Hydrochemical and Stable Isotope Analyses Show Limited Interactions Between Groundwater and Lake Water in the Lake Bosomtwi Impact Crater, Ghana.

Yvonne Sena Akosua Loh

University of Ghana

Obed Fiifi Fynn (✉ obedfynn24@gmail.com)

WRI: Water Research Institute <https://orcid.org/0000-0001-9338-6536>

Evans Manu

GFZ German Research Center for Geoscience, Fluid Systems and Modeling, Telegrafenberg, 14473
Potsdam, Germany

George Yamoah Afrifa

University of Ghana

Millicent Obeng Addai

University of Education Winneba

Bismark Awinbire Akurugu

WRI: Water Research Institute

Sadow Mark Yidana

University of Ghana

Research Article

Keywords: Lake Bosumtwi, Stable Isotopes, Kinetic Fractionation, Surface Water, Groundwater, Ghana

Posted Date: January 11th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1093447/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

**HYDROCHEMICAL AND STABLE ISOTOPE ANALYSES SHOW LIMITED
INTERACTIONS BETWEEN GROUNDWATER AND LAKE WATER IN THE LAKE
BOSOMTWI IMPACT CRATER, GHANA.**

Yvonne Sena Akosua Loh ^a, Obed Fiifi Fynn ^{b,*}, Evans Manu ^{b,c,d}, George Yamoah Afrifa ^a,
Millicent Obeng Addai ^e, Bismark Awinbire Akurugu ^b, Sandow Mark Yidana ^a

^a *Department of Earth Science, University of Ghana, P. O. Box LG 58, Legon, Ghana*

^b *Council for Scientific and Industrial Research, Water Research Institute, P. O. Box AH 38, Accra, Ghana*

^c *Germany Research Centre for Geosciences, Potsdam, Germany*

^d *University of Potsdam, Potsdam, Germany*

^e *Department of Geography Education, University of Education, Winneba, Winneba, Ghana*

**Corresponding author's e-mail address: obedfynn24@gmail.com*

Acknowledgements

We are grateful to the Office of Research, Innovation and Development (ORID), the Department of Earth Science Capacity Building Project, University of Ghana and the University of Rochester, New York. We are also grateful to the Ghana Geological Survey Department for availing to us the accommodation facilities at Mmrontuo during the fieldwork. We are greatly indebted to Profs. Asish Basu and Carmala Garzzone and Dr. Penny Higgins, all of the Department of Earth and Environmental Science, University of Rochester, for allowing us to use their laboratories and helping with the analysis of the samples.

Abstract

The relationship between groundwater and surface water in the Lake Bosumtwi impact crater has been assessed using hydrochemical data and stable water isotopes of $\delta^{18}\text{O}$ and δD . This study aimed to define likely groundwater flow and recharge zones, estimate the rate of evaporation, and examine the relationship between the lake and groundwater in the study area. The results of Q-Mode hierarchical cluster analysis (HCA) clearly differentiate the lake water from the groundwater based on their spatial relationship. These preliminary results indicated that groundwater recharge occurs on the hilltops of the crater, where it is slightly acidic with low levels of dissolved minerals, characterized 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 stable water isotopes of $\delta^{18}\text{O}$ and δD showed a high evaporation rate on the lake surface, of ~90% with a relatively significant evaporative enrichment, whereas groundwater showed a relatively lower evaporation rate ranging between 54-60%. 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

1. Introduction

Stable isotopes of hydrogen and oxygen are influenced by meteorological processes that provide specific fingerprints as a basis for studying meteoric evolution of ordinary waters within the water cycle. The investigation of environmental isotopes of natural waters has proven in recent studies to be a relevant tool in the management and assessment of water resources. This enables deductions with regard to the recharge mechanism, identification of recharge and discharge areas, (Gopinath et al., 2021; Leketa and Abiye, 2021), aquifer interconnectivity and groundwater turnover time (IAEA, 1983; Chen et al., 2006; Doveri and Mussi, 2014) and to identify interactions between groundwater and surface water (Ojiambo et al., 2001; Zhang et al., 2016, Zhu et al., 2019; Leketa and Abiye, 2021).

These isotopes have equally been valuable in tracking the groundwater flow paths, evaluate residence time and aquifer discharge, identifying paleo waters, -- investigating water-rock interactions (Abid et al., 2010; Pu et al 2020; Zhang et al., 2020; Zhou et al., 2021; Carreira et al., 2021). For instance, Leketa and Abiye (2021) used stable isotopes of $\delta^{18}\text{O}$ and δD to show that recharge into the fractured quartzite aquifer of the Upper Crocodile River Basin occurs through direct mechanisms. Likewise, stable isotopes were used by Dogramaci et al. (2012), to evaluate the groundwater recharge in dry and semi-arid areas where high-intensity rain is supposed to control recharge. Sukhija et al. (2006) in their attempt to investigate recharge mechanisms in a fractured competent rock aquifer with different weathered zone thicknesses combined isotope and geochemical data and concluded that the groundwater route configuration is complex and involves multiple sources.

A combined application of multivariate statistical methods with graphical techniques for hydrogeochemical data interpretation (Guler et al., 2002; Helstrup et al., 2007; Yidana et al., 2012a; Loh et al., 2016; Dash & Kalamdhad, 2021) has been helpful for the description of

hydrochemical schemes and the delineation of groundwater flow paths. For instance, Yidana et al. (2012b) used hierarchical cluster analysis (HCA) in the Q-Mode to establish the spatial connection between groundwater hydrochemical datasets from the Ankobra Basin and led to the identification of three major spatial groundwater relationships based on the main of disparity in the hydrochemistry. In addition, Loh et al. (2012) used R-mode HCA of groundwater to identify the effects of both man-made and natural factors that control groundwater hydrochemistry. Using multivariate methods to understand the chemistry of groundwater, and specifically environmental isotopes, provides water managers and hydrogeologists with a powerful tool for solving water-related problems. This tool provides an understanding of geochemical routes and dynamics in hydrochemical groundwater studies.

Groundwater and surface water interactions play a critical role in the functioning of riparian ecology, and the occurrence of water quality problems in regional and sub-regional aquifers are well documented in recent times (Sophocleous, 2002; Di Ciacca, 2020; Kebede et al., 2021). In Ethiopia, Kebede et al. (2021) used stable isotopes of $\delta^{18}\text{O}$ and δD to identify water loss from the Awash River. For the sustainable management of river basins, it is crucial to understand and measure interaction processes between groundwater and surface water. The exchanges between surface water in Lake Bosumtwi and the underlying aquifers has become a matter of passionate concern in recent years and has necessitated this study. Moreso, the wells situated along the crater rim are in close proximity to the lake and could obtain recharge from the lake. To further develop our understanding of the recharged dynamics in the aquifers surrounding the Lake, this study attempts to distinguish the isotopic signature of groundwater and lake water, identify possible recharge zones and groundwater flow paths, and outline potential geochemical transformation trends.

In due course, the study will use hydrochemical and environmental isotope data of groundwater and surface water to understand a possible hydraulic association between the lake and the aquifer system near the former. The results of the study are expected to serve as a reference point and provide essential data and interpretations for understanding of groundwater recharge, flow path and hydrochemical dynamics occurring within the Bosumtwi Impact Crater (BIC) and its environs..

2. 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 climatic condition of the study area is akin to semi-equatorial climate and characterized by two rainy seasons; major and minor rainy seasons. The major rainy season begins in March, peaks in June and ends in July, whilst the minor season spans 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°C in March and 20°C in August, with relative humidity ranging between 70 and 80 per cent (Turner et al., 1996 a). Details of the hydrological characteristics of the area are copiously discussed by other researchers (e.g., Turner et al., 1996; 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 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 early Proterozoic age, which are the Birimian Sedimentary Basins and Birimian Volcanic Belts (Kesse, 1985; Karikari et al., 2007) (**Fig. 1**). Extensive studies by various workers 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; Fougere et al., 2017; Kazapoe & Arhin, 2021). These studies showed that the Eburnean tectonothermal event, which stabilized 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 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 highs 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).

The hydrogeology of the study area is characterized by the Birimian Province. Here the hydrogeology is controlled by secondary porosity and permeability and 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 137m (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 regards 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. Average aquifer transmissivity value in this Province is 7.4 m²/d (Banoeng-Yakubo et al., 2011). Successful boreholes that have been drilled in this Province suggest there is an average borehole yield of 12.7m³/hr (Banoeng-Yakubo et al., 2010; Dapaah-Siakwan and Gyau-Boakye 2000).

3. Materials and Methods

Following conventional 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 sterilized polypropylene tubes. 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 (HNO₃) to pH less than 2 for cation analysis, and the other used for anion analysis. The $\delta^{18}\text{O}$ and δD isotopes concentrations 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 98280. In the field, the alkalinity (Alk) (as HCO₃⁻) 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 reanalyze samples that were over the required range (i.e., > 25 ppm of Na, K, and Sr; and > 100 ppm of Ca, Mg, and Si). Anions of chloride (Cl⁻), sulfate (SO₄²⁻), and nitrate (NO₃⁻), fluoride (F), nitrite (NO₂⁻), and phosphate (PO₄³⁻) were measured in milligram per liter (mg/l) using a Dionex DX 120 ion chromatograph (I.C).

168 Ten (10) rainfall samples collected in the months of April, May, June and July were analysed
169 for isotopes of $\delta^{18}\text{O}$ and δD . The Los Gatos Research Liquid Water Isotope Analyzer was used
170 to analyse these samples at the University of Rochester's Department of Earth and
171 Environmental Sciences. The findings were standardized (Coplen, 1994) on scales so that the
172 $\delta^{18}\text{O}$ and $\delta\text{DV-SMOW}$ values were 0.0‰ and 0.0‰, respectively, whereas the $\delta^{18}\text{O}$ and δD
173 values of SLAP were respectively -428‰ and -55.5‰. Unless otherwise stated, the 2-sigma
174 uncertainties for $\delta^{18}\text{O}$ and δD results were respectively 2.0‰ and 0.20‰. This suggests that
175 the result of isotopic analysis of the same sample would fall 95% of the time within the
176 uncertainty bounds if it were reanalysed.

177 Microsoft Excel and the statistical package for social sciences (SPSS) version 25.0 were
178 statistically used to conduct univariate, bivariate and multivariate analyses of the data sets
179 obtained. The multivariate statistical analyses were performed in order to constrain
180 relationships among multiple variables in the entire data set with emphasis on revealing
181 naturally, clusters/ groupings within the entire data, which on the contrary would not have been
182 noticed. In order to achieve optimal results from the statistical analysis, the normality of each
183 parameter was tested and those parameters which did not meet normality were transformed
184 accordingly. Log transformation was employed and then standardized to their respective z-
185 scores. In producing the spatial distribution maps, kriging was performed using different semi-
186 variogram models to determine the best model fit for the data set. Continuous adjustment was
187 made to the variogram parameters until all the criteria for an optimal model was arrived at. The
188 Gaussian model was the most accurate predictor for pH and EC data sets. The obtained
189 parameters ($C_0=0.00021$; $C_0+C=0.00654$; $A_0=0.03$; $r^2=0.786$; $\text{RSS}=1.056\text{E-}05$) from the
190 variogram model were then used to generate the spatial distribution maps of pH and EC in
191 ArcGIS version 10.7.

192 Following the model advanced by Craig and Gordon (1965) and applied by Yidana et al.,
 193 (2013), the surface evaporation rate from the Lake was estimated. This model determines the
 194 fraction of water lost to evaporation (f) (eqn 1).

$$195 \quad f = 1 - ((\delta_L - \delta^*)/(\delta_P - \delta^*))^{\frac{1}{m}}; \quad (1)$$

196 δ^* = local limiting isotopic signature, which is determined from equation 2:

$$197 \quad \delta^* = (h\delta_A + \varepsilon)/(h - \frac{\varepsilon}{1000}) \quad (2)$$

198 h = average relative humidity of the study area,

199 δ_A = ambient air vapour isotope signature and

200 ε = total isotope fractionation factor (Gat and Gonfiantini, 1981)

201 δ_P and δ_L represent the isotope signatures of the initial/source water for the lake and
 202 sampled lake water respectively while m , the index, is given by eqn. 3

$$203 \quad m = (h - \frac{\varepsilon}{1000})/(1 - h + \frac{\varepsilon_k}{1000}); \quad (3)$$

204 The isotopic kinetic fractionation factor, ε_k , is linked to the relative humidity between
 205 water (w) and water vapor (v) w.r.t $\delta^{18}\text{O}$ (eqn. 4) (Gonfiantini, 1986).

$$206 \quad \varepsilon_k^{18}\text{O}_{w-v} = 14.2(1 - h)\text{‰} \quad (4)$$

207 The $\varepsilon_k^{18}\text{O}_{w-v}$ value of 4.26‰ was estimated at a local humidity of 0.7 (Turner et al.,
 208 1996a) for the lake water.

209 ε provides the sum of both equilibrium and non-equilibrium (kinetic) fractionation
 210 factors in eqn. 5.

$$211 \quad \varepsilon = \varepsilon_{eq} + \varepsilon_k; \quad (5)$$

212 $\varepsilon_{eq} = 10^3 (1 - \alpha^{18} O_{w-v}^{-1})$ and $\alpha^{18} O_{w-v}$, which is temperature (T measured in Kelvin)
 213 dependent is expressed by eqn. 6 (Faure, 1998);

$$214 \quad 10^3 \ln \alpha^{18} O_{w-v} = \left(\frac{1.534 \cdot 10^6}{T^2} \right) - \left(\frac{3.206 \cdot 10^3}{T} \right) + 2.644 \quad (6)$$

215 For a mean annual T of 298.15K (25°C), ε_{eq} returned a value of 9.11‰. The overall
 216 enrichment under the prevailing conditions was $\varepsilon = \varepsilon_{eq} + = -13.37\text{‰}$. Peng et al.
 217 (2012) proposed that a relationship between δ_{IP} and δA presumes an isotopic
 218 equilibrium (eqn. 7).

$$219 \quad \delta A \cong \delta_{IP} - 10^3 (\alpha_{w-v} - 1) \quad (7)$$

220 **4. Results and Discussions**

221 *4.1 Major ion chemistry*

222 The summary statistics and distribution of hydrochemical parameters from the lake and
 223 groundwater (GW) are presented in **Fig. 2** and **Table 1**. The relative abundance of the major
 224 cations in the lake occur in the order $\text{Na} \gg \text{Mg} > \text{K} > \text{Ca}$, whilst in the groundwater, the cations
 225 occur as $\text{Ca} \geq \text{Mg} \approx \text{Na} \gg \text{K}$. The anions on the other hand occur in the order; $\text{HCO}_3^- > \text{Cl}^- \approx$
 226 $\text{SO}_4^{2-} \gg \text{NO}_3^-$ for groundwater and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ for Lake water (**Fig. 3a**),
 227 suggesting the dominance of meteoric waters.

228 Hierarchical cluster analysis (HCA) performed on the hydrochemical parameters using Q-
 229 mode, to discriminate samples based on their spatial relations resulted in four clusters, based
 230 on a phenon line drawn at a linkage distance of 3 on the resultant dendrogram (**Fig. 4**). The
 231 clusters are ordered from left to right, with clusters 1 to 3 being groundwater, and showing an
 232 increasing trend in ionic enrichment, whereas cluster 4 is composed of lake water samples.
 233 Cluster 1 (C1) members, generally located in the SW on the top of the crater rim, in higher
 234 elevations (about 308 m above sea level), exhibit relatively lower ionic content (median EC =
 235 188 $\mu\text{S}/\text{cm}$), dominated by acidic waters (median pH = 5.6); characteristic of recharge zones
 236 in the evolutionary sequence of groundwater flow regimes (**Table 1; Figs. 5 a and b**). The low
 237 mineralization also suggests short residence time and rapidly recharged groundwaters.

238 The relatively acidic waters observed in C1 members may have resulted from recharge from
 239 CO_2 -charged rainwater, and the dissolution of CO_2 in the root zone as a result of plant and
 240 animal respiration (Hem, 1985; Hasan and Tewari, 2020). ‘Hard’ rock and associated silicate
 241 mineral dissolution is aided by acidic conditions as a result of low pH, which explains the
 242 relatively high levels of Si in C1 members as compared to the other clusters as observed in
 243 Table 1. These processes cause the incongruent dissolution of mainly plagioclase, biotite and
 244 potassium feldspar, which are common minerals identified in the underlying geology of the
 245 study area (Garrels and Mackenzie, 1967; Dedzo et al., 2017).

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

assertion that the high levels of Si in C1 members resulted from the aforementioned processes while CO₂-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 gradient towards relatively lower elevations in the NE. Cluster 2 (C2) members occur at elevations around 251 m asl, characterized by a high ionic (EC=μS/cm) 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, located in a much lower elevation (163 m asl) with average pH of about 6.72 (**Table 1 and Figs. 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, Ca²⁺ 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 decreases along the flow path as the groundwater evolves, in the order; C1 > C2 > C3, suggesting possible crystallization 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 recharge composition, (e.g., Guler et al., 2002; Loh et al., 2016; Loh et al., 2020) which have been identified to influence the chemistry of groundwater, collectively influence the diverse water types that change in time and space. The analyses and observations made corroborates 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 resident and contact time with the aquifer material along its flow paths.

4.2 *Stable Isotopes*

Fig. 6 presents summary results of stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) for rainwater (RW), lake water (LW) and groundwater (GW) from the study area. The results revealed that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values varied from -3.6 ‰ to -2.3 ‰ for $\delta^{18}\text{O}$, and -16.5 ‰ to -7.6 ‰ for $\delta^2\text{H}$ for the groundwater in the study area. Average $\delta^{18}\text{O}$ values for the RW, LW and GW in the area are -4.47 ‰, -3.06 ‰ and 4.74 ‰ respectively, whereas their respective average $\delta^2\text{H}$ 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 stable isotopes of ^{18}O and ^2H is expected to be evident in such water bodies in the study area. However, comparing the isotopic signatures of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for GW and LW to the precipitation in the study area, a progressive enrichment is observed in their isotope compositions, suggesting that the rainwater may have undergone some modification (Clark and Fritz, 1997).

A biplot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ 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; characterized 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 minimizes the evaporation rate and subsequent enrichment of rainfall events (Fig 7) (Clark and Fritz, 1997).

To aid the discussions and further understanding of the relative isotopic enrichment or depletion of the various water sources sampled in this study, the regression line established by Akiti (1987) for the Accra plains was adopted as the LMWL (equation 8) due to the lack of sufficient precipitation data. The LMWL as established by Akiti (1987) is comparable as a result of the proximity and similar geographic and climatic conditions of Accra Plains to this current study area. Although the intercept and slope of the regression lines may be different depending on the prevailing local weather conditions (Hoefs, 2009; Lachniet et al., 2021; Smith et al., 2021).

$$\delta^2H = 7.87\delta^{18}O + 13.6 \quad (8)$$

It can be observed in Fig. 7 that most of the samples from the rain and groundwater plot between the LMWL (Akiti, 1987) and the GMWL, except for the LW samples, which plot far below both MWLs. The level of departure of the samples from the MWLs reveals the degree of relative enrichment. Samples that have undergone slight/no enrichment plot on/very close to the MWLs, but where evaporative enrichment or mixing is significant, the samples depart

from the MWLs, and fall to the right of the regression lines, with a relatively larger intercept (Alley, 1993; Mazor, 1997). Hence GW samples that plotted close to the MWLs have not undergone any significant evaporation and subsequently little/no enrichment occurred. This is probably due to the fact that groundwater is generally protected from the impacts of high temperature and evaporation on the land surface. On the other hand, the lake, due to its exposure to the harsh weather conditions is prone to high evaporation rates and subsequently relatively high enrichment. This explains the departure of the lake 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 adopted by 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 δA estimation resulted in -12.40 ‰ for $\delta^{18}\text{O}$ using equation 7. The resultant ~90% evaporation rate for the lake surface estimated is in tandem with the harsh climatic conditions that characterize 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.

Equation 9 represents a regression line for GW in the study area, with a $r = 0.7$, indicating a strong correlation. The slope and intercept in the regression line (eqn. 9) suggests that the rainwater, prior to infiltration and recharge, may have undergone relative evaporative enrichment, especially when compared with the LMWL and GMWL. This is in sync with what has been reported in the literature about d-excess values of less than 10 ‰ (Dogramaci et al., 2012; Sreedevi et al., 2021). Based on Equation 9, the evaporation rate for the groundwater

was estimated to range from 54 – 59.5%, using -17.03 ‰ and -3.89 ‰ respectively as initial $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope contents. This suggests that evaporation is an active process in the unsaturated zone and possibly after recharge has occurred as observed in some studies in Ghana (Addai et al., 2016; Akurugu et al., 2020). About more than half of the rainfall that transits the soil zone is lost to evaporation, suggesting that groundwater recharge probably largely results from vertical infiltration through fractures, implying less water availability as groundwater in the study area. The estimated initial value of -3.89 ‰ for $\delta^{18}\text{O}$ is comparable to the average $\delta^{18}\text{O}$ values of -4.47 ‰, -3.20 ‰, -3.10 ‰ obtained for the rainwater, Akiti (1987) and groundwater in the study area, which are characteristic of recent meteoric waters. This corroborates the claim that the groundwater may have been recharged through fissures and fractures by recent evaporated meteoric water.

Furthermore, it is evident in Figure 8a that the groundwater EC shows a general 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., 2010).

$$\delta^2\text{H} = 5.49\delta^{18}\text{O} + 4.33 \quad (9)$$

Depletion gradients in stable water isotopes has been observed per 100 m rise in elevation, ranging from -1 to -4 ‰ for $\delta^2\text{H}$ and -0.15 to -0.6 ‰ for $\delta^{18}\text{O}$ (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 common in isotopic content with samples located around the crater rim; 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. 8b; suggesting no seepage of water from the lake and 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 of the groundwater increases as one moves towards the lake in lower elevations, suggesting the direction of groundwater flow is from the crater rim to 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 impacts, land/cover change, population growth and urbanization.

5. Conclusions

Stable water isotopes of $\delta^{18}\text{O}$ and δD as well as hydrochemical data from groundwater and lake water from the Bosumtwi impact crater have been assessed. Results from the Q-mode HCA of the hydrochemical data distinguished four main clusters based on their spatial relation; uniquely discriminating the lake water from the groundwater. The Q-mode HCA also identifies hill tops of the crater as recharge zones, and as the groundwater moves downhill, it becomes more mineralized, influenced by the host rocks, as it evolves and flows towards the lake. Vertical infiltration in the area is thought to occur rapidly through fractures, resulting in slightly evaporated recent meteoric waters recharging the groundwater. The stable water isotopes indicate that both groundwater and the lake water are considerably enriched relative to the local meteoric water, with the open lake water being even more so, due to its exposure to harsh weather conditions on the surface. Evaporation rate of groundwater, which is thought to occur during infiltration is estimated at 54-59.5%, whereas evaporation over the Lake Bosumtwi surface is ~90% based on $\delta^{18}\text{O}$ and δD analysis, resulting in increased levels of univalent

cations in the groundwater system. The preliminary results also suggest that any hydraulic connection between the lake and groundwater may not be benefitting aquifers in the study area. However, further studies are recommended to fully determine the extent of the hydraulic connection between these two reservoirs.

Acknowledgements

Funding: This work has been partly supported by ORID, through the Faculty Development Grant Award, the Department of Earth Science Capacity Building Project, University of Ghana and the University of Rochester, New York. We are also grateful to the Ghana Geological Survey Authority for availing their accommodation facilities at Mmrontuo during the fieldwork. We are greatly indebted to Profs. Asish Basu and Carmala Garzione and Dr. Penny Higgins, all of the Department of Earth and Environmental Science, University of Rochester, for allowing us to use their laboratories and helping with the analysis of the samples.

References

- Abass, G., Shiloh, O., Tetteh T, A., Dickson, A., Samuel Y, G., Edward PK, B. and Alhassan, H., 2010. Origin of dissolve ions in groundwaters in the northern Densu River Basin of Ghana using stable isotopes of ^{18}O and ^2H . *Journal of water resource and protection*, 2010.
- Abid, K., Zouari, K. and Abidi, B., 2010. Identification and characterisation of hydrogeological relays of continental intercalaire aquifer of southern Tunisia. *Carbonates and Evaporites*, 25(1), pp.65-75.
- Addai, M.O., Yidana, S.M., Chegbeleh, L., Adomako, D. and Banoeng-Yakubo, B., 2016. Groundwater recharge processes in the Nasia sub-catchment of the White Volta Basin: analysis of porewater characteristics in the unsaturated zone. *Journal of African Earth Sciences*, 22, pp. 4–14.
- Akiti, T.T., 1986. Environmental isotope study of ground water in crystalline rocks of the Accra plains (Ghana).
- Akurugu, B. A., Chegbeleh, L. P., and Yidana, S. M., 2020. Characterisation of groundwater flow and recharge in crystalline basement rocks in the Talensi district, Northern Ghana. *Journal of African Earth Sciences*, 161, pp. 103-665.
- Alley, W.M. ed., 1993. *Regional ground-water quality*. John Wiley & Sons.
- Amu-Mensah, F.K., Amu-Mensah, M.A., Akrong, M.O., Addico, G. and Darko, H., 2019. Hydrology of the major water sources of Lake Bosomtwe in Ghana. *West African Journal of Applied Ecology*, 27(1), pp 42-51.
- Appelo, C.A.J. and Postma, D., 2004. *Geochemistry, groundwater and pollution*. CRC press.

440 Banoeng-Yakubo, B., Yidana, S. M., Ajayi, J. O., Loh, Y., & Asiedu, D. (2010). Hydrogeology
 441 and groundwater resources of Ghana: a review of the hydrogeology and hydrochemistry
 442 of Ghana.

443 Carreira, P.M., Marques, J.M., Guerra, A., Nunes, D., Marques, J.E., Teixeira, J. and Chaminé,
 444 H.I., 2021. Caldelas and Gerês hydrothermal systems (NW Portugal): a comparative
 445 study based on geochemical and isotopic signatures. *Environmental Earth*
 446 *Sciences*, 80(3), pp.1-20.

447 Cartwright, I., Hall, S., Tweed, S. and Leblanc, M., 2009. Geochemical and isotopic constraints
 448 on the interaction between saline lakes and groundwater in southeast
 449 Australia. *Hydrogeology Journal*, 17(8), p.1991.

450 Chen, Z., Nie, Z., Zhang, G., Wan, L. and Shen, J., 2006. Environmental isotopic study on the
 451 recharge and residence time of groundwater in the Heihe River Basin, northwestern
 452 China. *Hydrogeology Journal*, 14(8), pp.1635-1651.

453 Clark, I.D. and Fritz, P., 1997. Environmental Isotopes in Hydrology Lewis Publishers. *Boca*
 454 *Raton, New York*.

455 Cochand, M., Christe, P., Ornstein, P. and Hunkeler, D., 2019. Groundwater storage in high
 456 alpine catchments and its contribution to streamflow. *Water Resources*
 457 *Research*, 55(4), pp.2613-2630.

458 Coplen, T.B., 1994. Reporting of stable hydrogen, carbon, and oxygen isotopic abundances
 459 (technical report). *Pure and applied chemistry*, 66(2), pp.273-276.

460 Dar, F.A., Jeelani, G., Perrin, J. and Ahmed, S., 2021. Groundwater recharge in semi-arid karst
 461 context using chloride and stable water isotopes. *Groundwater for Sustainable*
 462 *Development, 14*, p.100634.

463 Dash, S. and Kalamdhad, A.S., 2021. Hydrochemical dynamics of water quality for irrigation
 464 use and introducing a new water quality index incorporating multivariate
 465 statistics. *Environmental Earth Sciences, 80*(3), pp.1-21.

466 Dedzo, M.G., Tsozué, D., Mimba, M.E., Teddy, F., Nembungwe, R.M. and Linida, S., 2017.
 467 Importance of rocks and their weathering products on groundwater quality in Central-
 468 East Cameroon. *Hydrology, 4*(2), p.23.

469 Di Ciacca, A., 2020. Spatially distributed recharge and groundwater–surface water interactions
 470 in groundwater models: from the field to the catchment scale.

471 Dogramaci, S., Skrzypek, G., Dodson, W. and Grierson, P.F., 2012. Stable isotope and
 472 hydrochemical evolution of groundwater in the semi-arid Hamersley Basin of
 473 subtropical northwest Australia. *Journal of Hydrology, 475*, pp.281-293.

474 Doveri, M. and Mussi, M., 2014. Water isotopes as environmental tracers for conceptual
 475 understanding of groundwater flow: An application for fractured aquifer systems in the
 476 “Scansano-Magliano in Toscana” area (Southern Tuscany, Italy). *Water, 6*(8), pp.2255-
 477 2277.

478 Fougereuse, D., Micklethwaite, S., Ulrich, S., Miller, J., Godel, B., Adams, D.T. and McCuaig,
 479 T.C., 2017. Evidence for two stages of mineralization in West Africa’s largest gold
 480 deposit: Obuasi, Ghana. *Economic Geology, 112*(1), pp.3-22.

481 Freeze, R.A. and Cherry, J.A., 1979. Groundwater. New Jersey: Prentice-Hall geochemical
 482 parameter distribution in a ground water system contaminated with petroleum
 483 hydrocarbons. *Journal of Environmental Quality*, 30, pp.1548-1563.

484 Garrels, R.M. and Mackenzie, F.T., 1967. Origin of the chemical compositions of some springs
 485 and lakes.

486 Gat, J.R. and Gonfiantini, R., 1981. Stable isotope hydrology. Deuterium and oxygen-18 in the
 487 water cycle.

488 Gonfiantini, R., 1986. Environmental isotopes in lake studies. *Handbook of environmental*
 489 *isotope geochemistry*, 2, pp.113-168.

490 Gonfiantini, R., Wassenaar, L.I., Araguas-Araguas, L. and Aggarwal, P.K., 2018. A unified
 491 Craig-Gordon isotope model of stable hydrogen and oxygen isotope fractionation
 492 during fresh or saltwater evaporation. *Geochimica et Cosmochimica Acta*, 235, pp.224-
 493 236.

494 Gopinath, G., Resmi, T.R., Pragath, M., Jesiya, N.P., Hameed, A.S. and Deshpande, R.D.,
 495 2021. Isotopic differentiation of groundwater recharge processes in a semi-arid region
 496 of southern India. *Environmental Earth Sciences*, 80(16), pp.1-12.

497 Gosselin, D.C., Harvey, F.E. and Frost, C.D., 2001. Geochemical evolution of ground water in
 498 the Great Plains (Dakota) Aquifer of Nebraska: Implications for the management of a
 499 regional aquifer system. *Groundwater*, 39(1), pp.98-108.

500 Güler, C., Thyne, G.D., McCray, J.E. and Turner, K.A., 2002. Evaluation of graphical and
 501 multivariate statistical methods for classification of water chemistry
 502 data. *Hydrogeology journal*, 10(4), pp.455-474.

503 Hasan, Z. and Tewari, D.D., 2020. Characteristics of Groundwater Quality in the Aquifer of
504 Indo-Nepal Border of Balrampur City. *INTERNATIONAL JOURNAL OF PLANT AND*
505 *ENVIRONMENT*, 6(02), pp.146-151.

506 Helstrup, T., Jørgensen, N.O. and Banoeng-Yakubo, B., 2007. Investigation of hydrochemical
507 characteristics of groundwater from the Cretaceous-Eocene limestone aquifer in
508 southern Ghana and southern Togo using hierarchical cluster analysis. *Hydrogeology*
509 *Journal*, 15(5), pp.977-989.

510 Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural waters. US
511 Geol. Survey Water Supply Paper 1473.

512 Hendry, M.J. and Schwartz, F.W., 1990. The chemical evolution of ground water in the Milk
513 River aquifer, Canada. *Groundwater*, 28(2), pp.253-261.

514 Herczeg, A.L., Simpson, H.J. and Mazor, E., 1993. Transport of soluble salts in a large semiarid
515 basin: River Murray, Australia. *Journal of Hydrology*, 144(1-4), pp.59-84.

516 Hirdes, W., Davis, D.W. and Eisenlohr, B.N., 1992. Reassessment of Proterozoic granitoid
517 ages in Ghana on the basis of U/Pb zircon and monazite dating. *Precambrian*
518 *Research*, 56(1-2), pp.89-96.

519 Hiscock, K.M., Dennis, P.F., Saynor, P.R. and Thomas, M.O., 1996. Hydrochemical and stable
520 isotope evidence for the extent and nature of the effective Chalk aquifer of north
521 Norfolk, UK. *Journal of Hydrology*, 180(1-4), pp.79-107.

522 Hoefs, J. and Hoefs, J., 2009. *Stable isotope geochemistry* (Vol. 285). Berlin: springer.

523 IAEA, 1983. *Guidebook on Nuclear Techniques in hydrology*. Vienna: IAEA, 91.

524 Jeon, S.W., Kang, J., Jung, H. and Lee, J., 2021. Review of Seawater Intrusion in Western
525 Coastal Regions of South Korea. *Water*, 13(6), p.761.

526 Jones, W.B., Bacon, M. and Hastings, D.A., 1981. The Lake Bosumtwi impact crater,
527 Ghana. *Geological Society of America Bulletin*, 92(6), pp.342-349.

528 Karikari, F., Ferriere, L., Koeberl, C., Reimold, W.U. and Mader, D., 2007. Petrography,
529 geochemistry, and alteration of country rocks from the Bosumtwi impact structure,
530 Ghana. *Meteoritics & Planetary Science*, 42(4-5), pp.513-540.

531 Kazapoe, R. and Arhin, E., 2021. Determination of local background and baseline values of
532 elements within the soils of the Birimian Terrain of the Wassa Area of Southwest
533 Ghana. *Geology, Ecology, and Landscapes*, 5(3), pp.199-208.

534 Kebede, S., Charles, K., Godfrey, S., MacDonald, A. and Taylor, R.G., 2021. Regional-scale
535 interactions between groundwater and surface water under changing aridity: evidence
536 from the River Awash Basin, Ethiopia. *Hydrological Sciences Journal*, 66(3), pp.450-
537 463.

538 Kesse, G.O., 1985. The mineral and rock resources of Ghana.

539 Kumar, S., Joshi, S.K., Pant, N., Singh, S., Chakravorty, B., Saini, R.K., Kumar, V., Singh, A.,
540 Ghosh, N.C., Mukherjee, A. and Rai, P., 2021. Hydrogeochemical evolution and
541 groundwater recharge processes in arsenic enriched area in central Gangetic plain,
542 India. *Applied Geochemistry*, 131, p.105044.

543 La Plante, E.C., Simonetti, D.A., Wang, J., Al-Turki, A., Chen, X., Jassby, D. and Sant, G.N.,
544 2021. Saline Water-Based Mineralization Pathway for Gigatonne-Scale CO2
545 Management. *ACS Sustainable Chemistry & Engineering*, 9(3), pp.1073-1089.

546 Lachniet, M.S., Moy, C.M., Riesselman, C., Stephen, H. and Lorrey, A.M., 2021. Climatic and
547 topographic control of the stable isotope values of rivers on the South Island of New
548 Zealand. *Paleoceanography and Paleoclimatology*, p.e2021PA004220.

549 Leketa, K. and Abiye, T., 2021. Using Environmental Tracers to Characterize Groundwater
550 Flow Mechanisms in the Fractured Crystalline and Karst Aquifers in Upper Crocodile
551 River Basin, Johannesburg, South Africa. *Hydrology*, 8(1), p.50.

552 Leube, A., Hirdes, W., Mauer, R. and Kesse, G.O., 1990. The early Proterozoic Birimian
553 Supergroup of Ghana and some aspects of its associated gold
554 mineralization. *Precambrian research*, 46(1-2), pp.139-165.

555 Loh, Y.S., Banoeng-Yakubo, B., Yidana, S.M., Asiedu, D., Akabzaa, T. and Jørgensen, N.O.,
556 2012. Hydrochemical characterisation of groundwater in parts of the Volta Basin,
557 Northern Ghana. *Ghana Mining Journal*, 13, pp.24-32.

558 Loh, Y.S.A., Akurugu, B.A., Manu, E. and Aliou, A.S., 2020. Assessment of groundwater
559 quality and the main controls on its hydrochemistry in some Voltaian and basement
560 aquifers, northern Ghana. *Groundwater for Sustainable Development*, 10, p.100296.

561 Loh, Y.S.A., Yidana, S.M., Banoeng-Yakubo, B., Sakyi, P.A., Addai, M.O. and Asiedu, D.K.,
562 2016. Determination of the mineral stability field of evolving groundwater in the Lake
563 Bosumtwi impact crater and surrounding areas. *Journal of African Earth Sciences*, 121,
564 pp.286-300.

565 Mazor, E., 1997. *Chemical and isotopic groundwater hydrology: the applied approach* (No.
566 Ed. 2). Marcel Dekker Inc..

567 Mirzavand, M., Ghasemieh, H., Sadatinejad, S.J. and Bagheri, R., 2020. An overview on
568 source, mechanism and investigation approaches in groundwater salinization
569 studies. *International Journal of Environmental Science and Technology*, 17(4),
570 pp.2463-2476.

571 Ojiambo, B.S., Poreda, R.J. and Lyons, W.B., 2001. Ground water/surface water interactions
572 in Lake Naivasha, Kenya, Using $\delta^{18}\text{O}$, δD , and $3\text{H}/3\text{He}$ age-
573 dating. *Groundwater*, 39(4), pp.526-533.

574 Panno, S.V., Hackley, K.C., Cartwright, K. and Liu, C.L., 1994. Hydrochemistry of the
575 Mahomet Bedrock Valley Aquifer, east-central Illinois: Indicators of recharge and
576 ground-water flow. *Groundwater*, 32(4), pp.591-604.

577 Pazand, K., Khosravi, D., Ghaderi, M.R. and Rezvanianzadeh, M.R., 2018. Identification of
578 the hydrogeochemical processes and assessment of groundwater in a semi-arid region
579 using major ion chemistry: A case study of Ardestan basin in Central
580 Iran. *Groundwater for Sustainable Development*, 6, pp.245-254.

581 Peng, T.R., Huang, C.C., Wang, C.H., Liu, T.K., Lu, W.C. and Chen, K.Y., 2012. Using
582 oxygen, hydrogen, and tritium isotopes to assess pond water's contribution to
583 groundwater and local precipitation in the pediment tableland areas of northwestern
584 Taiwan. *Journal of Hydrology*, 450, pp.105-116.

585 Pu, H., Song, W. and Wu, J., 2020. Using Soil Water Stable Isotopes to Investigate Soil Water
586 Movement in a Water Conservation Forest in Hani Terrace. *Water*, 12(12), p.3520.

587 Reimold, W.U., Brandt, D. and Koeberl, C., 1998. Detailed structural analysis of the rim of a
588 large, complex impact crater: Bosumtwi crater, Ghana. *Geology*, 26(6), pp.543-546.

589 Ren, X., Li, P., He, X., Su, F. and Elumalai, V., 2021. Hydrogeochemical processes affecting
590 groundwater chemistry in the central part of the Guanzhong Basin, China. *Archives of*
591 *Environmental Contamination and Toxicology*, 80(1), pp.74-91.

592 Smith, D.F., Saelens, E., Leslie, D.L. and Carey, A.E., 2021. Local meteoric water lines
593 describe extratropical precipitation. *Hydrological Processes*, 35(2), p.e14059.

594 Sophocleous, M., 2002. Interactions between groundwater and surface water: the state of the
595 science. *Hydrogeology journal*, 10(1), pp.52-67.

596 Sreedevi, P.D., Sreekanth, P.D. and Reddy, D.V., 2021. Deuterium Excess of Groundwater as
597 a Proxy for Recharge in an Evaporative Environment of a Granitic Aquifer, South
598 India. *Journal of the Geological Society of India*, 97(6), pp.649-655.

599 Stimson, J., Frape, S., Drimmie, R. and Rudolph, D., 2001. Isotopic and geochemical evidence
600 of regional-scale anisotropy and interconnectivity of an alluvial fan system,
601 Cochabamba Valley, Bolivia. *Applied geochemistry*, 16(9-10), pp.1097-1114.

602 Stuyfzand, P.J., 1999. Patterns in groundwater chemistry resulting from groundwater
603 flow. *Hydrogeology Journal*, 7(1), pp.15-27.

604 Sukhija, B.S., Reddy, D.V., Nagabhushanam, P., Bhattacharya, S.K., Jani, R.A. and Kumar,
605 D., 2006. Characterisation of recharge processes and groundwater flow mechanisms in
606 weathered-fractured granites of Hyderabad (India) using isotopes. *Hydrogeology*
607 *Journal*, 14(5), pp.663-674.

608 Turner, B.F., Gardner, L.R., Sharp, W.E. and Blood, E.R., 1996. The geochemistry of Lake
609 Bosumtwi, a hydrologically closed basin in the humid zone of tropical
610 Ghana. *Limnology and Oceanography*, 41(7), pp.1415-1424.

611 Yidana, S.M., 2013. The stable isotope characteristics of groundwater in the Voltaian Basin–
612 An evaluation of the role of meteoric recharge in the basin. *Journal of Hydrogeology*
613 *and Hydrol. Eng*, 2, p.2.

614 Yidana, S.M., Banoeng-Yakubo, B. and Sakyi, P.A., 2012a. Identifying key processes in the
615 hydrochemistry of a basin through the combined use of factor and regression
616 models. *Journal of earth system science*, 121(2), pp.491-507.

617 Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. and Samed, A.A., 2012b. A factor model to
618 explain the hydrochemistry and causes of fluoride enrichment in groundwater from the
619 middle Voltaian sedimentary aquifers in the northern region, Ghana.

620 Zhang, B., Song, X., Zhang, Y., Ma, Y., Tang, C., Yang, L. and Wang, Z.L., 2016. The
621 interaction between surface water and groundwater and its effect on water quality in the
622 Second Songhua River basin, northeast China. *Journal of Earth System*
623 *Science*, 125(7), pp.1495-1507.

624 Zhang, Q., Luo, Z., Lu, W., Harald, Z., Zhao, Y. and Tang, J., 2020. Using water isotopes and
625 hydrogeochemical evidences to characterize groundwater age and recharge rate in the
626 Zhangjiakou area, North China. *Journal of Geographical Sciences*, 30, pp.935-948.

627 Zhou, J., Liu, G., Meng, Y., Xia, C., Chen, K. and Chen, Y., 2021. Using stable isotopes as
628 tracer to investigate hydrological condition and estimate water residence time in a plain
629 region, Chengdu, China. *Scientific reports*, 11(1), pp.1-12.

630 Zhou, Y., Li, P., Xue, L., Dong, Z. and Li, D., 2020. Solute geochemistry and groundwater
631 quality for drinking and irrigation purposes: a case study in Xinle City, North
632 China. *Geochemistry*, 80(4), p.125609.

Zhu, M., Wang, S., Kong, X., Zheng, W., Feng, W., Zhang, X., Yuan, R., Song, X. and
Sprenger, M., 2019. Interaction of surface water and groundwater influenced by
groundwater over-extraction, waste water discharge and water transfer in Xiong'an
New Area, China. *Water*, 11(3), p.539.

STATEMENT AND DECLARATION

Funding: This work has been partly supported by the Office of Research, Innovation and
Development (ORID), through the Faculty Development Grant Award of the University of
Ghana, Ghana and the Rochester International Council Fellowship for Doctoral Thesis
Completion, University of Rochester, New York.

Competing 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.

AUTHOR CONTRIBUTIONS

Yvonne Sena Akosua Loh: Conceptualization, Methodology, Data curation, Writing–original
draft, Visualization, Funding acquisition. **Obed Fiifi Fynn:** Formal analysis, Investigation,
Visualization. **Bismark Awinbire Akurugu:** Methodology, Writing–review and editing.
George Yamoah Afrifa: Writing–review and editing, Investigation, Resources. **Millicent**
Obeng Addai: Investigation, Validation. **Evans Manu:** Writing–review and editing,
Investigation, Resources. **Sadow Mark Yidana:** Conceptualization, Writing–review and
editing, Supervision, Project administration, Funding acquisition.

Figures

Figure 1

Geological map of the study area showing sample points

Figure 2

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

Figure 3

a and b: Stiff diagrams for the mean concentration of the major ions in groundwater/ lake water and Schoeller diagram showing the arithmetic mean of the major ions in each cluster

Figure 4

Dendrogram generated from HCA of hydrochemical data from groundwater and lake water showing associations between the samples

Figure 5

a and b: Spatial distribution of EC (μS/cm) and pH (pH units) in relation to sample clusters

Figure 6

Box plot of the stable isotope contents of the analysed water samples

Figure 8

a, b and c: Relationship between EC and $\delta^{18}\text{O}$ for the groundwater and lake water, relationship between Elevation and $\delta^{18}\text{O}$ for the groundwater and relationship between Elevation and EC for the groundwater