ORIGINAL ARTICLE

Groundwater - surface water interactions: application of hydrochemical and stable isotope tracers to the lake bosumtwi area in Ghana

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Abstract

This research demonstrated the application of hydrochemical data and stable water isotopes of $\delta^{18}O$ and δD (or delta 2H) for evaluating the relationship between surface water in Lake Bosumtwi and the underlying groundwater system. It aimed at determining the presence or absence of a hydraulic relationship and for evaluating the possible direction of flow at the interface between the two reservoirs. The study also estimated evaporative losses of infiltrating rainwater as it transits the unsaturated zone and provided important information on the hydrological processes prevailing in the area. The results of Q-Mode hierarchical cluster analysis (HCA) clearly differentiate the lake water from the groundwater based on their spatial relationship. These results indicated that groundwater recharge occurs on the hilltops of the crater, where it is slightly acidic with low levels of dissolved ions, characterised by short residence time and rapid unrestricted vertical infiltration and recharge. The groundwater becomes more mineralized with longer contact times and deeper circulation with the host rock, while it flows from the recharge areas towards the lake at lower elevations. Analyses of $\delta^{18}O$ and δD showed a high evaporation rate on the lake surface (90%) with a significant evaporative enrichment, whereas groundwater showed no significant isotopic variations. Thus suggesting that the aquifers have been recharged by recent meteoric water that has undergone some evaporative enrichment since the study established an evaporation rate of water infiltrating the unsaturated zone ranging from 54 to 60%. Both reservoirs do not appear to be hydraulically connected, and where such a connection exists, it is expected to favour the lake.

Keywords Lake Bosumtwi · Stable isotopes · Kinetic fractionation · Surface water · Groundwater · Ghana

Introduction

In the wake of the recent report of the Intergovernmental Panel on Climate Change (IPCC) on climate projections, there have been conscious efforts at building resilience against the unremitting impacts of climate change, especially on vulnerable communities. One of the most important strategies for enhancing resilience and improving upon the adaptive capacities of vulnerable communities is the development of groundwater resources. Globally, there have been various strategies for improving the knowledge base on groundwater resources to facilitate effective development and sustainable management (eg., Yira et al. 2017; Mustafa et al. 2019; Perera et al. 2019; Yu et al. 2019). Most of these investigations have assessed the relationship between groundwater and other hydrological systems and have proffered strategies for improving resource resilience. For instance, Mustafa et al (2019) used a 3D numerical groundwater flow model to evaluate the relationship between surface and groundwater resources and suggested essential recommendations for improving upon effective groundwater resources sustainably. There are many other studies which have applied numerical

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process-based approaches which are data-intensive and are not effective in data-poor regions such as most parts of sub-Saharan Africa. In such regions, the development of novel techniques, involving the use of tracers (natural and artificial) is critically important for improving understanding of the relationship between hydrological systems.

Hydrochemical and isotope tracers have been copiously used to study various aspects of hydrogeology and hydrological systems. They have been used to evaluate sources of variation in water quality and for delineation of groundwater flow paths (e.g. Cloutier et al. 2008; Banoeng-Yakubo et al. 2010; Loh et al. 2012, 2016; Yidana et al. 2012a, b). However, there are few studies that have effectively used hydrochemical and isotope studies to characterize the relationship between surface and groundwater reservoirs to provide the basis for developing conceptual models on the relationship between the two reservoirs (e.g., Nuan et. al. 2021). An accurate depiction of the conceptual relationship between surface and groundwater resources is critical in the development of useful decision-support systems for managing both resources. Thus, large-scale basin-wide investigations must first begin with an adequate conceptual understanding of the beneficial relationship between surface and groundwater systems so that it will be possible to evaluate the effect of stresses on one reservoir on the other.

This research demonstrates the application of hydrochemical and isotope tracers for evaluating the relationship between a lake and the underlying groundwater system. It is aimed at determining the presence or absence of a hydraulic relationship and for evaluating the possible direction of flow at the interface between the two reservoirs. This will serve the purpose of managing both resources effectively. In the context of Lake Bosumtwi, a natural crater and a subject of many global research endeavours, this research provides important information on the hydrological processes prevailing in the area. Although similar techniques have been applied in other parts of the world (e.g., Abid et al. 2010; Dogramaci et al. 2012; Pu et al. 2020; Zhang et al. 2020; Zhou et al. 2021; Carreira et al. 2021; Kebede et al. 2021), very few have quantitatively evaluated surface–groundwater relationships in the manner demonstrated in this study using stable isotopes and hydrochemical datasets. The objective of this study is to demonstrate the use of hydrochemical and isotopic tracers to facilitate an understanding of the hydraulic relationship between two major reservoirs and for estimating evaporative losses of infiltrating rainwater. The processing of the hydrochemical datasets provides insights into the net direction of groundwater flow, which is relevant for the designation of groundwater recharge and discharge areas.
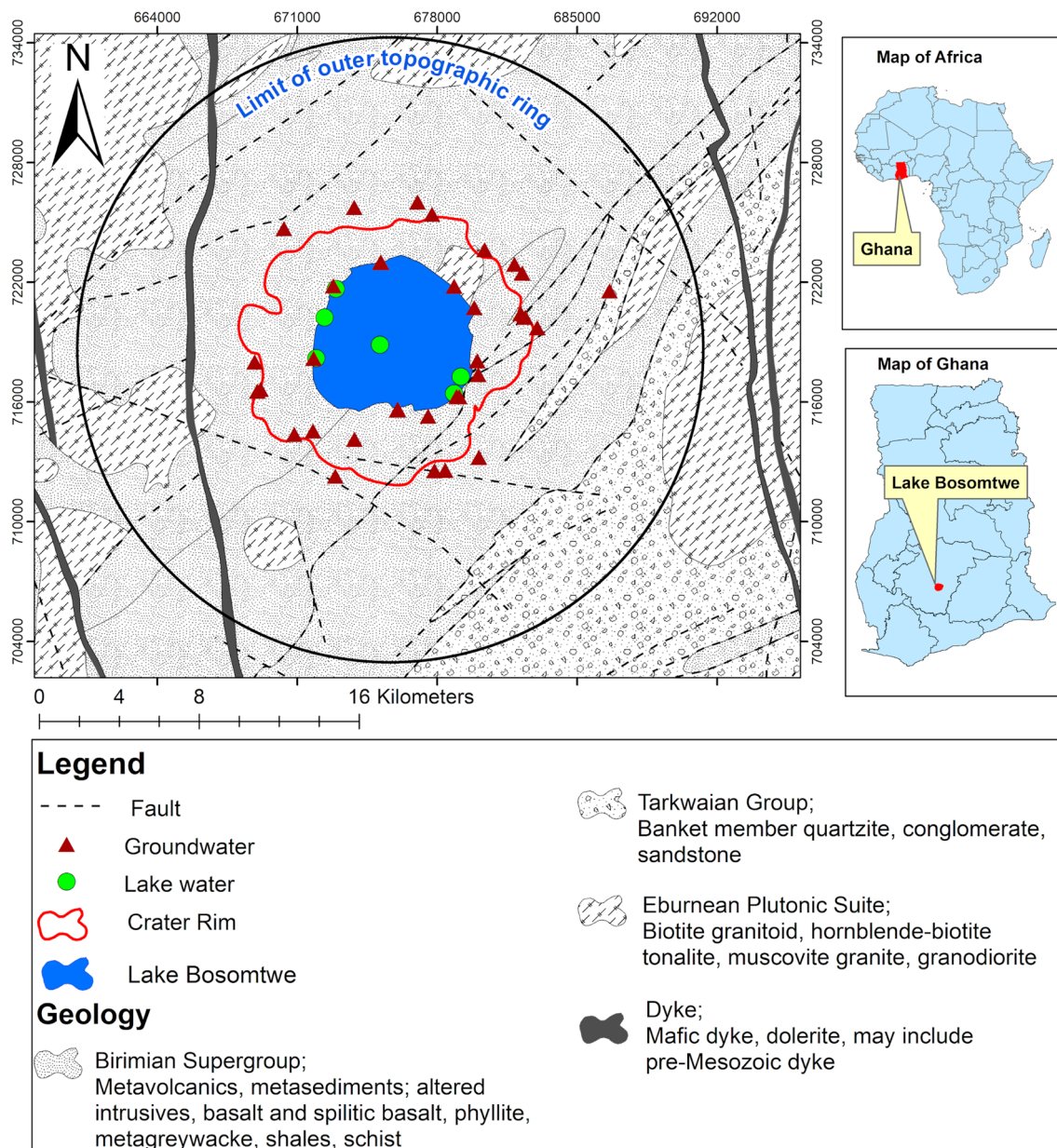
Study area

The study area, Lake Bosumtwi and its environs, is one of the major tourist sites in Ghana, which attracts both leisure and educational visits. The Lake is close to Kumasi, the second largest city in Ghana (Fig. 1). The study area is situated within the deciduous forest zone and is strongly influenced by the West Africa monsoon winds (Balek 2011). The climate is generally warm with variable temperatures masked by seasons and elevation and characterised by two rainy seasons; major and minor rainy seasons. The major rainy season begins in March, peaks in June and ends in July, while the minor season spans from September to November with a peak in October. Rainfall amounts range between 1.6 m and 1.8 m per annum. On average, there are about 150 rainy days.

Temperatures range between 32 ℃ in March and 20 ℃ in August, with relative humidity ranging between 70 and 80% (Turner et al. 1996a). Details of the hydrological characteristics of the area are copiously discussed by other researchers (e.g., Turner et al. 1996a; Amu-Mensah et al. 2019).

Extensive farming, illegal mining and lumbering have changed the vegetation cover in the study area from semi-deciduous and rainforest to mosaic secondary forest. Dendritic drainage pattern is the drainage type pertaining to the area. However, around Lake Bosumtwi, there is internal drainage where the streams flow from the surrounding highlands into the Lake, forming a dense network due to the double maxima rainfall regime.

Lake Bosumtwi falls within the Birimian Supergroup of West Africa and made up of two major lithostratigraphic units of the early Proterozoic age, which are the Birimian Sedimentary Basins and Birimian Volcanic Belts (Kesse 1985; Karikari et al. 2007) (Fig. 1). Extensive studies have established that these rocks host most of Ghana's mineral deposits such as gold and diamond (Leube et al. 1990; Hirdes et al. 1992; Fougerouse et al. 2017; Kazapoe & Arhin 2021). These studies showed that the Eburnean tectonothermal event, which stabilised the West African Craton, caused the Birimian Supracrustal rocks to become folded and metamorphosed under greenschist-facies conditions, and intruded by granitoids. The impact crater has a steep rim rising up to 300 m above the present lake level. It is surrounded by an irregular circular depression with a rim-to-rim diameter of 10.5 km, as well as an outer ring of minor topographic elevations with a diameter of about 20 km (Jones et al. 1981; Reimold et al. 1998). Rocks at and around Lake Bosumtwi are dominated by meta-sandstones, shales, phyllites, and schist (Leube et al. 1990; Hirdes et al. 1992). These metasediments are rich in quartz, feldspars and micas (biotite, muscovite).

Fig. 1 Geological map of the study area showing sample points

The hydrogeology of the study area is characterised by the Birimian Province. Here the hydrogeology is controlled by secondary porosity and permeability and the extent of weathering. These secondary porosity and permeability in the rocks of the study area were created during the Eburnean orogeny that occurred about 2.1 Ga ago (Kesse 1985) and impact cratering (Reimold et al. 1998). Where there are tectonic lines of weakness as a result of the Eburnean orogenic event, deep weathering of the rocks occurs in the study area. Weathering is enhanced where the fractures, joints, faults, folds and quartz veins are extensive. Thick weathering zones are known to be reservoirs for delivering huge volumes of

water (Banoeng-Yakubo et al. 2010). In some places, the weathered zones can be as thick as 137 m (Kesse 1985; Dapaah-Siakwan and Gyau-Boakye 2000). In the Birimian Province, the lower part of the saprolite and the upper part of the saprock forms the most productive section with regard to groundwater. These complement each other in terms of transmissivity and storage (Carrier et al. 2008). A conceptual model developed by Carrier et al. (2008) shows that the hydrostratigraphy of the Birimian Province starts with topsoil/laterite, followed by the saprolite then the saprock and eventually the competent bedrock. Borehole depths completed within the weathered and fractured units ranged

between 26 and 64 m with an average of 43 m (Loh et al. 2016) and static water levels ranging between 3 and 43 m below ground level (Banoeng-Yakubo et al. 2010). Average aquifer transmissivity value in this Province is 7.4 m^2/d (Banoeng-Yakubo et al. 2010). Successful boreholes that have been drilled in this Province suggest there is an average borehole yield of 12.7m^3/hr (Banoeng-Yakubo et al. 2010; Dapaah-Siakwan and Gyau-Boakye 2000). Loh et al. (2016) established that drilled and developed boreholes within the study area tap water under semi-confining conditions.

Materials and methods

Water sampling was carried out over a generally cold and dry period from late July to early August 2012. Thirty-four groundwater samples and seven lake water samples were collected in triplicate into 50 mL sterilised polypropylene bottles. Out of the three samples, two were filtered via a 0.45-micron membrane. One of the filtered samples was subsequently acidified with nitric acid (HNO_3^-) to pH less than 2 for cation analysis, and the other was used for anion analysis. Duplicate samples were taken as a quality control measure for the obtained analytical results. The concentrations of $\delta^{18}O$ and δD were determined using the third unfiltered sample. Physical parameters such as total dissolved solids (TDS), water temperature (T), salinity (Sal), electrical conductivity (EC), pH, dissolved oxygen (DO) and oxidation–reduction potential (ORP) were measured in situ for all samples collected with a HANNA Instruments HI 98,280. In the field, the alkalinity (Alk) (as HCO_3^-) was measured using a Hach digital titrator. Major cation and trace element concentrations were determined using an inductively coupled plasma-mass spectrometer (ICP-MS) at Activation Laboratories Ltd in Canada. Inductively coupled plasma optical emission spectrometry (ICP-OES) was then used to reanalyse samples that were over the required range (i.e., > 25 ppm of Na^+, K^+, and Sr^{2+}; and > 100 ppm of Ca^{2+}, Mg^{2+}, and Si^{4+}). The analytical precision for both ICP-MS and ICP-OES was estimated to be within 5% based on repetitive sample analysis and duplicate sample results. Anions of chloride (Cl^-), sulphate (SO_4^{2-}), and nitrate (NO_3^-), fluoride (F^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) were measured in milligram per litre (mg/l) using a Dionex DX 120 ion chromatograph (I.C) with an analytical precision of 5%. Additionally, the standard error for the obtained results of individual elements was calculated by dividing the sample standard deviation by the square root of the total number of samples.

Ten rainfall samples collected in the months of April, May, June and July were analysed for isotopes of $\delta^{18}O$ and δD. The Los Gatos Research Liquid Water Isotope Analyzer was used to analyse these samples at the University of Rochester's Department of Earth and Environmental Sciences. The findings were standardised (Coplen 1994) on scales so that the $\delta^{18}O$ and δD of the Vienna Standard Mean Ocean Water (V-SMOW) values were 0‰ and 0‰, respectively, whereas the $\delta^{18}O$ and δD values of Standard Light Antarctic Precipitation (SLAP) were, respectively, − 428‰ and − 55.5‰. Unless otherwise stated, the 2-sigma uncertainties for $\delta^{18}O$ and δD results were 2.0‰ and 0.20‰, respectively. This suggests that the result of isotopic analysis of the same sample would fall 95% of the time within the uncertainty bounds if it were reanalysed.

Microsoft Excel and the statistical package for social sciences (SPSS) version 25.0 were used to conduct univariate, bivariate and multivariate statistical analyses of the data sets obtained. The multivariate statistical analyses were performed to constrain relationships among multiple variables in the entire data set with an emphasis on revealing the intrinsic clusters/ groupings within the entire data, which on the contrary would not have been noticed. To achieve optimal results from the statistical analysis, the normality of each parameter was tested and those parameters which did not meet normality were transformed accordingly. Log transformation was employed and then standardised to their respective z-scores. In producing the spatial distribution maps, kriging was performed using different semi-variogram models to determine the best model fit for the data set. Continuous adjustment was made to the variogram parameters until all the criteria for an optimal model was arrived at. The Gaussian model was the most accurate predictor for pH and EC data sets. The obtained parameters ($C_o = 0.00021$; $C_o + C = 0.00654$: $A_o = 0.03$: $r^2 = 0.786$: Residual Sum Square $= 1.056E\text{-}05$) from the variogram model were then used to generate the spatial distribution maps of pH and EC in ArcGIS version 10.7.

Following the model developed by Craig and Gordon (1965) and applied by Yidana et al., (2013), the surface evaporation rate from the Lake was estimated. This model determines the fraction of water lost by evaporation (*f*) (Eq. 1).

$$f = 1 - \left(\left(\delta_L - \delta^* \right) / \left(\delta_P - \delta^* \right) \right)^{\frac{1}{m}} \tag{1}$$

$\delta^* =$ local limiting isotopic signature,

which is determined from Eq. 2:

$$\delta^* = (h\delta A + \varepsilon)/\left(h - \frac{\varepsilon}{1000} \right) \tag{2}$$

h is the average relative humidity of the study area, δA ambient air vapour isotope signature and ε isotopic enrichment factor (Gat and Gonfiantini 1981).

δ_p and δ_L represent the isotope signatures of the initial source water for the lake and sampled lake water, respectively, while the index (m) is given by Eq. 3

$$m = \left(h - \frac{\varepsilon}{1000} \right) / \left(1 - h + \frac{\varepsilon_k}{1000} \right) \tag{3}$$

The kinetic isotopic enrichment factor, ε_k, is linked to the relative humidity between water (w) and water vapour (v) with regards to $\delta^{18}O$ (Eq. 4) (Gonfiantini 1986).

$$\varepsilon_k^{18}O_{w-v} = 14.2(1-h)‰ \tag{4}$$

The $\varepsilon_k^{18}O_{w-v}$ value of 4.26‰ was estimated at a local humidity of 70% (Turner et al. 1996a) for the lake water.

ε provides the sum of both equilibrium and non-equilibrium (kinetic) enrichment factors in Eq. 5.

$$\varepsilon = \varepsilon_{eq} + \varepsilon_k; \tag{5}$$

$\varepsilon_{eq} = 10^3(1 - \alpha_{w-v}^{-1} =$ and α_{w-v}^{-1}, which is temperature (T measured in Kelvin) dependent is expressed for ^{18}O by Eq. 6 (Faure 1998);

$$10^3 ln\alpha^{18}O_{w-v} = \left(\frac{1.534 \times 10^6}{T^2} \right) - \left(\frac{3.206 \times 10^3}{T} \right) + 2.644 \tag{6}$$

For a mean annual T of 298.15 K (25 °C), ε_{eq} returned a value of 9.11‰. The overall enrichment under the prevailing conditions was −13.37‰. Peng et al. (2012) proposed that a relationship between initial precipitation (δ_{IP}) and ambient air vapour isotope signature (δA) presumes an isotopic equilibrium (Eq. 7).

$$\delta A \cong \delta_{IP} - 10^3 (\alpha_{w-v} - 1), \text{ where } (\alpha w - v) \text{ is the fractionation factor,} \tag{7}$$

Results and discussions

Major ion chemistry

The summary statistics and distribution of hydrochemical parameters from the lake and groundwater (GW) are presented in Fig. 2 and Table 1. The relative abundance of the major cations in the lake water occur in the order $Na^+ >> Mg^{2+} > K^+ > Ca^{2+}$, while in the groundwater, the cations occur as $Ca^{2+} \geq Mg^{2+} \approx Na^+ >> K^+$. The anions on the other hand occur in the order; $HCO_3^- > Cl^- \approx SO_4^{2-} >> NO_3^-$ for groundwater and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ for lake water (Fig. 3a). The dominance of HCO_3^- suggests both the lake water and groundwater are dominated by meteoric waters (Freeze and Cherry 1979). The HCO_3^- may have resulted largely from the dissociation of carbonic acid (H_2CO_3) when falling
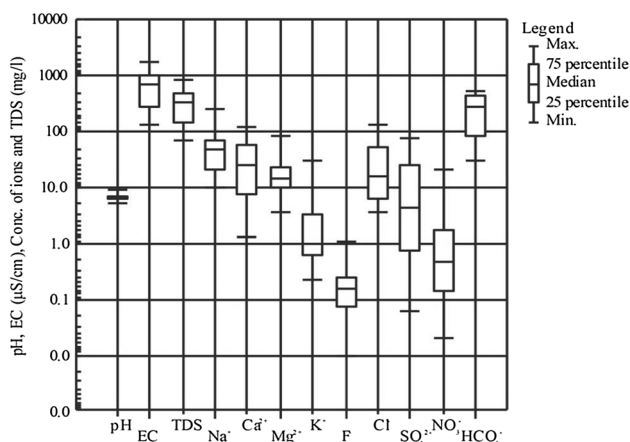

Fig. 2 Box plot for the physical and major ions for the water samples from the study area

precipitation dissolved CO_2 in the atmosphere, which process is well described by Freeze and Cherry (1979).

Hierarchical cluster analysis (HCA) performed on the hydrochemical parameters using Q-mode, to discriminate samples based on their spatial relations resulted in four clusters, based on a phenon line drawn at a linkage distance of 3 on the resultant dendrogram (Fig. 4). The clusters are ordered from left to right, with clusters 1–3 being groundwater, and showing an increasing trend in ionic enrichment, whereas cluster 4 is composed of lake water samples. Cluster 1 (C1) members, generally located in the southwest, on the top of the crater rim, in higher elevations (about 308 m above sea level), exhibit relatively lower ionic content (median EC = 188 µS/cm), dominated by acidic waters (median pH = 5.6); characteristic of recharge zones in the evolutionary sequence of groundwater flow regimes (Table 1; Fig. 5a and b) (Chebotarev 1955; Freeze and Cherry 1979). The low mineralization also suggests a short residence time of infiltrated and rapidly recharged groundwater (Table 2).

The relatively acidic waters observed in C1 members may have resulted from recharge from CO_2-charged rainwater, and the dissolution of CO_2 in the root zone as a result of plant and animal respiration (Hem 1985; Hasan and Tewari 2020). Indeed, comprehensive research by Akoto et al. (2011) on the chemical composition of rainwater sampled in the Pra River Basin suggests acidic rainwater with a pH range of 4.0–5.6 averaging 4.76 ± 0.47. Turner et al. (1996a) also observed that the decomposition of organic matter within the root zone lowers the pressure of CO_2^-, resulting in low pH within lake Bosumtwi. Even though there are fault zones distributed near the metavolcanic rocks, extensive research by various authors (e.g., Koeberl et al. 1997, 1998; Reimold et al. 1998; Boamah and Koeberl 2002; Karikari et al. 2007) on the rocks of the area do not indicate an abundance of CO_2^- so the migration and dissolution of

Table 1 Statistical summary of the physico-chemical parameters of the clusters

|	Elevation (m)	pH	T (°C)	EC (μS/cm)	TDS (mg/l)	K$^+$ (mg/l)	Na$^+$ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	Sr^{2+} (mg/l)	Si^{4+} (mg/l)	F$^-$ (mg/l)	Cl$^-$ (mg/l)	NO$_3^-$ (mg/l)	SO$_4^{2-}$ (mg/l)	HCO$_3^-$ (mg/l)
Cluster 1																
Min	259	5.08	25.04	138	69	0.23	9.64	3.49	13	0.07	23.8	0.01	3.53	0.15	0.13	31
Max	358	5.73	26.03	270	135	4.80	18.8	11.7	11.6	0.17	52	0.26	6.16	3.13	1.98	70
Mean	308	5.51	25.48	189	95	1.05	15.07	5.74	4.95	0.12	36.14	0.1	4.47	0.87	0.9	52
Std.Dev	28	0.26	0.36	46.14	23	1.53	3.35	2.68	3.44	0.03	9.5	0.1	0.82	1.02	0.74	16
Median	306	5.61	25.39	188	94	0.57	15.75	4.81	4.6	0.12	35.2	0.08	4.15	0.54	0.61	51
Cluster 2																
Min	111	5.54	24.55	295	147	0.28	17.2	7.97	1.6	0.178	13.9	0.02	4.3	0.02	0.06	57
Max	448	7.29	28.23	662	331	4.4	67.2	23.8	69.9	0.52	38.4	1.11	60.1	13.5	22.5	290
Mean	251	6.43	26.48	510.2	255	1.28	37.75	16.23	34.45	0.32	25.74	0.23	20.17	3.04	9.71	183
Std.Dev	121	0.55	1.31	105.08	53	1.26	17.87	4.86	20.88	0.13	6.47	0.32	21.89	5.42	8.57	88
Median	253	6.56	26.19	507	254	0.87	33.7	16.05	38.75	0.33	26.55	0.14	7.73	0.62	10.02	199
Cluster 3																
Min	108	6.2	25.46	599	300	0.44	26.7	9.9	18.8	0.2	8.1	0.02	8.63	0.02	17.9	182
Max	244	7.04	29.18	1746	873	4.89	105	84	120	0.86	22.4	0.38	69.6	21.3	79.3	494
Mean	163	6.7	27.43	959	480	1.46	59.03	31.52	65.91	0.42	16.68	0.15	31.44	4.17	36.27	354
Std.Dev	58	0.23	1.18	293.26	147	1.24	21.92	18.7	28.21	0.21	3.95	0.11	19.54	6.14	17.54	93
Median	129	6.73	27.57	888.5	444	0.97	60.6	24.1	65.2	0.36	17	0.14	26.55	1.8	28.6	361
Cluster 4																
Min	103	8.39	26.59	1262	634	119	80.8	6.79	4.5	0.105	4.6	0.18	107	0.04	0.6	500
Max	112	9.06	27.50	1344	672	28.8	260	14.3	9.2	0.2	11.6	0.41	138	0.32	0.9	526
Mean	107	8.87	27.24	1313.29	658	25.04	224.97	12.63	7.73	0.19	9.94	0.26	112	0.13	0.79	514
Std.Dev	3	0.23	0.34	36.2	17	6.29	66.31	2.72	1.52	0.04	2.6	0.07	11.47	0.11	0.12	10
Median	109	8.95	27.41	1337	669	28.1	257	14	8	0.2	11.2	0.24	108	0.08	0.78	516
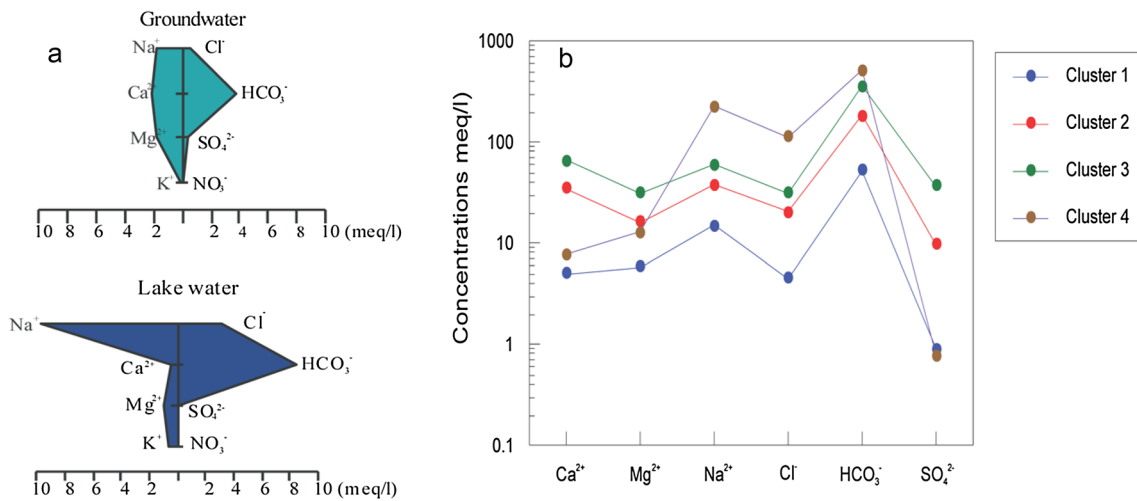
Fig. 3 Stiff diagrams for the mean concentration of the major ions in groundwater (**a**) and lake water (**b**) and Schoeller diagram showing the arithmetic mean of the major ions in each cluster
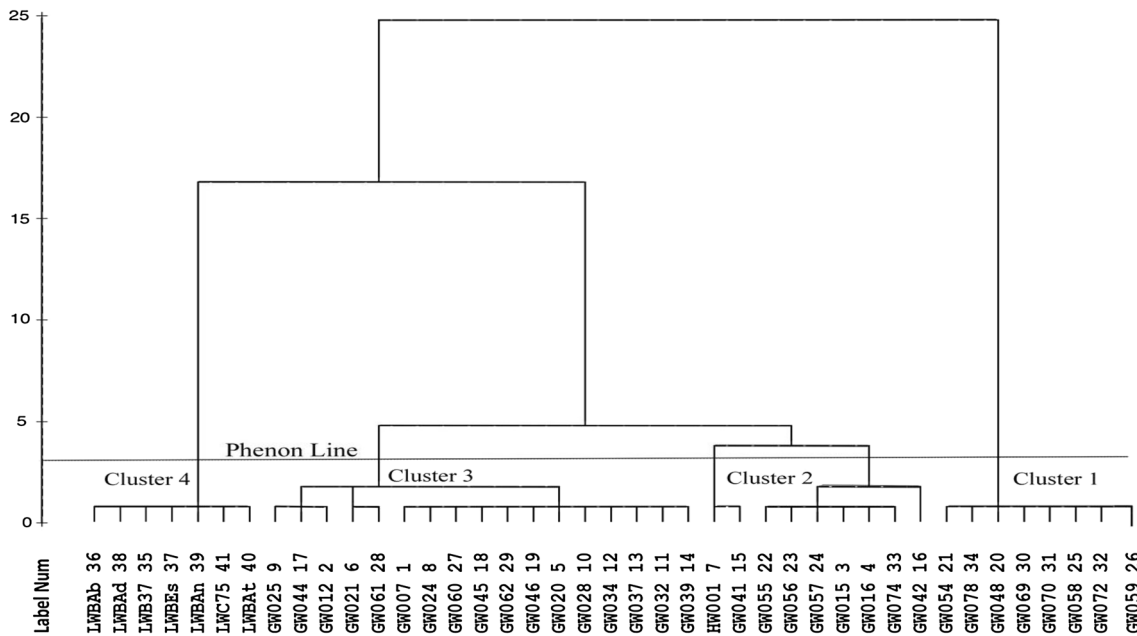
Fig. 4 Dendrogram generated from HCA of hydrochemical data from groundwater and lake water showing associations between the samples

deep mantle-derived CO_2^- with groundwater may not be an important reason for the low pH values. 'Hard' rock and associated silicate mineral dissolution is aided by acidic conditions as a result of low pH, which explains the relatively high levels of Si in C1 members as compared to the other clusters (Table 1). These processes cause the incongruent dissolution of mainly plagioclase, biotite and potassium feldspar, which are common minerals identified in the underlying geology of the study area (Garrels and Mackenzie 1967; Dedzo et al. 2017).

Average concentration of the major ions used to plot a Schoeller diagram (Fig. 3b) corroborated the evolutionary sequence observed above; Na^+ level is higher than Mg^{2+} and Ca^{2+} for C1 members. The dissolution of Si is enhanced under conditions of high CO_2 and low pH. Under such conditions, the groundwater gains high Si content over relatively short residence time. And where the dissolution of plagioclase is present, a 2:1 Si to Na ratio is expected (Garrels and Mackenzie 1967; La Plante et al. 2021). This is consistent with the assertion that the high levels of Si in
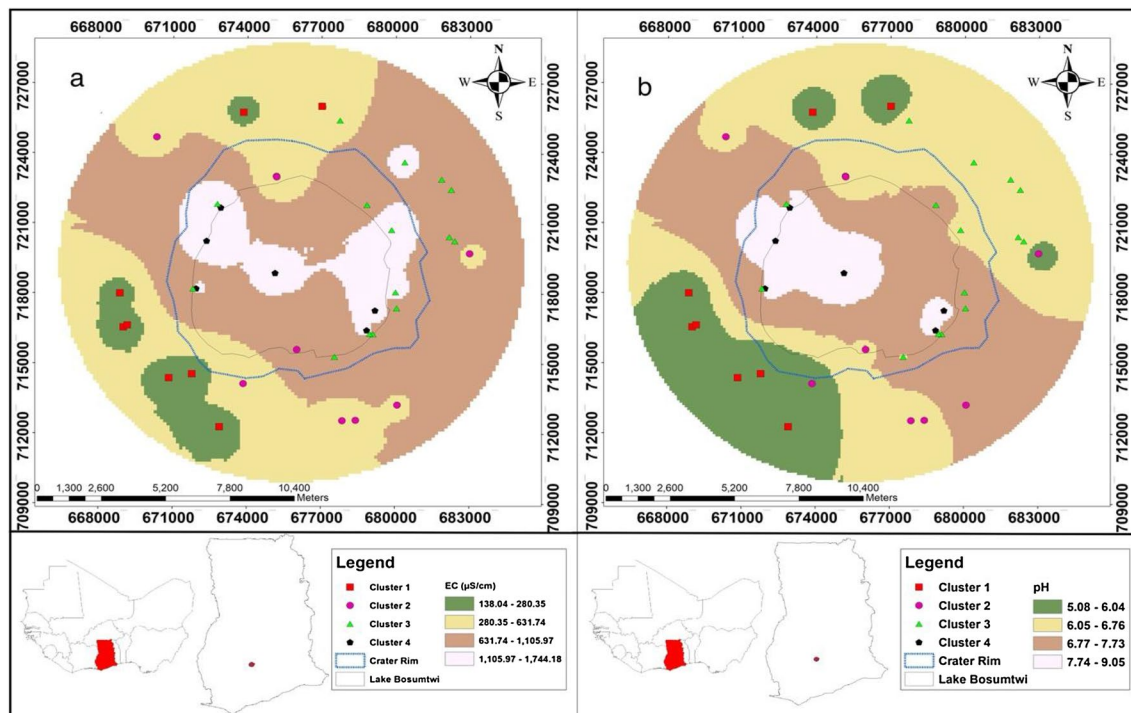
Fig. 5 Spatial distribution of EC (**a**) and pH (**b**) in relation to sample clusters

Table 2 Analytical standard error values for measure major ions

Elements	Analytical technique	Precision	Standard error
K^+	ICP-OES	0.1	0.06
Na^+	ICP-OES	0.1	0.05
Mg^{2+}	ICP-OES	0.1	0.06
Ca^{2+}	ICP-OES	0.1	0.10
Sr^{2+}	ICP-OES	0.01	0.05
Si^{4+}	ICP-MS	0.2	0.03
F^-	IC	0.01	0.06
Cl^-	IC	0.03	0.07
NO_3^-	IC	0.01	0.14
SO_4^{2-}	IC	0.03	0.15
HCO_3^-	HDT		0.07

Where ICP-OES is inductively coupled plasma optical emission spectrometry, ICP-MS is inductively coupled plasma mass spectrometry, IC is ion chromatograph and HDT is hach digital titrator

C1 members resulted from the aforementioned processes while CO_2-charged meteoric waters recharged groundwater, and in the process dissolved a sodium-rich plagioclase feldspar such as albite, which is common among the rocks of the study area. The weathering of silicate minerals such as albite is probably the cause of the high levels of Na^+ in C1 members. Samples from C1 are most likely groundwater collected from boreholes located in areas designated as potential recharge zones. The groundwater evolved from

Cluster 1 to Clusters 2 & 3 as one moves down the gradient towards relatively lower elevations in the northeast (NE). Cluster 2 (C2) members occur at elevations around 251 m above sea level (asl), characterised by a high ionic content and a slightly acidic (pH = 6.55) system. Cluster 2 appears to be the transmission zone members, which evolved into a more mineralized group (EC = 888.5 μS/cm) in Cluster 3 (C3), located in a much lower elevation (163 m asl) with average pH of about 6.72 (Table 1 and Fig. 5 a and b). The relatively high mineralization in Cluster 3 members is attributable to the relatively longer residence time and increased interaction with aquifer materials as the groundwater transits and evolves from C1 to C3 (Freeze and Cherry 1979; Stuyfzand 1999; Appelo and Postma, 2005; Cochand et al. 2019; Ren et al. 2021). Although C2 and C3 appear to be equally balanced on the cations, with no particular cation dominating, Ca^{2+} appears to be the most abundant cation in most of the C2 and C3 members. While various studies (e.g. Hendry and Schwartz 1990; Herczeg et al. 1993; Hiscock et al. 1996; Zhou et al. 2020; Mirzavand et al. 2020; Kumar et al. 2021) have employed major ion chemistry to ascertain the main sources of solutes and to better evaluate and understand groundwater evolution, several other studies (Panno et al. 1994; Gosselin et al. 2001; Stimson et al. 2001; Pazand et al. 2018; Jeen et al. 2021) have demonstrated that the study of regional hydrogeochemistry is valuable to the management of regional aquifers, tracing flow and salinisation of groundwater.

It can be observed from Table 1 that the Si levels decrease along the flow path as the groundwater evolves, in the order; C1 > C2 > C3, suggesting possible crystallisation of some secondary mineral other than kaolinite that may have substituted silica in the groundwater (Garrels and Mackenzie 1967). Various factors such as aquifer mineralogy and characteristics, climate and topography and composition of recharge, (e.g., Güler et al. 2002; Loh et al. 2016, 2020) have been identified to influence the chemistry of groundwater, and collectively influence the diverse water types that change in time and space. The analyses and observations corroborate the assertion that hydrochemical facies analysis can be applied to adequately delineate and trace potential groundwater recharge source(s). Hence it is cogent to conclude that the observed pattern is in tandem with the general hydrogeological principle that groundwater becomes relatively more mineralized, with increased residence and contact time with the aquifer material along its flow paths. Detailed work on the hydrochemistry and quality of groundwater and lake water in the study area for various uses are presented by Loh et al. (2016) and Loh et al., (2021).

Stable isotopes

Figure 6 presents summary results of $\delta^{18}O$ and δ^2H for rainwater (RW), lake water (LW) and groundwater (GW) from the study area. The results revealed that $\delta^{18}O$ and δ^2H values varied from -3.6 to -2.3 ‰ for $\delta^{18}O$, and -16.5 ‰ to -7.6 ‰ for δ^2H for the groundwater in the study area. Average $\delta^{18}O$ values for the RW, LW and GW in the area are -4.47 ‰, -3.06 ‰ and 4.74 ‰ respectively, whereas their respective average δ^2H are -25.49 ‰, -12.46 ‰ and 23.98 ‰, although samples from the lake and rainfall were limited in number. Since water from natural water bodies such as rivers, lakes, dams, groundwater etc. is derived from precipitation, its characteristic signatures in ^{18}O and ^2H are expected to be evident in such water bodies in the study area. However, comparing the isotopic signatures of $\delta^{18}O$ and δ^2H for GW and LW to the precipitation in the study
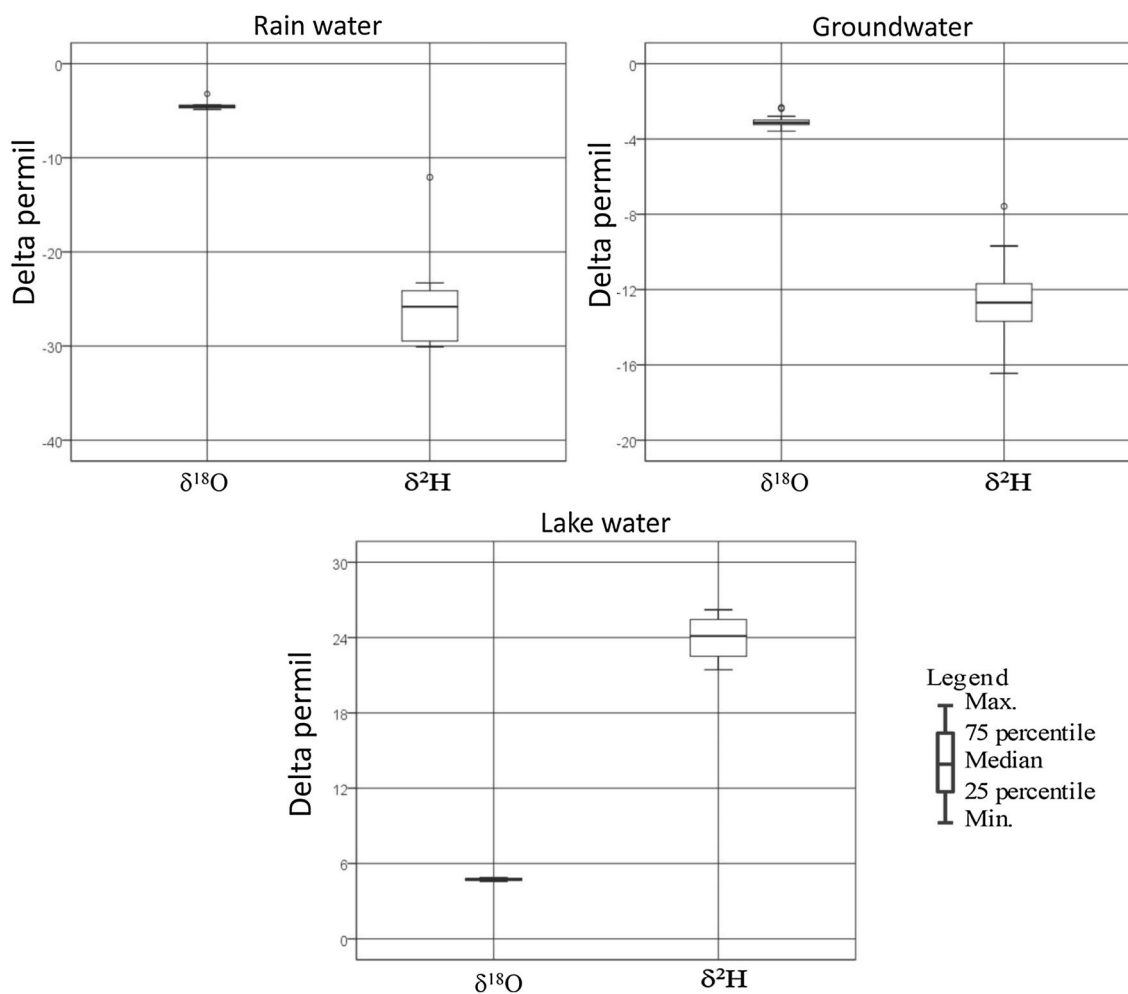

Fig. 6 Box plot of the stable isotope contents of the analysed water samples

area, a progressive enrichment was observed in their isotope compositions, suggesting that the rainwater may have undergone some modification (Clark and Fritz 1997).

A biplot of δ^2H against $\delta^{18}O$ for the various water sources sampled in this study is presented in Fig. 7. Rainfall event RW04, which was sampled at the beginning of the rainy season, around April is relatively isotopically enriched, compared to latter events in May to July, and exhibit similar signature as groundwater in the areas. RW04 was particularly an early and light rainfall event that commenced the rainy season. The enrichment of RW04 is attributable to the harsh weather conditions associated with the onset of the rainy season; characterised by high temperatures and evaporation rates (Fig. 7). The harsh weather conditions in the study area lessens once the rainy season begins, leading to a much cooler environment since the dry air column and the ground gets saturated with water. This minimises the evaporation rate and subsequent depletion of rainfall events (Fig. 7) (Clark and Fritz 1997).

To further understand the relative isotopic enrichment or depletion of the various water sources in this study, the regression line established by Akiti (1986) for the Accra plains was adopted as the local meteoric water line (LMWL) due to the lack of sufficient precipitation data. The LMWL established by Akiti (1986) as: $\delta^2H = 7.87\delta^{18}O + 13.6$ is comparable as a result of the proximity and similar geographic

and climatic conditions of Accra Plains to this current study area. The intersection of the LMWL and the LEL produced an initial isotope content (Clark and Fritz 1997; Marfia et al., 2004; Dogramaci et al. 2012) of $-29.76‰$ δ^2H and $-5.51‰$ $\delta^{18}O$ that is more negative than the mean isotope composition ($\delta^2H = -25.49‰$ and $\delta^{18}O = -4.47‰$) of rainwater but comparable to the isotopic composition ($\delta^2H = -30.07‰$ and $\delta^{18}O = -4.88‰$) of the heaviest rainfall event collected in May. This agrees with the findings of Turner et al. (1996a) that the lake water input budget is dominated by heavy and intense rainfall events who estimated that about 80% of the water that enters the lake annually is sourced from rainfall on its surface.

It can be observed in Fig. 7 that most of the samples from the rain and groundwater plot between the LMWL (Akiti 1986) and the global meteoric water line (GMWL), except for the LW samples, which plot far below both MWLs. The level of departure of the samples from the meteoric water lines (MWLs) reveals the degree of relative enrichment. Samples with little or no enrichment plot more closely to the MWLs as compared to more enriched samples. Significantly enriched samples fall to the right of the regression line generating larger intercept value (Alley 1993; Mazor 1997). Hence GW samples that are plotted close to the MWLs have not undergone any significant evaporative enrichment. This is probably due to the fact that groundwater

Fig. 7 A scatter diagram of δ^2H—$\delta^{18}O$ of the samples analysed in this study
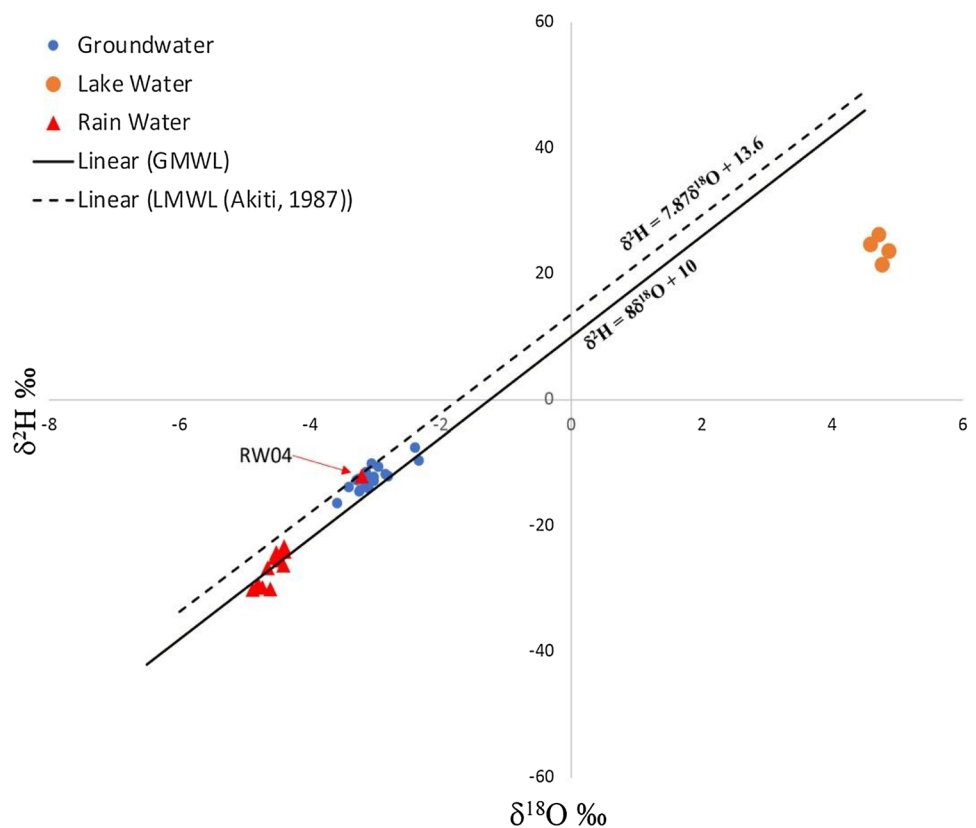
is generally protected from the impacts of high temperature and evaporation on the land surface. On the other hand, the lake water, due to its exposure to harsh weather conditions is prone to high evaporation rates and subsequently relatively high enrichment. This explains the divergence of the lake water samples from the MWLs (Fig. 7).

A model proposed by Craig and Gordon (1965) has been adopted to estimate the rate of evaporation from the lake surface. This model, which has been used in several studies (Dogramaci et al. 2012; Yidana 2013; Gonfiantini et al. 2018; Dar et al. 2021) employed average temperature in the area, slope of the local evaporation and the initial isotopic signature of the precipitation to estimate evaporation rate for the lake. The isotopic signature of RW04 sampled in April was considered as the initial precipitation, and the ambient air vapour isotope signature (δA) estimation resulted in -12.40 ‰ for $\delta^{18}O$ using Eq. 7. The observed ~90% evaporation rate from the lake surface is in tandem with the harsh climatic conditions that characterise the study area. This further corroborates the assertion that water from the lake has undergone some intense evaporation, and as a result it is isotopically enriched.

The GW samples from the study area, fit nicely with a least square regression line, given as: $\delta^2H = 5.49\delta^{18}O + 4.33$ with a strong correlation ($r = 0.7$). The slope and intercept, 5.49 and 4.33, respectively, suggest that the rainwater, prior to infiltration and recharge, may have undergone relative evaporative enrichment within the unsaturated zone, especially when compared with the LMWL and GMWL. This agrees with what has been reported in the literature about d-excess values of less than 10 ‰ (Dogramaci et al. 2012; Sreedevi et al. 2021). The evaporation rate for groundwater was estimated to range from 54% to 59.5%, using -17.03 ‰ and -3.89 ‰, respectively, as initial δ^2H and $\delta^{18}O$ isotope contents. This suggests that in the study area, more than half of the rainwater that begins transit through the unsaturated zone is lost to evaporation and aquifer recharge probably resulted from vertical infiltration or passage along flow paths in fractures. Thus, rainwater available for groundwater recharge is reduced at most locations within the area. This corroborates the assertion that evaporation is an active process in the unsaturated zone prior to recharge as observed in some studies in Ghana (Addai et al. 2016; Akurugu et al. 2020). The observed groundwater evaporation rate could be attributed to the matrix of flow mechanisms within the unsaturated zone before recharge. In a system where the piston and preferential flow are characteristic, a mix of old and new waters could impact the isotopic signature of the final recharging water (Cheng et al. 2014). Fynn et al., (2016) in an attempt to characterize the unsaturated zone of the Nabogo basin in Ghana, established the effect of the flow mechanism on isotopic signature of recharged groundwater. The estimated initial value of $\delta^{18}O$ (-3.89 ‰)

is comparable to the average $\delta^{18}O$ values obtained for the rainwater (-4.47 ‰), Akiti (1986) (-3.20 ‰) and groundwater (-3.10 ‰) in the study area, which are characteristic of recent meteoric waters. This supports the claim that the groundwater may have been recharged through fissures and fractures by recently evaporated meteoric water.

Furthermore, it is evident in Fig. 8 that the groundwater EC (138 – 1746 μS/cm) shows a generally increasing trend whereas the isotopic composition remains the same. This suggests that one of the main factors influencing the hydrochemistry of the groundwater is rock mineralization and not evaporation. Therefore, the isotopic signature as observed in the groundwater could only have resulted from direct precipitation (Gibrilla et al. 2017).

Depletion gradients in stable water isotopes have been observed per 100 m rise in elevation, ranging from -1 to -4 ‰ for δ^2H and -0.15 to -0.6 ‰ for $\delta^{18}O$ (Clark and Fritz 1997; Dogramaci et al. 2012). Groundwater samples in lower elevations and close to the lake were relatively lighter in isotopic signatures than the lake water but with isotopic content close to that of the samples located around the crater rim with an elevation difference of about ~300 m. This shows that the isotopic contents of the various groundwater samples had no relationship with elevation in the study area (Fig. 8a) suggesting no seepage of water from the lake towards groundwater. However, this does not exclude a possible hydraulic connection between the lake and shallow aquifers in the study area.

Figure 8c shows the relationship between elevation and EC. It can be deduced that the EC (138–1746 μS/cm) of the groundwater increases as water moves towards the lake in lower elevations, suggesting that the direction of groundwater flow is from the crater rim into the lake. Hence the claim that the crater rim areas are the plausible recharge zones is in tandem with results from the cluster analysis (Fig. 4). Since the groundwater flows towards the lake, a detailed study may be required to establish the possible connection between the lake and groundwater if any. This is important to establish the impacts of low or high groundwater levels on the lake and vice versa, in the wake of climate change, land cover change, population growth and urbanisation.

Conclusions

This study has successfully demonstrated the utility of hydrochemical and stable isotopic tracers to determine the possible hydraulic connection between surface and groundwater reservoirs. The study finds that there is no obvious hydraulic connection that benefits the underlying aquifers through seepage from the Lake; the reverse situation whereby groundwater discharges into the Lake is more plausible, based on the stable isotopic data and the
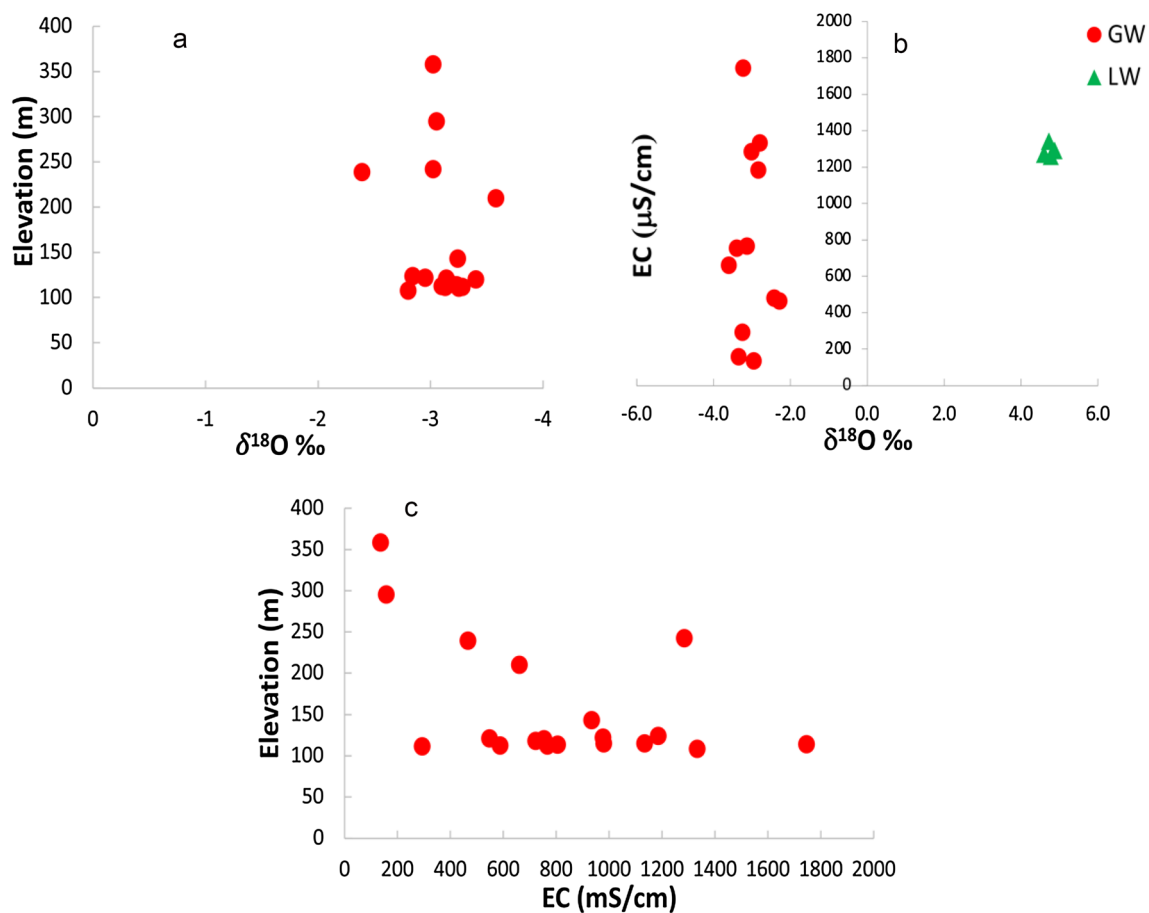
Fig. 8 Relationship between elevation and $\delta^{18}O$ for the groundwater (**a**), EC and $\delta^{18}O$ (**b**) and elevation and EC (**c**)

hydrochemistry. The data suggest that large volumes of evaporative losses of water from both the Lake and infiltrating rainwater in transit into the groundwater system. A conceptual framework inspired by the processed hydrochemical data suggests net groundwater discharge into the Lake. Evaporation rate of precipitation, which is thought to occur during infiltration prior to recharging the groundwater is estimated at 54–59.5%, whereas evaporation over the Lake Bosumtwi surface is ~ 90% based on $\delta^{18}O$ and δD analysis, resulting in increased levels of univalent cations in the groundwater system. The results also suggest that any hydraulic connection between the lake and groundwater may not be benefitting aquifers in the study area. The significantly high levels of evaporative losses of water from both the infiltrating groundwater system and surface water in the Lake may even be exacerbated by the predictions of regional and global climate models which indicate rising temperatures and evapotranspiration rates in the West African sub-region. Prudent management strategies are therefore recommended to safeguard water resources for sustainable development.

Data Availability Statement The data employed in this research would be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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