Available online at www.elixirpublishers.com (Elixir International Journal)

Agriculture

Elixir Agriculture 39 (2011) 4888-4894

Stable isotopes of water as indicator of Groundwater-Volta Lake interactions in the southwestern margin of the Volta Lake, Ghana E. A. Kaka^{1,2}, T.T. Akiti² and V.K. Nartey^{2,3}

¹National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon-Accra, Ghana ²School of Nuclear and Allied Sciences, University of Ghana, P. O. Box AE 1, Legon-Accra, Ghana ³Department of Chemistry, University of Ghana, P. O. Box LG 58, Legon-Accra, Ghana.

ARTICLE INFO Article history: Received: 25 July 2011; Received in revised form: 22 September 2011; Accepted: 29 September 2011;

Keywords

Stable isotopes, Groundwater, Stream water, Infiltration, Volta Lake.

ABSTRACT

Stable isotopes of hydrogen (δ^2 H) and oxygen (δ^{18} O) in groundwater, streams and Volta Lake collected in southwestern margin of the Volta Lake were investigated. While the spatial distribution of δ^{18} O in groundwater (-3.61 to -2.17 ‰ vs VSMOW) showed that most of the heavy-isotope depleted samples were located in the higher portion of the study area (northeastern) on the Kwahu Plateau, more positive values (from -2.62 to -2.17‰ vs VSMOW) were found in areas in proximity of the Volta Lake. The isotope composition of streams (δ^{18} O) varied closely from -2.80 to -2.61‰ vs VSMOW with most depleted being the most forested stream. The Volta Lake showed relatively enriched and homogenous isotope composition (δ^{18} O between -0.66 and -0.43) reflecting high evaporation of the Lake. Stable isotope signature of the water samples point to meteoric origin of recharge to groundwater in the area also show possible intrusion of Volta Lake into the aquifers near the banks of the Volta Lake.

© 2011 Elixir All rights reserved.

Introduction

Major irrigation facilities in Ghana take their water directly from surface water bodies such as rivers, dams and dug outs. However, long spell of dry seasons cause drying up some of these resources and therefore are not available for yearlong farming. Consequently, there have been increasing demands for groundwater for use in irrigation of various crops besides domestic consumption in the Volta basin for example. In order to further the exploitation of groundwater for these uses, various studies have been conducted to understand the properties of aquifers in the basin. In most cases hydrochemical characterization of aquifers and assessment of groundwater quality were achieved as are conspicuous in works of Kortatsi et al. (2008), Yidana et al. (2008), Acheampong and Hess (1998). What did not receive much attention is the study of interrelationship between groundwater and the Volta Lake.

The Volta covers 70% of the total drainage systems in Ghana. The Volta Lake resulted from the construction of the Akosombo Dam on River Volta in 1965 chiefly to generate hydroelectricity.

Infiltration from rivers or other surface water bodies is critical component of recharge to many groundwaters particularly where heavy extraction occurs (Clark and Fritz, 1997). Isotopes have been recognized as useful tracers for such investigations, complementing physical hydrology, geophysics and geochemistry (Burnett et al., 2006; Povinec et al., 2006a; Swarzenski et al., 2006; Gattacceca et al., 2007).

Meteoric processes, for instance, modify the stable isotopic composition of water, and so the recharge waters in a particular environment will have a characteristic isotopic signature. This signature serves as a natural tracer for the area of groundwater recharge.

The isotopes of oxygen and hydrogen have found the widest application in hydrology studies.

These elements form part of the water molecule, which makes them ideal for tracing water movement. The evaporation of water from water bodies produces a water vapour that is depleted in the heavier isotopes (¹⁸O and ²H) relative to the remaining water. As regional or continental atmospheric circulation systems move the water vapour inland, and as the process of condensation and precipitation is repeated, rain becomes characterized by low concentrations of these isotopes (Saayman et al., 2003).

The plotting of the observed global oxygen and hydrogen isotope concentrations in precipitation produces a line known as the global meteoric water line. Values however differ for different parts of the world. Variation in the equation for the meteoric line at a specific location is a function of its climate, geographic location and the source region of the evaporation.

Water with an isotopic composition that falls on the meteoric water line is assumed to have originated from the atmosphere and to be unaffected by other isotopic processes. Deviations from the meteoric water line result from other isotopic processes. In most cases these processes affect the relationship between δ^2 H and δ^{18} O in such a unique way that the position of the data points can help to identify the process. Two of the more commonly observed processes are evaporation from open water bodies and isotopic exchange between minerals and groundwater in deep, basinal flow or geothermal systems (Domenico and Schwartz, 1990).

Stable environmental isotopes are measured as the ratio of the two most abundant isotopes of a given element. This is reported in delta (δ) notation as permil (∞) which represents the deviation from a standard. The following general equation is used to calculate the deviation of the isotope ratios from a standard:

 $\delta = \left(\frac{\text{R sample} - \text{R standard}}{\text{R sample}}\right) X \ 1000$ R standard





Here $R = {}^{18}O/{}^{16}O \text{ or } {}^{2}H/{}^{1}H \text{ (Craig, 1961)}$

The deuterium and oxygen⁻¹⁸ content of water are usually measured with respect to the VSMOW (Vienna Standard Mean Ocean Water) standard.

Pioneering work in Ghana on isotope hydrology can be attributed to Akiti (1980). Akiti (1980) applied environmental isotopes such as 2 H, 18 O, 3 H (tritium), and 14 C to study groundwater in the Upper Regions of Ghana, the foothills of the Accra Plains, and the Keta Basin. Pelig-Ba et al (1990), Kortatsi and Sekpe (1994), Acheampong and Hess (2000), Yidana (2008), Pelig-Ba (2009), Adomako et al (2010) also applied 2H and 18 O as natural tracers in groundwater and surface water studies in some parts of the country.

In this study, stable isotopes (deuterium (²H) and oxygen-18 (¹⁸O)) have been used in conjunction with physicochemical parameters to determine the source of recharge to groundwater in the Manya Krobo area and explore possible interaction between groundwater and Volta Lake water in the catchment. The Manya Krobo area was identified as suitable the kind of research that is envisaged for the following reasons: It is largely bounded by Lake Volta; there is considerable distribution of boreholes in the area; its close proximity to requisite laboratories in Accra (Ghana Atomic Energy commission); its close proximity to the Akosombo dam means that results would be relevant and applicable to managers at that facility.

The study area

Location

The study area is located in Upper Manya Krobo District of the Eastern Region under the Afram arm of the Volta Lake. It lies between latitude 6.10N and 6.30N and longitude 0.08W and 0.20W. The topography of the area can be generally described as undulating. The highest point in the area is over 660 meters above sea level located in the south-western part of Sekesua. The lowest area, which is located at the south-eastern part of the area, is about 50 meters above sea level. The average height of the land is about 452 meters above sea level. The north-eastern part of the area is generally low lying towards Akotue and Akateng at the bank of the Volta Lake.

The area is drained by several rivers such as the Afram, Ponpon, Dawado, Alabo, Asesewa, Kabo, Anyaboni, Fefedo, Pleyo, and Akohia. The rivers and their tributaries exhibit mainly the trellised pattern of flow. With the exception of the Afram, almost all these rivers are seasonal with most of them overflowing their banks during the rainy season and flow towards the Lake.

The Manya Krobo area lies within the semi-equatorial climate belt of Ghana. The area experiences two major seasons, namely wet and dry seasons. The rainy season exhibits double maxima: the main rainy season occurs between April and July, whilst the minor one falls between September and October of every year. June is usually the wettest month in the area. Mean annual rainfall ranges between 900mm and 1500mm. Average relative humidity during the wet and the dry seasons are between 70% to 80% and 55% to 60% respectively. The dry and warm seasons are experienced from November to March. Temperatures are generally high with averages ranging between 26° C and 32° C.

However, August is dry, but cold. The area falls under the influence of two winds: the wet southwest monsoon winds which blow across the area from the Atlantic Ocean between March and early November and the northeastern trade winds (Harmattans) from Sahara Desert blow between November and early March.

The area falls under the transitional forest zone of Ghana. Human activities, however, on the vegetation have resulted in scattered patches of secondary or broken forests.

Geology and hydrogeology

The area under study (Fig. 1) is underlain by rocks of the Voltaian Super-group and the Buem structural unit. The Voltaian Super Group is made up of Neo-proterozoic to Early Cambrian, lithologically diverse platform sediments. The Voltaian terrain consists of 1000 to 950 Ma old Kwawu-Morago Group at the base, followed by a hiatus of 300 Ma by Oti-Pendjari Group, which was deposited after 630 Ma, and the late Neoproterozoic to Early Cambrian Obosum Group at the top. Detailed geology of this area is contained in reports by Junner and Service (1936)Junner, Hirst (1946), Saunders, 1970 and Anani, 1999. Anani, 1999 identified Kwahu Sandstone Members and Anyaboni Sandstone Members as hydrostagraphic units in the study area. Borehole success rate in the area is about 56% and well depth ranges between 222.0 and 55.0 metres. Mean static water level in the area is 6.6m. The average borehole yield is 8.5m³/h (Dapaah-Siakwan and Gyau-Boakye, 2000). Aquifer transmissivity values in the area fall within the range of 0.18-197.7 m²/day with a mean of 21 m²/day (Yidana et al., 2008).

The Buem is formed by the rocks of Pan-African Dahomeayide orogenic belt which are highly deformed and metamorphosed. It is made of quartzose and minor feldspathic sandstone, locally quartzite, minor siltstone, shale, phyllite and limestone. Rocks of the Buem formation are largely inherently impervious, but fracturing and weathering create secondary permeability in them at some locations to form high yielding aquifers (Dapaah-Siakwan and Gyau-Boakye, 2000).



Figure 1. Generalized geological map of the West African Craton. Modified after Ako and Wellman (1985). Belts and basins in the Birimian are defined after Leube et al. (1990) as follows: A = Kibi–Winneba belt; B = Cape Coast Basin; C

= Ashanti belt; D = Kumasi Basin;

E = Sefwi belt; F = Sunyani basin; G = Bui belt; H = Maluwe Basin; I = Bole-Navrongo belt; J = Lawra belt.

Methodol ogy

A total of 33 water samples (25 groundwater, 3 streams and 5 locations along the Volta Lake) were collected across the catchment during the periods of September, 2009. The geographical location of all sampling sites was recorded using a hand-held global positioning system (GPS) (Fig. 2).

Field investigations

Alkalinity and physical parameters such as electrical conductivity (EC), total dissolved solids (TDS), temperature and pH of the samples were measured in the field using Hatch field titration kit and portable EC and pH meters. For groundwater samples, boreholes were purged until stable readings for the physical parameters were obtained.

Samples were subsequently filtered through 0.45 micron membranes and collected in acid-washed, well-rinsed polyethylene bottles. Filtered and acidified (1% v/v HNO3) samples were used for major cations, while filtered unacidified samples were used for anion analysis. Unfiltered water samples (surface water and groundwater) were collected in 30-ml glass bottles and tightly sealed for stable isotopes analysis.



Figure 2: Geological and sampling location map showing hydrostratigraphic units of Voltaian and Buem formations of the study area

Laboratory analyses

Chemical and isotopic analysis of the water samples was performed at the National Nuclear Research Institute, Ghana Atomic Energy Commission. Calcium and magnesium ions were analyzed using Varian AA240 Fast Sequential Atomic Absorption Spectrometer. Sodium and potasium ions were also measured using flame emission photometer (Sherwood model 420). The sulphate and nitrate ions were analyzed using a UV-Visible spectrophotometer (Shimadzu). The chloride ion concentrations in the water samples were determined by titration. Stable isotopes of oxygen and hydrogen were determined using isotope mass spectrometry.

An off-axis integrated cavity output spectroscopy (OA-ICOS) Los Gatos Research DT-100 Liquid-Water Isotope Analyser (Model 908-008-2000) was used to measure $\delta^2 H$ and $\delta^{18}O$ of the water samples (IAEA-TCS-35, 2009). The analytical reproducibility was $\pm 0.2\%$ and $\pm 1.0\%$ for the oxygen and deuterium, respectively.

Results and discussions

Hydrogeochemistry

The results and statistical summary of physicochemical parameters of groundwater are presented in Table 1.

The pH of the groundwater in the study area varies from 5.20 to 6.92 with mean and median values of 6.60 and 6.69. These could be described as moderately acidic waters. Thus, all the samples fall within the natural water pH range of 4.5-7.0 (Langmuir, 1997).

Redox potential (Eh) of the groundwater samples have ranges between -33.5 and 70.8mV. The sign of the potential is positive if the reaction is oxidizing and negative if it is reducing. About 84% of the samples have negative Eh potentials. A plot of Eh vs. pH (Fig. 3) for all the groundwater samples shows values concentrating near the lower limit of the diagram. This indicates the environment of the groundwater samples in the area is generally isolated from the atmosphere, thus, under reducing conditions.

The conductivity of water within a temperature range $25.3 - 29.4^{0}$ C had a range of 125.3 to 2970 μ S cm⁻¹ with mean and median values of 614.96 and 286.00 μ S cm⁻¹ respectively. But

within this range, only six boreholes had values above 1000 $\mu S~cm^{-1}.$

The total dissolved solids (TDS) in the groundwater vary from 53.7 to 1274.0 mg/L. The mean TDS is 261.7 mg/L. The lowest TDS occurs in borehole at Sekesua, which has the highest altitude of 342m in the study area. The highest value of 1274mg/L occurs in borehole at Oborpa West in the extreme southern section (Fig.2). Areas of low TDS correspond to recharge areas and normally referred to as young waters, whereas areas of high TDS are described as discharge areas and referred to as relatively old waters.



Figure 3: The Eh-Ph relationship of groundwater samples collected at study area.

On the basis of classification by Davis and Dewiest (1966) and Freeze and Cherry (1979) (ranges 0–1,000 mg/l as fresh, 1,000–10,000 mg/l as brackish, 10,000–100,000 mg/l as saline water and more than 100,000 mg/l as brine), groundwater samples in the study area are fresh and potable for drinking except that at Oborpa.

A plot of altitude versus conductivity (Fig. 4) shows that low conductivities are found at higher elevations and higher conductivities found at lower elevations near the bank of the lake. It follows that the low conductivities at high altitudes could be due to short residence time. High conductivity at low altitudes also means long residence time. This may also indicate that groundwater is recharged at higher altitude and flows towards the Lake hence more ions get dissolved at discharge area.



In terms of major dissolved constituent (Kaka, 2010), the studied waters are characterized by significant heterogeneity.

This is clearly evidenced by the Piper (1944) diagram (Fig. 5) which shows compositions ranging from Na-K-HCO₃-Cl, Na-HCO₃, to Na-Cl water types, reflecting different geochemical environments.



Figure 5: Piper diagram showing groundwater samples from Manya Krobo area

Isotope geochemistry

The results and statistical summary of stable isotopic composition of groundwater and surface water samples are presented in Tables 2 and 3 respectively.

Stable isotopic composition in Volta Lake

Values of $\delta 180$ for the Volta Lake waters in the Manya Krobo area falls between -0.66 to -0.43‰ vs. VSMOW with a mean value of -0.57‰ vs. VSMOW. The δ 2H for the lake waters at five different locations during this study range between -4.62 at Akrusu-saisi and -1.47‰ vs. VSMOW at Treboanya. The values are narrowly spread showing that the Volta lake water is homogeneous in the area. The isotopic compositions of the lake are relatively enriched and this can be attributed to the fact that the large opened lake might have been subject to high level of evaporation. However, the oxygen-18 content of the Volta Lake from Kasakope through Akrusu-Saisi-2, Akrusu-Saisi-1, Treboanya to Akateng did not show any trend of isotopic variation. The lake water at Kasakope (-0.66‰ vs. VSMOW) is relatively depleted. It is possible that the lake water at this point is mixing with waters from the Pleyo stream which might be depleted.

The most enriched lake water was recorded at Treboanya (-0.43‰ vs. VSMOW). It could be due to the fact that no stream of more depleted waters mixed with the lake at this point.

Stable isotopic composition in streams

The Ponpon, Sekesua and Dawado streams were sampled for stable isotope analysis. The δ^{18} O values were -2.8, -2.76 and -2.61‰ vs. VSMOW respectively while the respective $\delta^2 H$ were -11.83, -10.19, -9.82‰ vs. VSMOW. The values vary narrowly signifying similar source of water for the streams probably rain water. The Ponpon stream had the most depleted δ^{18} O composition perhaps because the stream was the most forested hence little evaporation of the stream water.

Stable isotopic composition in groundwater

The groundwaters in the study area have δ^{18} O in the ranges from -6.61 at Seseaman-Kperti to -2.17‰ vs. VSMOW at Oterkpolou and have $\delta^2 H$ in the ranges from -15.63 at Ban-Dawa to -7.92‰ vs. VSMOW at Akrusu-Saisi. The respective mean values of δ^{18} O and δ^{2} H are -2.91‰ vs. VSMOW and -11.18 vs. VSMOW. The relatively wide variation in isotopic composition may be due to variability in recharge events in the area or relationship between surface water and groundwater.

The $\delta 2H$ - $\delta 18O$ correlation of the water samples

Stable isotope compositions of both groundwater and surface water were plotted as shown in Figure 6.

Two meteoric water lines were inserted. These include that obtained by Craig (1961): $\delta 2H = 8\delta^{18}O + 10$, i.e, Global Meteoric Water Line

(GMWL);

And that obtained by Akiti (1980):

 $\delta 2H = 7.86\delta^{18}O + 13.6$, i.e., a Local Meteoric Water Line (LMWL).



Figure 6: A graph of delta deuterium against delta oxygen-18 of water samples

Akiti's work was in the Accra plains in the south-eastern part of Ghana and the Upper Regions of Ghana. Since the lower part of Manya Krobo area falls within the Accra plains, the local meteoric water line obtained in Akiti (1980) will be most appropriate for use in this study.

In Figure 6, majority of the groundwater samples cluster between global meteoric water line and Akiti's local meteoric water line. This indicates the meteoric origin of groundwater in the Manya Krobo area. However, plot of $\delta^2 H vs. \delta^{18} O$ shows that majority of the groundwater is located at the top of the Global Meteoric Water Line (GMWL). This reflects local climatic conditions.

The groundwater in ring IV (Figure 6) though close to the GMWL but more depleted with δ^{18} O content lower than -3.42‰ vs. VSMOW is located at Seseaman-Kperti. The sample seemed to correspond to a recharge by a more depleted rainfall event which entered the saturated zone very rapidly to escape evaporation.

The groundwater (ring III in Figure 6) at Apimsu-2 with isotopic values of δ^2 H and δ^{18} O as -3.42‰ vs VSMOW and -12.82‰ vs. VSMOW respectively would be the average of rainwater capable of recharging the groundwater. This value corresponds to the value obtained in the Accra plains by Akiti (1980). Those waters that plotted closer or on the LMW line are likely to be recharged directly from local rainfall with little evaporation.

The slope of the fitting line of groundwater data (the black line in Figure 6) given as:

 $\delta^2 H = 3.64 \delta^{18} O - 0.59 (r^2 = 0.62);$

is significantly lower than either the Local or Global Meteoric Water Lines. Such a low slope in the $\delta^2 H - \delta^{18} O$ relationship may be therefore due to evaporation as a result of isotopic fractionations before groundwater infiltration and its underground circulation.

About 40% of groundwater data plotted below the line (evaporation line) indicative of evaporative processes in the soil during infiltration.

Interaction between the Volta Lake and groundwater

Stable isotope results of water samples show that generally Volta lake water was more enriched than stream waters. The stream waters were also more enriched than groundwater. This is consistent with the fact that the lake is vast and was more exposed to evaporation than the forested streams and groundwater.

However, in this study, some groundwaters (ring II in Figure 6) were more enriched than the stream waters. These waters were around the intersection point of evaporation line and GMWL. Their isotopic compositions are closer to those of Volta Lake waters (ring I) and these are boreholes at Akotue, Treboanya, Akrusu-Saisi, Oterkpolu and Kasakope. Incidentally. these boreholes are between 50 to 200 metres away from the Volta Lake.

Two assumptions can be responsible for this observation. One, storm from the evaporating lake results into enriched rain events in the proximity of the lake and recharges aquifers at the bank of the Lake. Thus, there could be cycle of evaporationrainfall in the area. Two, enriched Volta lake water infiltrates into aquifers at the lakeshore and mixes with groundwater flowing towards the lake.

Validation of the first assumption requires that rain samples far and near the Volta Lake be sampled and its stable isotope composition be measured. However, this was not done due the limited time within which the research was carried out and also that there were no rains in the area at the time of sampling. The second assumption was further investigated by performing isotopic mass balance calculations. In this, the proportion of recharged water from the lake water is estimated using the formula

 $\delta^{18}O_{BH} = p \times \delta^{18}O_{VL} + (1-p) \times \delta^{18}O_{LG},$ with $\delta^{18}O_{BH}, \delta^{18}O_{VL}, \delta^{18}O_{LG}$ respectively being the composition of δ^{18} O in a borehole, Volta lake water and local groundwater. The $\delta^{18}O_{VL}$ is determined with the average value of -0.57‰ vs. VSMOW. After determining the stable isotope composition of groundwater in 25 boreholes distributed around the study area, the value of -2.91‰ vs. VSMOW for δ^{18} O were chosen for $\delta^{18}O_{LG}$ with standard deviation of 0.37‰ vs. VSMOW. The p is the proportion of the Volta Lake water in groundwater of a borehole.

The calculated proportion of the Volta Lake water in groundwater (Table 4) at Oterkpolu, Bormase Tenya-1, Kasakope, Akrusu-Saisi, Treboanya, and Akotue are 32, 28, 25, 18, 16 and 12% respectively.

The ¹⁸O mass balance calculations show that the Volta lake water could infiltrates into groundwater in proximity of the lake but the influx may not be the same along the lake. This is because the bank of the lake is bounded by varied geological formations that may not have the same permeability. It could also be that the aquifer has a stronger influence on the distribution of groundwater fluxes through the lakebed than the lake itself.

It was also noticed that most of the depleted groundwater (δ^{18} O between -3.03‰ and -3.61‰ vs. VSMOW) as depicted in Figure 6 was found on the upper Anyaboni formation. The groundwater here seems to have a short residence time. Groundwater at Kponyokope also at the bank of the lake, in contrast, has depleted oxygen-18 value of -3.22‰ vs. VSMOW. This arm of the lake is between two opposite hills which are 450 and 590m above mean sea level. The borehole is located at foot of one the hills (450m a.m.s.l). The bank of the lake here may be underlain by hard Buem volcanic rock that prevents infiltration of lake water into groundwater.

Elevation and δ^{18} O relationship

In order to investigate the effect of altitude on the isotopic composition of groundwater samples in the study area, a graph of elevation versus δ^{18} O was plotted (Figure 7).

It can be seen that groundwater in the Manya Krobo area groundwater is generally enriched in δ^{18} O with decreasing elevation. This confirms groundwater in the area is recharged at higher altitudes and discharge at lower altitudes.



Figure 7: A graph of elevation vs. δ^{18} O

The observation may be because at lower altitude surface runoff after rain may be slow and water is subjected to evaporation before recharging the aquifer. The higher grounds

are around Sekesua whereas the lower places are at areas along the Volta Lake in out-crops of Obosum and Oti beds. Conductivity vs. $\delta^{18}O$ covariance

In an attempt to delineate a relationship between specific conductance and stable isotope composition of groundwater in the catchment, a scatter diagram of conductivity vs. δ^{18} O was plotted (Figure 8). Generally, conductivity increases as δ^{18} O composition of groundwater narrowly varied. The figure indicates dissolution of minerals in the formations as a process leading to evolution of dissolved species in the groundwater samples.



Figure 8: A scatter diagram of conductivity against δ^{18} O Conclusion

Groundwater, stream water and Volta Lake water in the Manya Krobo area have been assessed for their physicochemical and isotopic compositions. Groundwater in the area is moderately acidic under reducing conditions while total dissolve solute (TDS) fell within potable water range. The Na-K-HCO3-Cl, Na-HCO₃ and Na-Cl water types have been delineated. The stable isotope (δ^{18} O and δ^{2} H) composition of the waters shows that the order of enrichment of the water samples is Volta Lake water>stream water>groundwater. The study has shown that groundwater was recharged predominantly from rainfall at higher elevations on the Kwahu Plateau. However, the recharging water might have undergone some evaporation in the atmosphere or in the soil zone before reaching the groundwater table.

Comparison of δ^{18} O and δ^{2} H of groundwater, stream water and Volta Lake water shows that infiltration of Volta Lake water is possible at the bank of the lake. But because the infiltration may not be intense, ambient groundwater is not clearly distinguished from dam recharged groundwater. Boreholes that probably received recharge from the Volta Lake were identified as groundwaters which are more enriched than stream waters.

Acknowledgements

The authors are very grateful to the National Nuclear Research Institute, Ghana Atomic Energy Commission and School of Nuclear and Allied Sciences in Accra for equipment and expertise support for making this work a success. We also thank Alfred Anim, Edward Bam, and Oware Kesse for their selfless support during the sampling campaign.

References

Acheampong, S.Y. (1996). Geochemical evolution of the shallow groundwater system in the southern Voltaian Sedimentary Basin of Ghana. Ph.D. Thesis, University of Nevada, Reno, USA.

Acheampong, S.Y., Hess, J.W. (1998). Hydrogeologic and hydrochemical framework of the shallow groundwater system in the southern Voltaian Sedimentary Basin, Ghana. Journal of Hydrogeology 6: 527–537.

Acheampong, S.Y., Hess, J.W. (2000). Origin of the shallow groundwater system in the southern Voltaian Sedimentary Basin of Ghana: an isotopic approach. Journal of Hydrology 233:37-53.

Adomako, D., Osae, S., Akiti, T.T., Faye, S., Maloszewski, P. (2010). Geochemical and isotopic studies of groundwater conditions in the Densu River Basin of Ghana. Environ Earth Sci. DOI 10.1007/s12665-010-0595-2

Akiti T. T. (1987). Environmental isotope study of groundwater in crystalline rocks of the Accra Plains, Ghana. Proceedings of the 4th Working Meeting, Isotopes in Nature, Leipzig, September 1986.

Akiti, T.T. (1980). Etude Geochemique et Isotope de quelque aquifers du Ghana. These Dr. Ing. Univ. de Paris.

Akiti, T.T. (1981). Groundwater in hard rocks. UNESCO African Regional Seminar, Arusha-Tanzania, September 1981.

Akiti, T.T. (1985). Environmental isotope study of the Groundwaters of the Island of Santiago, Cape Verde. IAEA, Vienna.

Ako, J.A., Wellman, P. (1985). The margin of the West African craton: the Voltaian Basin. J. Geol. Soc. London 142, 625–626.

Anani, C. (1999). Sandstone petrology and provenance of the Neoproterozoic Voltaian Group in the southeastern Voltaian Basin, Ghana. Sedimentary Geology 128: 83–98

Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdorfer, J.A., Oliveira, J., Ozyurt, N., Povinec, P.P., Privitera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M., Turner, J.V., (2006). Quantifying submarine groundwater discharge in the coastal zone via multiple methods. The Science of the Total Environment 367, 498–543.

Cahen, L., Snelling, N.J., Delhal, J., Vail, J.R. (1984). The Geochronology and Evolution of Africa. Clarendon Press, Oxford, pp. 363–37

Clark, I.D., Fritz P. (1997). Environmental Isotopes in hydrogeology (eds). pp 1-256. CRC, London.

Dapaah-Siakwan, S., Gyau-Boakye, P. (2008). Hydrogeologic framework and borehole yields in Ghana. Hydrogeology Journal 8:405–416.

Davis, S.N., De Wiest, R.G.M. (1966). Hydrogeology. New York. Willey, London, p 463.

Domenico, P. A., and Schwartz, F. W., (1990). Physical and Chemical Hydrogeology, John Wiley & Sons, New York.

Freeze, R.A., Cherry, J.A. (1979). Groundwater. Prentice-Hall, Englewood Cliffs

Gattacceca, J.C., Vallet-Coulomb, C., Mayer, A., Radakovitch, O., Conchetto, E., Sonzogni, C., Claude, C., Hamelin, B., 2007. Isotopic characterization of saline intrusion into the aquifers of a coastal zone: case study of the southern Venice Lagoon, Italy. In: Sanford, W., Langevin, C., Polemio, M., Povinec, P. (Eds.), A New Focus on Groundwater–Seawater Interactions, vol. 312. IAHS, Wallingford, pp. 212–218.

IAEA-TCS-35 (2009). Laser Spectroscopic Analysis of Liquid Water Samples for Stable Hydrogen and Oxygen Isotopes. IAEA, Vienna, ISSN 1018-5518.

Junner, N.R., Hirst, T. (1946). The geology and hydrogeology of the Volta Basin. Memoir 8, Gold Coast Geological Survey.

Junner, N.R., Service, H. (19360). Geological notes on Volta River District and Togoland under British mandate. Annual Report on the Geological Survey by the Director, 1935-1936. Kaka, E.A. (2010). Hydrogeoghemical and Isotopic study of groundwater along the Vollta Lake: Manya Krobo area, Ghana. M. Phil, University of Ghana, Legon, Ghana.

Kortatsi, B. K. (1994). Groundwater utilization in Ghana. Paper presented in the Proceedings of the Helsinki Conference, June 1994. In: Future Groundwater Resources at Risk. IAHS Publ. no. 222, 149

Kortatsi, B. K. and Sekpey N. K. (1994). Chemical and isotopic techniques for the origin of groundwater in the crystalline basement complex of the Upper Region of Ghana. Regional trends in Geolgy in African Geology. Proceedings of the 9th International Geological Conference, Accra, 2nd–7th November, 1992). Geological Society of Africa.

Kortatsi, B.K., Anku, Y. S. A., Anornu, G. K. (2008). Characterization and appraisal of facets influencing geochemistry of groundwater in the Kulpawn sub-basin of the White Volta Basin, Ghana. Environ Geol. DOI 10.1007/s00254-008-1638-9

Lis, G.,Wassanar, L.I., Hendry, M.J. (2008). High precision Laser Spectroscopy D/H and 18O/16O Measurements of Microliter Natural Water Samples. Anal.Chem. 80:287-293

Pelig-Ba K. B., Kortatsi B. K. and Edmunds W. M. (1990). Application of isotope techniques in Groundwater studies in the Upper Regions of Ghana. Paper presented at the Regional Seminar on Isotope in Hydrology for Developing Countries in Africa from 15th to 19th October 1990 in Vienna, Austria.

Pelig-Ba, K.B. (2009). Analysis of Stable Isotope Contents of Surface and Underground Water in Two Main Geological Formations in the Northern Region of Ghana. West African Journal of Applied Ecology, vol.15.

Povinec, P.P., Aggarwal, P.K., Aureli, A., Burnett, W.C., Kontar, E.A., Kulkarni, K.M., Moore, W.S., Rajar, R., Taniguchi, M., Comanducci, J.-F., Cusimano, G., Dulaiova, H., Gatto, H., Hauser, S., Levy-Palomo, I., Ozorovich, Y.R., Privitera, A.M.G., Schiavo, M.A. (2006a). Characterization of submarine groundwater discharge offshore south-eastern Sicily– SGD Collaboration. Journal of Environmental Radioactivity 89, 81–101.

Saayman, I. C. D. Scott, F. Prinsloo, F. W. Moses, G. Weaver, J. M. C. and Talma, S. (2003). Evaluation of the application of natural isotopes in the identification of the dominant streamflow generation mechanisms in TMG catchments, CSIR, Environmentek, South Africa, WRC Report No.1234/1/03

Schiavo, M.A., Hauser, S., Povinec, P.P. (2009). Stable isotopes of water as a tool to study groundwater–seawater interactions in coastal south-eastern Sicily. Journal of Hydrology 364:40-49.

Sophocleous, M. (2002). Interactions between groundwater and surface water: the state of the science. Hydrogeology Journal 10:52-67.

Swarzenski, P.W., Burnett, W.C., Weinstein, Y., Greenwood, W.J., Herut, B., Peterson, R., Dimova, N., 2006. Combined time-series resistivity and geochemical tracer techniques to examine submarine groundwater discharge at Dor Beach, Israel. Geophysical Research Letters 33, L24405. DOI: 10.1029/2006GL 028282.

Yidana, S.M. (2008). Groundwater resources management for productive uses in the Afram Plains area, Ghana. Doctoral Dissertation, Montclair State University, USA.

Sampling location	ling location Latitude Longitude Elevation $\delta^2 H$ $\delta^{18}O$			δ ¹⁸ Ο	
	(N)	(W)	(m)	(% vs VSMOW)	(‰ vs VSMOW)
Oborpa west	6.17335	0.08315	111	-13.44	-3.18
Bweyonye	6.18203	0.0901	127	-11.05	-2.79
Oterkpolou	6.2098	0.11727	103	-8.76	-2.17
Bormase Tenya-1	6.29656	0.16052	282	-10.66	-2.32
Bormase Tenya-2	6.29861	0.16526	280	-12.44	-2.91
Sekesua	6.31356	0.19294	342	-10.58	-2.67
Akatawia	6.28446	0.13022	221	-9.95	-2.78
Abetima	6.3086	0.10405	197	-11.27	-2.90
Ban Dawa	6.32149	0.08849	168	-15.63	-3.42
Kasakope	6.27331	0.05528	96	-8.64	-2.25
Kponyokope	6.26135	0.05772	102	-12.96	-3.22
Apimsu-1	6.30576	0.08399	169	-11.50	-3.15
Apimsu-2	6.30316	0.08376	168	-12.82	-3.42
Seseaman sisi	6.30815	0.08375	169	-12.13	-3.29
Seseaman kperti	6.44248	0.16867	304	-12.00	-3.61
Brepaw Kperti	6.41119	0.16361	280	-11.22	-3.11
Asesewa	6.38974	0.15041	312	-12.99	-3.05
Akrusu sisi	6.47227	0.08814	87	-7.92	-2.48
Aworworso	6.4465	0.10602	229	-11.62	-2.86
Seseaman north	6.45571	0.15261	285	-10.45	-3.14
Akotue	6.48901	0.11975	90	-9.72	-2.62
Treboanya	6.5119	0.10947	89	-8.75	-2.54
Akrusu Yiti-1	6.44729	0.12493	205	-10.49	-2.97
Akrusu Yiti-2	6.43666	0.13638	238	-11.42	-3.03
Mensa Dawa	6.31801	0.13154	207	-11.20	-2.94
Ponpon (stream)	6.18203	0.0901	94	-11.83	-2.8
Sekeswa (stream)	6.31013	0.1877	820	-10.19	-2.76
Dawado (stream)	6.32209	0.08849	167	-9.82	-2.61
Kasakope(Voltalake)	6.27249	0.05263	90	-2.89	-0.66
Akrusu sisi-1 (Volta lake)	6.47154	0.08238	86	-4.12	-0.59
Akrusu sisi-2 (Volta lake)	6.47276	0.08767	88	-4.62	-0.63
Akaken (Volta lake)	6.52243	0.15517	85	-3.18	-0.55
Treboanya (Volta lake)	6.5136	0.11112	82	-1.47	-0.43

Table 1: Stable isotope content of water samples in the Manya Krobo area

Table 2: Statistical summary of stable isotope results of water samples in the Manya Krobo area.

Permil(% vs. VSMOW)	Water	Ν	Min	Max	Mean	Median	Std. dev
	Groundwater	25	-3.61	-2.17	-2.91	-2.94	0.37
$\delta^{18}O$	Stream water	3	-2.80	-2.61	-2.72	-2.76	0.10
	Volta Lake	5	-0.66	-0.43	-0.57	-0.59	0.09
	Groundwater	25	-15.63	-7.92	-11.18	-11.22	1.73
$\delta^2 H$	Stream water	3	-11.83	-9.82	-10.61	-10.19	1.07
	Volta Lake	5	-4.62	-1.47	-3.26	-3.18	1.22

Table 3: Proportion	of Volta	lake water	in some bore	holes in the Manya	Krobo area

Sampling points	Distance from Volta Lake	Mean isot ope content	Proportion of Volta Lake (%)
Groundwater	-	-2.91	0
Volta Lake	0	-0.57	100
MK3	5	-2.17	32
MK4	500	-2.32	28
MK10	100	-2.25	25
MK18	10	-2.48	18
MK22	120	-2.54	16