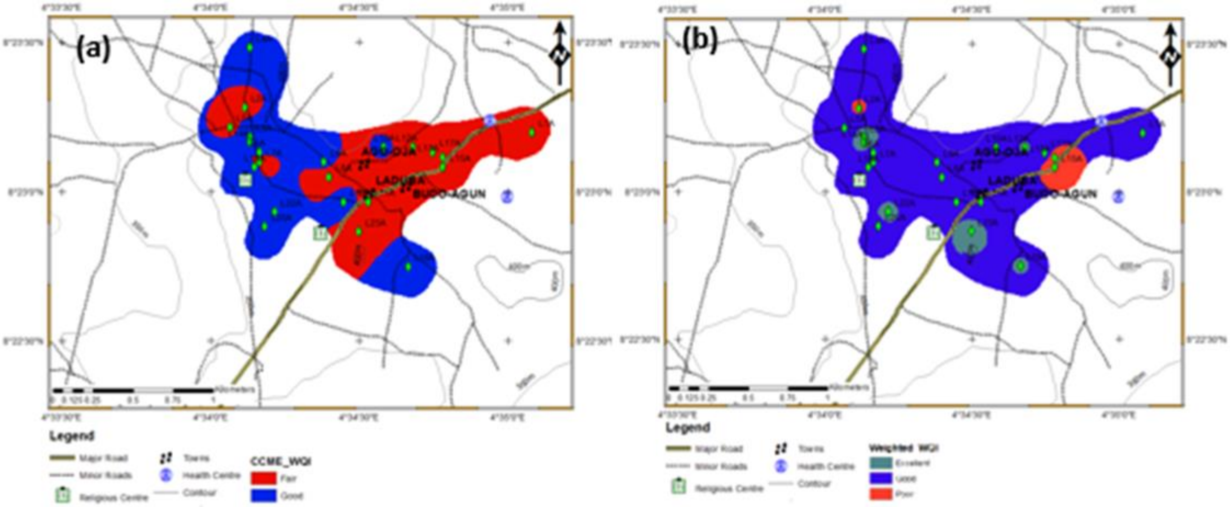

Figure 4. Water quality index maps. (a) CCME water quality index map (b) Arithmetic weighted water quality map

Stable Isotope Geochemistry

Hydrogen and Oxygen Isotopes Composition of Groundwater

The hydrogen and oxygen isotopic compositions of groundwaters are shown in Table 4. The entire ranges of $\delta^{18}O$ and $\delta^{2}H$ values observed are -4.1 ‰ to -2.6 ‰, and -15.0 ‰ to -24.6 ‰ in groundwater, respectively. The relationships between $\delta^{2}H$ and $\delta^{18}O$ are shown in Figure 5a. The hydrogen and oxygen isotopic compositions of precipitation and infiltrating waters are controlled by various physical factors, e.g., latitudinal and altitudinal effects, intensity and duration of rainfall, temperature, and evaporation and condensation in recharge and drainage areas [32; 33]. Unfortunately, no isotopic precipitation data are available for the study area. The general meteoric relationship between the oxygen and hydrogen isotopes has been described by the global meteoric water line (GMWL) with the equation:

$\delta^{2}H_{vsmow}=8*\delta^{18}O_{vsmow}+10$ ‰ [34; vsmow: Vienna Standard Mean Ocean Water] (11)

The deviation from this global meteoric water line (GMWL), called the local meteoric water line (LMWL), can be expressed through the deuterium excess parameter (d).

The d-parameter is defined as $d= \delta D-8*\delta^{18}O$ [33] (12)

While precipitation is characterized by an excess deuterium d of 10-13 ‰, the groundwater shows d values less than 10 ‰ except in three samples (L1, L2, and L10) (Table 4). Since a decrease in the parameter d is an expression of evaporation processes [35], these data indicate that the groundwater represents evaporated meteoric water.

The data location on the LMWL indicates the origin of the air moisture [11; 12]. Therefore, the $\delta^{18}O$ value was plotted against d-excess (Figure 5d) and the distribution has a range from 3.84 ‰ to 15.20 ‰ for the groundwater. These ranges of values reflect the influence of both local and regional moisture circulation as well as evaporative enrichment from regional circulation in the area.

The local meteoric water line (LMWL) from Kano GNIP station close to the study area was adopted for comparison, and this line is described as:

$$\delta^{2}H = 7.1 * \delta^{18}O + 4.1\ ‰\ (R^{2}=0.90) \qquad (13)$$

Table 4. Stable isotope data of ^{18}O and ^{2}H and calculated d-excess for groundwater of the study area

Wells ID	**Lat.**	**Long.**	**Well depth (m)**	**Salinity (ppm)**	**EC (µs/cm)**	**$\delta^{2}H$ (‰)**	**± ^{2}H StD ev (‰)**	**$\delta^{18}O$ (‰)**	**± ^{18}O StDev (‰)**	**d-excess (‰)**
					Hand-dug wells					
L01	8°23′12"N	4°35′5"E	4.7	0.03	653	-20.9	0.4	-3.95	0.1	10.65
L03	8°23′11"N	4°34′8"E	4.4	0.05	263	-17.7	0.4	-3.61	0	7.99
L04	8°23′29"N	4°34′8"E	4.3	0.04	1130	-18.7	0.4	-3.21	0	8.14
L06	8°23′8"N	4°34′10"E	4.3	0.04	897	-18.7	0.2	-3.36	0.1	9.91
L07	8°23′6"N	4°34′10"E	4.8	0.05	695	-19.7	0.2	-2.91	0.2	8.24
L08	8°23′3"N	4°34′24"E	5.6	0.01	876	-18.5	0.6	-3.58	0	8.74
L09	8°23′6"N	4°34′23"E	5.5	0.01	1049	-18.8	0.4	-3.50	0	9.28
L10	8°23′9"N	4°34′35"E	5	0.01	226	-17.4	0.1	-3.40	0.1	15.20
L12	8°23′9"N	4°34′41"E	5.1	0.01	260	-18.9	0.2	-3.51	0.1	6.67
L13	8°23′7"N	4°34′47"E	4.7	0.01	217	-21.0	0.5	-4.08	0.1	7.02
L15	8°23′5"N	4°34′47"E	6.3	0.02	154	-17.4	0.6	-2.91	0.1	6.06
L20	8°22′53"N	4°34′11"E	4.2	0.02	225	-20.1	0.3	-3.20	0.1	4.84
L22	8°22′56"N	4°34′13"E	4.8	0.03	390	-19.3	0.5	-3.51	0.2	3.84
L23	8°22′52"N	4°34′30"E	11.3	0.01	701	-21.8	0.1	-2.84	0.1	8.60
L24	8°32′52"N	4°34′30"E	9.5	0.01	512	-20.5	0.4	-2.93	0.1	5.91
				Boreholes						
L02	8°23′17"N	4°34′7"E	95	0.01	712	-18.2	0.4	-2.56	0.1	10.69
L05	8°23′13"N	4°34′4"E	90	0.03	463	-15.0	0.2	-3.51	0	8.25
L11	8°22′58"N	4°34′32"E	85	0	202	-17.7	0.5	-2.80	0.1	5.59

L14	8°23′10"N	4°34′8"E	65	0.01	505	-15.3	0.2	-3.86	0.1	7.42
L16	8°23′5"N	4°34′9"E	55	0.03	512	-16.1	0.5	-3.12	0.1	4.40
L17	8°23′8"N	4°34′45"E	45	0.02	155	-22.3	0.3	-3.06	0.1	5.84
L18	8°22′58"N	4°34′27"E	75	0.01	778	-17.4	0.4	-2.89	0.2	5.00
L19	8°22′45"N	4°34′40"E	120	0.02	217	-24.6	0.3	-3.80	0.1	6.25
L21	8°22′5"N	4°34′24"E	80	0	253	-19.4	0.7	-3.30	0.1	5.05

The slope is close to that of the global meteoric water line, but the line has a smaller y-intercept as shown in Figure 5a. The LMWL shows low vapor humidity relative to the GMWL resulting from its lower slope value. A slope is a function of humidity, temperature, and other factors [36; 37; 11] of a particular groundwater territory.

Similarly, in Figure 5a, the stable isotope compositions expressed as δD versus $\delta^{18}O$ plot of groundwater is shown with the corresponding GMWL and LMWL. The plots revealed stable isotopic compositions that essentially clustered below the GMWL and scattered around and along the LMWL indicating meteoric origin as the source of recharge to the groundwater. The slope and interception (d-excess) of the regression line of the groundwater data were lower than that of the LMWL:

$$\delta^2H = 3.4^* \, \delta^{18}O - 7.8 \text{ ‰} \tag{14}$$

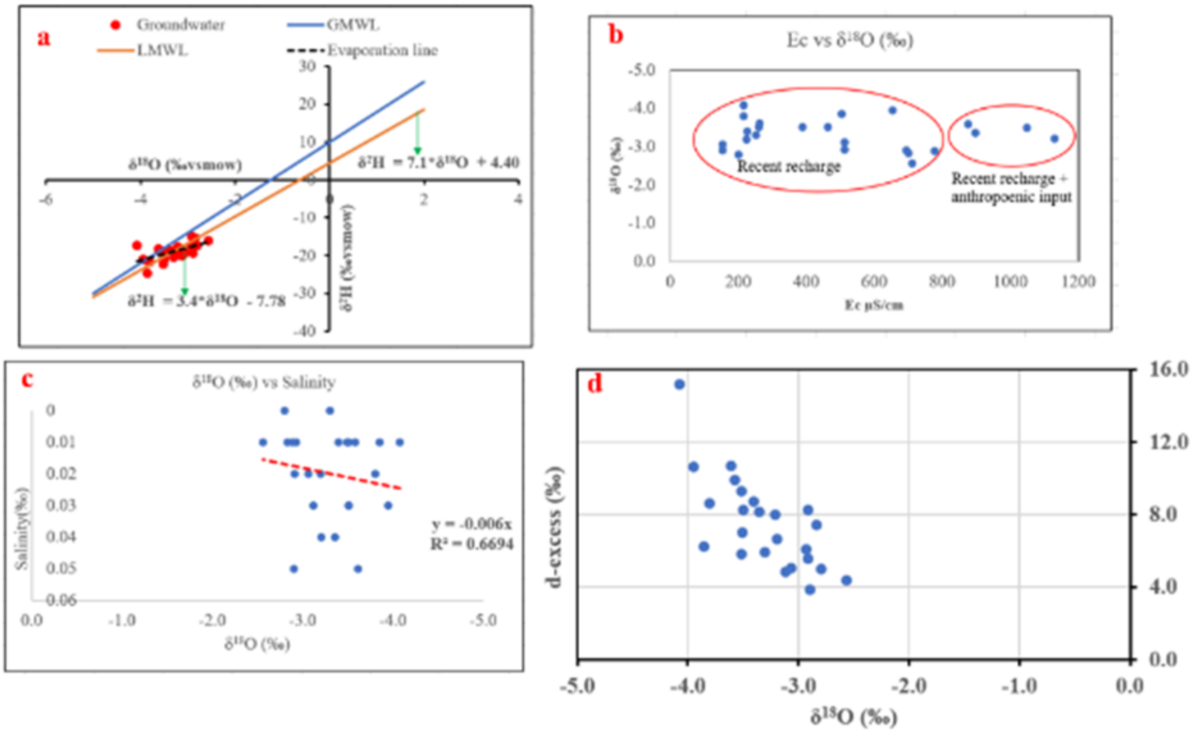

Figure 5. (a) A plot of δ^2H vs $\delta^{18}O$ (‰) relation for the groundwaters in the study area (b) Plot of EC versus $\delta^{18}O$ for the groundwater samples (c) Plot of stable oxygen isotopes ($\delta^{18}O$) vs. salinity for groundwater (d) Plot of $\delta^{18}O$ vs. d-excess in groundwater samples showing a decrease in ^{18}O with an increase in d-excess values

This shows that groundwater is affected by evaporation during recharge. In general, most groundwater isotopes distribute along their corresponding MWLs as commonly observed in groundwater studies [36;8] and Isotope signals in groundwater normally represent long-term average values [38; 11]. Furthermore, the samples plotted above the MWLs indicate rapid infiltration of recharge water before evaporation, while samples plotted below the MWLs are subject to evaporation before recharge. The mean isotope contents of modern precipitation could be calculated from these groundwater samples by projecting their contents back to the world meteoric line [3]. The mean contents calculated in this manner are close to those in modern precipitation in this area [39; 11]. Therefore, the mean isotopic composition of parent precipitation that recharged the aquifer at the point of regression line intercepts the LMWL gives δ^2H = -19.9 ‰ and $\delta^{18}O$ = -3.5 ‰.

Evaluation of Groundwater Residence Time

Figure 5b shows the relationship between electrical conductivity and oxygen-18 and it is adopted essentially to deduce the recharge history of the waters characterizing the aquifer. In general, the groundwater from both shallow and deep aquifers is both recent and relatively enriched in isotopic composition. However, two distinct groups of water may be defined.

- The young recently recharged groundwater, in this group is isotopically enriched with low electrical conductivity value (EC).

- The current or recent recharge but polluted groundwater, is also isotopically enriched but with high electrical conductivity values, the exhibited high EC may be attributed to possible human influence through agricultural and/or other urban pollution. The affected samples are L04, L06, L08, and L09 all of which are located in the shallow hand-dug wells (Table 4).

The similarities and statistical indistinguishable in the isotopic composition values of both shallow and deep aquifers may suggest an interaction between the two aquifers. This is possible where any or all of the following is involved: (i) the presence of porous or fractured overburden which accelerates infiltration, (ii) types of episodic rainfall that recharge the aquifer (iii) and over-exploitation of groundwater that enhances upward leakage of the deep-seated waters towards the shallow surficial aquifer (11; 12). In the presence instance, all the aforementioned are possibilities

Groundwater Quality

Like TDS and electrical conductivity, groundwater salinity can be used as a surrogate for ionic content and is indicative of processes that raise the solute concentration of water. The salinity of the groundwater in the study area is less than the marginal quality (<1%), indicating that the groundwater is fresh. Also, the lower salinity levels may reflect limited weathering of the crystalline basement rocks as well as lower evapo-concentration indicated by more depleted ^2H and ^{18}O in groundwater in the research area.

The link between the ^{18}O (or ^2H) and solute concentrations, which in the present instance is expressed by salinity, can be utilized to evaluate the impacts of rainfall and evaporation vs water-rock interaction on groundwater quality [40]. If evapo-concentration was responsible for the increase in solute concentrations in groundwater, then there should be a positive relationship between the ^{18}O and salinity. The findings show that high salinity does not necessarily correspond with high ^{18}O (Figure 5c), although the negative indication of the trendline may suggest other sources of solute concentration other than evaporation. The poor relationship between salinity and the ^{18}O signifies that salinity in the groundwater of the study area is dominantly due to rock-water interactions. This submission is in tandem with the hydrochemical investigation.

CONCLUSION

The stable isotopes of $\delta^{18}O$ and δ^2H, WQI, and hydrogeochemical investigations have provided useful information about the recharge origin, residence time, groundwater quality, and factors controlling groundwater quality in North Central, Nigeria. The physicochemical parameter values of the groundwaters are within the acceptable standard of WHO 2017 except for some samples of EC, TDS, Fe, Ca, Na, and K with elevated concentrations. The trace elements (Mn, Cd, Cu, Ni) except Zinc exhibit higher concentration values than the WHO standard indicating anthropogenic influence. This highlights the need for regular monitoring and management of groundwater quality to prevent water-borne diseases. The order of cationic and anionic abundance in the groundwater are Ca > K > Na > Mg and HCO_3 > Cl

>SO4 and this accounted for the dominance of Ca-Mg-HCO3, Na-HCO3, and Mixed Ca-Na-HCO3 water types indicating an early stage of groundwater transformation. In addition, carbonate and silicate weathering control the groundwater chemistry. Hydrochemical interpretation revealed that water-rock interaction and little evaporation are the notable geochemical processes that control groundwater evolution. The WQI indexes adjudged the groundwater fit for drinking purposes except in a few instances. The WQI maps provide a valuable tool for assessing and managing groundwater quality in the study area and can inform decision-making and policy development related to water resources management. The stable isotope relationship of $\delta^{18}O$ and $\delta^{2}H$ revealed the groundwater plot along and close to the LMWL with little deviation towards evaporation. This indicates that recent meteoric water origin has little influence on evaporation. A comparison of the results with the Global Meteoric Water Line and regional precipitation data of GNIP station Kano showed groundwater in the study area is dominated by localized young water recharge with a relatively short residence time. The observed similarities and interwoven in the stable isotope values of shallow and deep aquifers may suggest the presence of porous or fractured overburden which enhanced the interaction between the shallow and the deep aquifer. The relationship between $\delta^{18}O$ and EC identified two water categories; unpolluted recently recharged groundwater and polluted recently recharged groundwater which suggests anthropogenic influence on the shallow aquifer. This emphasizes the need for sustainable land use practices, proper waste management, and regulation of industrial activities to prevent groundwater pollution. In addition, the poor relationship between salinity and $\delta^{18}O$ suggests that salinity in groundwater is dominantly due to rock-water interaction. Comparing hydrochemistry results with the stable isotope deductions shows a complementary agreement between the duo. Although groundwater is under active recharge, judicious exploitation, efficient use practices, regular monitoring programs, protection, and management of the limited resources are crucial for the region's economic advancement and sustainable development.

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