Environ Monit Assess (2015) 187:264
DOI 10.1007/s10661-015-4498-2

# Tracing stable isotopes ($\delta^2$H and $\delta^{18}$O) from meteoric water to groundwater in the Densu River basin of Ghana

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Received: 15 July 2014 / Accepted: 1 April 2015


**Abstract** This study represents the first attempt to study soil water $\delta^{18}$O profiles in Ghana using a mechanical auger. In this paper, the characteristics of $\delta^{18}$O and $\delta^2$H in rain water, surface water, soil water and groundwater have been used to understand the transformation mechanism of rain water to groundwater. Rain waters were sampled in Koforidua and Accra. Surface water and groundwater were sampled from the Densu River and selected boreholes in the basin, respectively. Soil waters were taken from three typical sites, namely, Potroase (POT), Teacher Mante (TM) and Ayikai Doblo (AD) in the northern, middle and southern zone from 0.00- to 6-m depth. The soil water was extracted using vacuum distillation method. The distribution of the stable isotopes of rain water is influenced by rainfall amount with minimal temperature effect. In general, the soil water is of meteoric origin undergoing fractionation-controlled evaporation. In the middle zone, the soil water shows some evidence of recharge from enriched source. The three profiles show similar trend of enriched values in the upper depths with gradual depletions of $\delta^{18}$O with depth. The POT profile showed relatively more depleted values suggesting a fast infiltration. In all the three profiles, soil waters below 3 m were found to contribute to groundwater recharge with piston flow as the dominant mechanism. The study also revealed that there is a significant contribution of enrich source to the groundwater system leading to the dilution of the infiltrating water by the large aquifer.

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**Keywords** Stable isotope · Soil water movement · Infiltration · Groundwater recharge · Groundwater · Densu River basin

## Introduction

Groundwater plays an important role in the socio-economic development of many rural communities in Ghana. The study of groundwater systems requires data on hydrogeochemistry, piezometric and isotopic data. Groundwater studies in Ghana are mainly focused on water quality using hydrogeochemical and piezometric methods. However, due to large areal extent, complex hydrogeological conditions (multiple aquifers and flow systems) and scarce data, the use of these traditional methods for groundwater studies does not adequately provide deep understanding on groundwater recharge, circulation, flow mechanism, aquifer continuity, sources of ion in the water, etc. which are key issues for groundwater development and management. The use of

Published online: 17 April 2015

environmental isotopes of water ($^{18}O$ and $^{2}H$) in hydrological systems is gaining worldwide attention and proves to be a valuable tool in bridging the knowledge gap (Fontes 1980; IAEA 2001).

The stable isotopic composition of soil water has also been found useful in gaining insight about soil water fluxes (evaporation, transpiration and downward infiltration) (Li et al. 2007). Earlier studies on the effect of soil water evaporation on stable isotope ($^{2}H$ and $^{18}O$) from soil water profile of a saturated sand column in the laboratory were reported by Zimmermann et al. (1967). This study was followed by many unsaturated zone field studies by several authors (Barnes and Allison. 1983; Allison and Hughes 1983; Gazis and Feng 2004; Gehrels et al. 1998; Munnich et al. 1980; Song et al. 2009; Walker et al. 1988).

The mechanism of infiltration of rain water and subsequent downward percolation in the unsaturated zone are a complex process due the dependence on factors such as climatic conditions, soil conditions (texture, structure, moisture) and vegetation cover. Soil water movement mechanism has a significant effect on the distribution and cycle processes of water, salt and other nutrients (Song et al. 2009). The knowledge of water movement in the unsaturated zone is essential for deciding the process of rain water infiltration and recharging of groundwater and subsequent transformation of rain water to soil water to groundwater.

One of the simplest models to view the infiltration of water through the soil is the piston flow model. In this model, water from the more recent rainfall (newer water) pushes the older soil water to flow downward (Li et al. 2007; Zimmermann et al. 1967). Due to the differences in isotopic composition of each rainfall event, different isotopic profiles of the infiltrating water are observed. A number of several studies documenting tracer movement in the soil column have pointed to the existence of preferential flow, in which water is channelled through more permeable pathways through macropores. This can be caused by cracks (in dried soils), decayed plant roots, earthworm burrows, rocks, etc. (Komor and Emerson 1994; Van Ommen et al. 1989; Vincent et al. 2001). Additionally, fingered flow, in which wetting front instability gives rise to flow through "fingers" rather than uniformly through a porous medium, is a common phenomenon in coarser soils (Ritsema et al. 1997; Ritsema and Dekker 1998). Different flow mechanisms result in different isotopic profiles, particularly when successive rainfall events are isotopically distinct. Preferential flow allows newer rainwater to pass older water that remains in the soil matrix. In Piston flow, an isotopically distinct rainfall event results in an abrupt "isotopic front" within the soil. Consequently, identification of the infiltrating rain water, recharge depth to groundwater, mixing of water from different rainfall events and flow mechanism dominating a given soil profile are possible by measuring the isotopic composition of rain water, groundwater and soil water.

Groundwater studies using stable isotopes in Ghana date back to 1980s (Akiti 1986). Later studies on isotopes focused on origin of groundwater (Acheampong and Hess 2000), identification of sources of dissolved ions in groundwater (Gibrilla et al. 2010), groundwater recharge (Adomako et al. 2010a) and role of meteoric recharge in the voltain basin (Yidana 2013). One of the major limitations of previous studies of stable isotopes is the lack of the consideration of the effect of unsaturated zone on the infiltrating water. This study represents the first attempt in Ghana to trace stable isotope signal from rainwater to groundwater using rainwater, surface water, soil profile and groundwater stable isotopes of $^{18}O$ and $^{2}H$. The objective of the study, therefore, is to investigate rainfall infiltration process; soil water movement mechanism; and the relationship among rain water, soil water and groundwater in the study area.

## Study area

### Location

The Densu River basin (5° 30′–6° 20′ N; 0° 10′–0° 35′ W) is a coastal river catchment located in the south-eastern part of Ghana (Fig. 1). The basin has an area of 2564 km$^2$, spans ten district assemblies and lies within three regions of Ghana (Eastern, Greater Accra and Central regions). There are about 200 settlements in the basin with a population density ranging from 150 to 200 per square kilometre, which is above the national average of 77 persons per square kilometre (Ghana Statistical Service 2000).

### Climate

The study area lies between two distinct climatic zones: the dry equatorial climate of the south-eastern coastal plains and the wet semi-equatorial climate further north

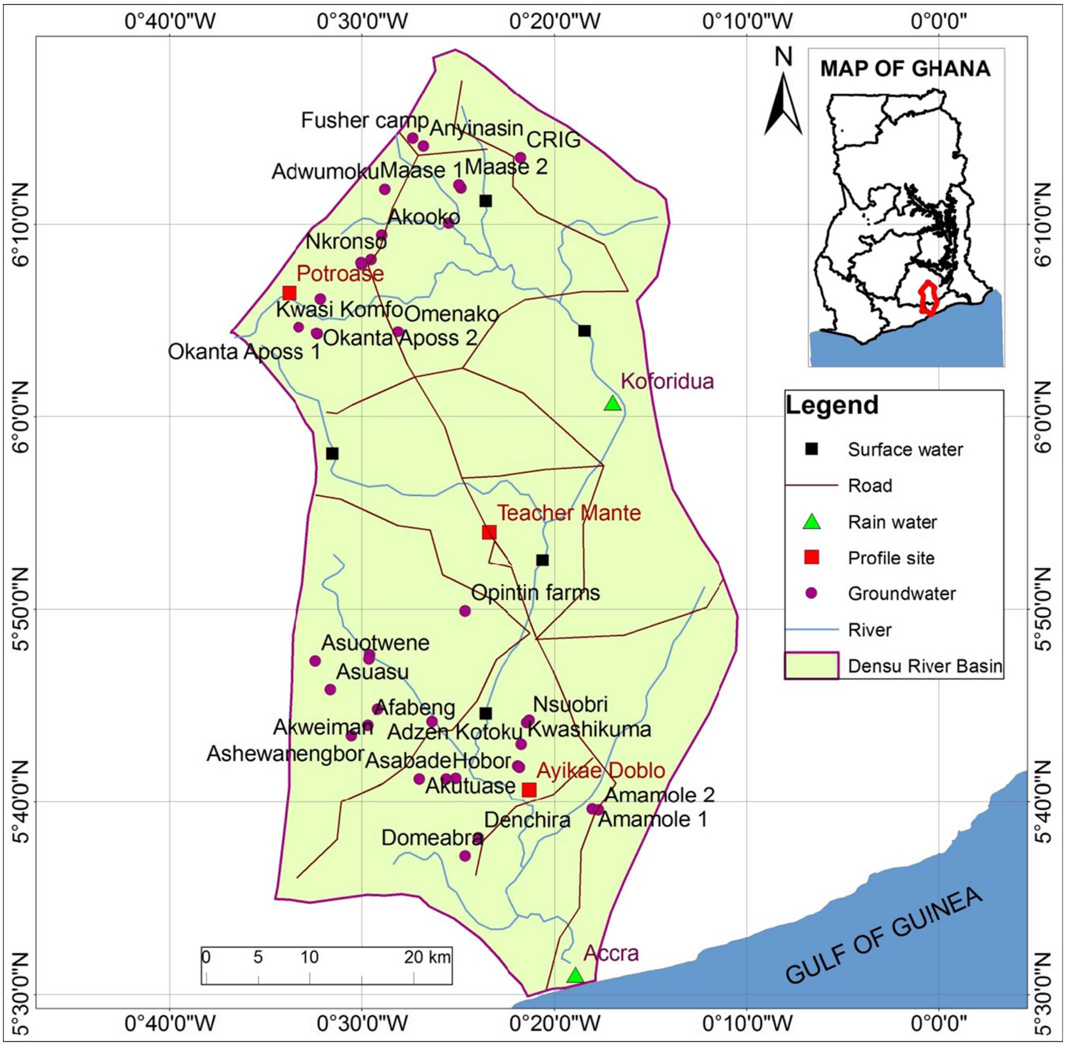



**Fig. 1** The Densu River basin, a coastal river catchment located in the south-eastern part of Ghana

from the coast. Both climatic zones are characterized by two rainfall seasons with different intensities (Dickson and Benneh 1998). April/May to July marks the period of the major rainy season which attains a peak in June. The minor season occurs between September and November which is then followed by the dry season. The total annual rainfall ranges from 1700 mm in the wet interior to 800 mm in the dry equatorial zone near the coast.

The climate of the study area is usually characterized by high temperatures throughout the year. The mean annual temperature is about 28 °C, with March/April being the hottest month (32 °C) and August being the coldest month (23 °C). The maximum relative humidity values vary from 89 to 93 % and the minimum from 41 to 72 %. Maximum and minimum monthly temperatures, normal rainfall distributions and relative humidity are shown in Fig. 2.

## Geology, hydrogeology and groundwater occurrence

The Densu River basin spans through three geological formations, namely, Cape Coast granite complex, Birimian and the Togo series (Fig. 1). The Cape Coast granitoid is underlain by the Proterozoic basin-type granitoid batholiths which are associated with gneiss. This geological formation covers a large part of the basin (90 %) and is composed of quartz, muscovite, orthoclase and albite. The Birimian formation, which occurs at the watershed of the river in the north-west,

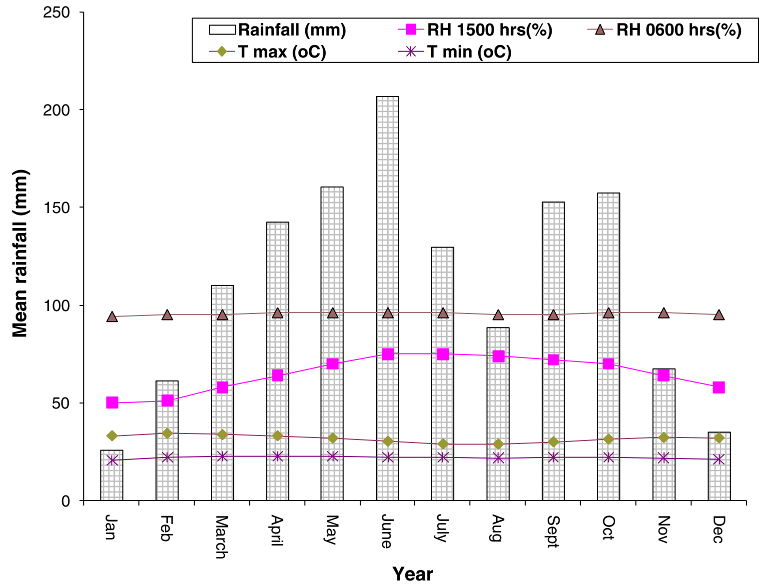



**Fig. 2** Distribution of rainfall, temperature and relative humidity in the study area

covers approximately 4 % of the basin. The Birimian Supergroup is subdivided into Lower and Upper Birimian (Junner 1935, 1940). The Lower Birimian consists of dacitic/rhyodacitic volcaniclastics, greywackes, phyllites, argillites and chemical sediments (Leube and Hirdes 1986). The Upper Birimian is mainly made up of tholeiitic basalts with intercalated volcaniclastics, pyroclastic lava and hypabyssal basic intrusions. Most of the rocks have metamorphosed into calcareous chlorite schists and amphibolites (greenstones). Rocks belonging to the Birimian formation are sandstones, tuffs, grit, quartzites and some breccia. The Togo Series occurs in the south-eastern part of the area and forms the estuary of the Densu River. It covers about 6 % of the catchment, and the rocks are highly folded and jointed and form the chain of hills known as the Akwapim–Togo Ranges, which extend from the coast near Accra to the Togo border. The Togo Series consists of sandstone, quartzite and quartz schist, shale, phyllite and some talc mica schist.

The basement rocks underlying about 90 % of the basin have very little intergranular pore space and are thus characterized by little or negligible primary porosity and permeability; hence, the major part of the groundwater flow occurs in secondarily formed structures, mostly fractures, joinings, shearings and deep weathering in the rocks (Banoeng-Yakubu 1989; Ganyaglo et al. 2006). The development of the secondary porosity gives rise to two distinct types of aquifers in the basin, i.e. the fractured zone aquifer and the weathered zone aquifers. The fractured zone aquifers develop in the bedrock at a depth of about 20 m or more. They tend to be localized in nature, and groundwater occurrences, yield and recharge are controlled by degree of fracturing (Buckley 1986). Transmissivity varies between 1 and 72 $m^2$/day. The weathered zone aquifer has thickness ranges from 4 to 20 m as a unit. They occur mainly in the forested area and vary greatly depending on the climatic conditions of the rocks (Seismos 1984). In most communities, the weathered zone aquifer is developed for water supply by hand-dug wells, but most of these wells dry up during the dry season (Acheampong and Hess 2000). A formation which combines the thick weathered zone with well-fractured bedrock provides the most productive aquifers. The granites in the basin are less fractured and weathered; hence, groundwater occurrence is moderately low. The granitic aquifers thus formed are usually phreatic to semi-confined in character, structurally dependent and often discontinuous in occurrence (Buckley 1986; Seismos 1984). However, in the northern portion of the granitic formation, relatively high-productive wells exist. The Birimian formation to the north-western portion of the basin is generally well folded and deeply weathered; hence, groundwater occurrence in this formation is very high. The Togo formation in the south-eastern portion of the basin is highly folded, jointed and fractured. The contact zone between the granites and the Togo formation provides a favourable condition for groundwater accumulation.

The thickness of the mean weathered zone ranges from 1.0 to 32.0 m, 5.0 to 27.0 m and 3.0 to 36.0 m in the granites, Birimian and Togo series, respectively. The depth of the borehole varies from 9.1 to 103.0 m in the granites, 23.0 to 40.0 m in the Birimian and 28.0 to 97.0 m in the Togo series (WRI 1994). Borehole yields are highly variable and lie in the range of 0.1–30.0 $m^3 h^{-1}$ with mean value of 2.0 $m^3 h^{-1}$ in the granite. In the Togo and the Birimian, borehole yields are within 0.6–6.0 and 0.7–9.0 $m^3 h^{-1}$ with the mean values of 2.8 and 3.7 $m^3 h^{-1}$, respectively (Seismos 1984). However, borehole yields vary from location to location and the chemistry of the groundwater also varies from well to well (Akiti 1986).

During the wet seasons, the water table generally gets higher supplying water to a number of shallow wells. This also permits the movement of fresh recharge water beyond the weathered zone into the fractured aquifer, particularly in places where there is hydraulic continuity between the weathered zone and the underlying fractures or fissures (Buckley 1986).

## Methodology

The three sampling sites selected represent the three main geological formations in the basin (Potroase–Birimian, Teacher Mante–Cape Coast granite and Ayikai Doblo–Togo series). These sites differ in altitude and vegetation (Fig. 1).

## Field work

A mechanical auger from the Ghana Geological Survey (GGS) was used for drilling soil profiles. The depths of the profiles at the sites Potroase, Teacher Mante and Ayikai Doblo were 500, 550 and 600 cm, respectively. Bulk samples were taken at a regular interval of 25 cm. About 500–1000 g of the bulk soil was collected in polyethylene bags, tightly sealed and later packed in an ice chest to prevent moisture loss due to evaporation. The texture was analyzed with a resolution of 1 m in all soil profiles using the hydrometer method according to the US Department of Agriculture soil classification. Gravimetric water content and bulk density were determined by drying 150 g of each soil sample in an oven at a temperature of 105 °C for 24 h (Blake and Hartge 1986). From these data, volumetric water contents and the total porosity were calculated.

Forty rainwater samples were collected from Koforidua on event basis (2006–2008) and seven (7) samples from Accra for isotope analysis. The rain water samples were collected in a 500-ml vial through a 200-mm-diameter funnel with a ping-pong ball to avoid evaporation. The rain water samples were then collected into 60-ml air-tight polyethylene vials soon after the rain event for the analysis.

A total of 51 groundwater samples were collected from the aquifers across the catchment from wells with depths ranging from 24 to 65 m. In addition, 15 surface waters (River Densu) were collected at intervals of 15 km from upstream to downstream. The geographical locations of all the sampling sites were recorded using a hand-held global positioning system (GPS).

## Laboratory analysis

### Method of soil extraction

The soil water was extracted from the bulk soil samples for stable isotope analysis as described by (Aragua's-Aragua's et al. (1995)). A vacuum extraction line consisting of three parallel units with cryogenic collection of the extracted soil water was used. At the beginning of each extraction run, the system was degassed, and a static vacuum was applied. Each soil sample of approximately 250 g was placed in a 1000-ml Pyrex round-bottomed flask and connected to a vacuum line. The samples were heated in a 70 °C water bath for 6 h. The temperature was maintained below 100 °C to reduce the risk of removing any loosely bound water (i.e. immobile water) in the clay lattice, which otherwise will introduce errors in the isotope composition of the extracted water (Aragua's-Aragua's et al. 1995). The water vapour was collected by a connected glass tube using liquid nitrogen traps. Subsequently, the nitrogen traps were taken off and the frozen water in the glass tubes turned into liquid water. The extracted water was then poured into 30-ml glass bottles and tightly sealed to prevent evaporation. Comparing the weight of the obtained water to the loss of weight of the soil samples confirmed the completion of the extraction and was taken as a reference to exclude evaporation loss during the procedure.

### Isotope analysis

Water isotopes $^{18}O$ and $^{2}H$ of the extracted soil water, groundwater, rain water and the surface water were determined using Thermo Finnegan Delta isotope mass spectrometry. The water samples for oxygen isotope analysis were prepared by conventional $H_2O$–$CO_2$ equilibration (Epstein and Mayeda 1953) where 5 ml of each sample was equilibrated with $CO_2$ gas at 25± 0.1 °C for 24 h. The $CO_2$ gas was then extracted and cryogenically purified in a vacuum line. For deuterium analysis, Cr at 850 °C was used to produce hydrogen gas (Coleman et al. 1982). Both $^{18}O$ and $^{2}H$ contents were determined relative to internal standards that were calibrated using Vienna Standard Mean Ocean Water (V-SMOW). The data were normalized and reported in the delta notation (Coplen 1988):

$$\delta = \left(\frac{R_S}{R_{\text{V-SMOW}}} - 1\right) * 1000$$

where $R_S$ represents either $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio of the sample and $R_{\text{V-SMOW}}$ is the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio of the V-SMOW. The analytical reproducible is ±0.1 ‰ for $\delta^{18}O$ and ±1.0‰ for $\delta^{2}H$. Deuterium excess (*d* in abbreviation) value was calculated as (Dansgaard 1964):

$$d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$$

## Results and discussion

The statistical summary of soil water content; total porosity; isotopic composition in rain water, soil water, groundwater and surface water; and *d* excess are shown in Table 1.

### Rain water and its isotopic composition

The majority of the rain water stable isotopes (40) were sampled at Koforidua covering a 2-year period (2007–2008) with few samples from Accra (7) from March to July 2007. The relationship between $\delta^{2}H$ and $\delta^{18}O$ based on the 47 samples of the rain water together with the weighted monthly averages is shown in Fig. 3. The rainfall monthly volume weighted was calculated using the equations

$$\partial^{18}O_{\text{sample}} = \frac{\sum_{i=\text{sample}}^{\text{month}} \partial^{18}O P_i}{\sum_{i=\text{sample}}^{\text{month}} P_i} \quad \text{and}$$

$$\partial^{2}H_{\text{sample}} = \frac{\sum_{i=\text{sample}}^{\text{month}} \partial^{2}H P_i}{\sum_{i=\text{sample}}^{\text{month}} P_i}$$

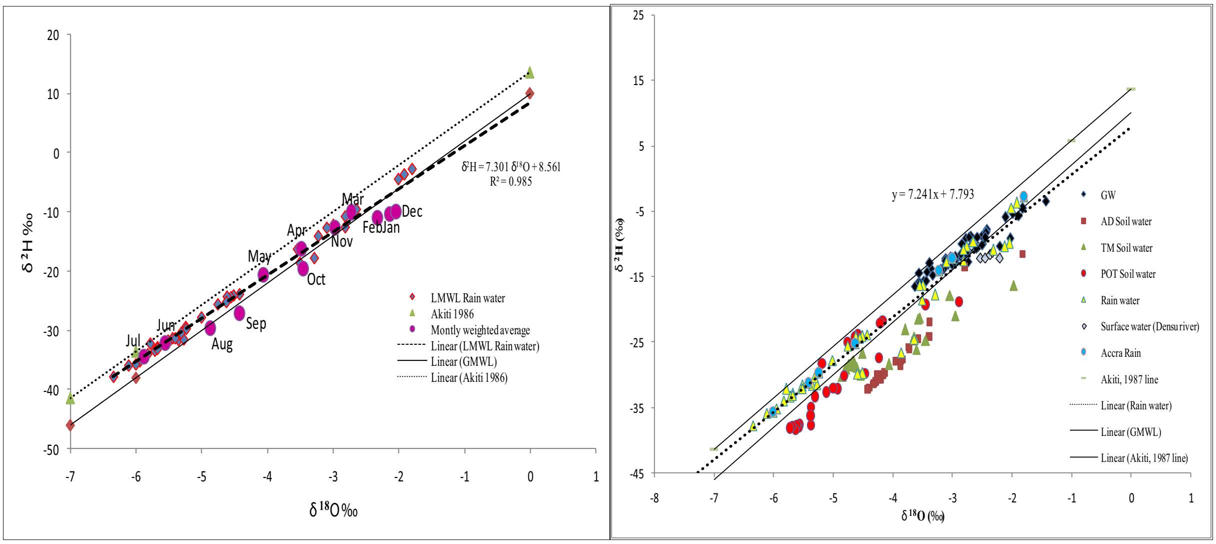
The $\delta^{18}O$ values of the rainfall in the Densu River basin ranged from −6.01 to −1.80‰ with a mean value of −4.25, and the $\delta^{2}H$ ranged from −35.70 to −2.80 with a mean value of −22.59. Based on the measured $\delta^{2}H$ and $\delta^{18}O$ in the 47 sets of rainfall, the data define a linear trend that represents the local meteoric water line (LMWL) for the Densu River basin.

$$\delta^2\text{H} = 7.30^{18}\text{O} + 8.56,\ R^2 = 0.985$$

The physical basis for this correlation lies in the fractionation of isotopes during evaporation–condensation process (Gourcy et al. 2005). The slope of 7.3 and

**Table 1** Statistical summary of the soil water content, total porosity, *d* excess and stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) in the three profiles

| Profiles | Soil water content ($cm^3\ cm^{-3}$) | | | Total porosity | | | $\delta^{18}O$‰ | | | $\delta^{2}H$‰ | | | *d* excess (‰) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean |
| Potroase | 0.22 | 0.38 | 0.36 | 0.39 | 0.41 | 0.4 | −5.72 | −2.89 | −4.89 | −38.2 | −18.9 | −30.6 | 4.22 | 13.22 | 8.55 |
| Teacher Mante | 0.11 | 0.38 | 0.25 | 0.34 | 0.41 | 0.34 | −4.85 | −1.98 | −4.11 | −30.2 | −16.3 | −26 | −0.46 | 9.48 | 6.95 |
| Ayikai Doblo | 0.10 | 0.40 | 0.25 | 0.34 | 0.41 | 0.35 | −4.42 | −1.83 | −3.88 | −32.3 | −11.5 | −27.5 | 2.34 | 8.72 | 3.58 |
| Groundwater | | | | | | | −3.63 | −1.43 | −2.82 | −16.46 | −3.48 | −11.24 | 7.01 | 14.08 | 11.35 |
| Rainwater | | | | | | | −6.35 | −1.92 | −4.33 | −37.80 | −3.70 | −23.75 | 4.28 | 14.12 | 10.91 |
| Surface water | | | | | | | −3.34 | −2.21 | −2.76 | −16.10 | −10.30 | −12.54 | 5.58 | 11.22 | 9.50 |




a b

**Fig. 3** (**a**) Relationship between $\delta^{18}O$ and δD isotopic composition of rain water, monthly weighted average and LMWL in the study area. (**b**) Relationship between $\delta^{18}O$ and δD isotopic composition of rain water, groundwater, soil water, surface water, GMWL and LMWL in the study area

intercept of 8.6 are both slightly below the global meteoric water line (GMWL) (Craig 1961). The LMWL is controlled by local climatic factors and may differ from the slope of 8 and intercept of 10 developed by Craig (1961). The GMWL is the representation of many LMWLs controlled by local climatic conditions such as origin of vapour mass, re-evaporation during rainfall and seasonality of precipitation (Clark and Fritz 1997). The lower slope of the LMWL indicated the occurrence of secondary evaporation which is more pronounced in the lighter rains.

Stable isotopes of rainfall are influenced by altitude, latitude, temperature and rainfall amount (Gat et al. 2001). Several authors have reported a correlation between isotopic fractionations that occurs during condensation and evaporation with temperature (Mazor 2004; Mook 2006). As a result, precipitation normally has higher isotopic values during warmer summers and lower values during cooler winters.

In the Densu River basin, the monthly weighted average samples exhibit these typical seasonal variations in isotopic composition. The most depleted sample was collected during 8 July 2008 with the lowest temperature ($\delta^{18}O=-6.01$, $\delta^2H=-35.3$, average temperature 25.1 °C), while the most enriched sample was taken in 8 March 2008 ($\delta^{18}O=-1.92$, $\delta^2H=-3.70$, average temperature 27.9 °C), the month with the highest temperature. The monthly surface temperatures ($T$) and $\delta^{18}O$ during the study period are described by the following least-squares fit linear regression

$$\delta^{18}O_{\text{weighted monthly mean}} = 0.85\ T_{\text{monthly}} - 26.41\ \left(R^2 = 0.37\right)$$

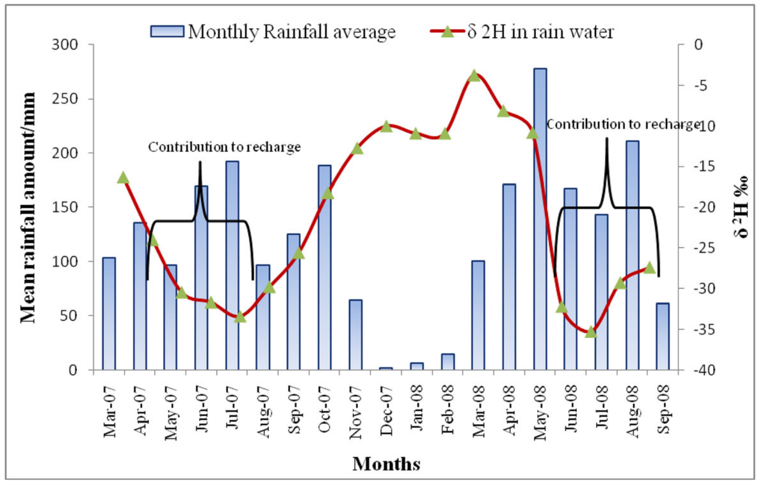
The variation pattern of isotope composition with the temperature gave a weak correlation; this could be due to narrow range in temperature (about ~2.8 °C) in the basin. The weak correlation of $\delta^{18}O$ and temperature suggests that temperature is not the only factor controlling the isotope fractionation. Studies by Fontes and Olivry 1976 also established weak relationship between temperature measured on the ground and the isotopic compositions of tropical rain.

For this reason, the relation between $\delta^{18}O$ and rainfall amount was also examined. In this case, there is a good correlation between average monthly rainfall (P) and $\delta^{18}O$ and described by the linear regression

$$\delta^{18}O_{\text{weighted monthly mean}} = -0.015\ P_{\text{monthly}} - 2.41\ \left(R^2 = 0.48\right)$$

Similarly, in Fig. 3a, the volume-weighted monthly averages show monthly variations with the lighter isotopes coinciding with the wetter months and the heavier isotopes coinciding with the drier months. Similar seasonal variation was also observed in the rainfall amount against $\delta^2H$ as shown in Fig. 4. From the plot, the lighter isotopic values are observed in May to September in both years. These months represent the period of heavy

Fig. 4 Seasonal variation of rainfall amount and $\delta^2$H in the study area




rainfall events, where the humidity is high in both years. This indicates that the amount effect is the dominant process controlling the isotopic composition of the rainfall in the area.

## Soil water content and total porosity

The soil water content, total porosity and stable isotope contents of the three profiles are summarized in Table 1 while Fig. 5a–c shows the distribution of water content, total porosity and lithology of the soil samples along the depths of the cores of the three sampling sites. Careful analysis of the data reveals that there is no significant difference between the mean total porosity of Teacher Mante and Ayikai Doblo. The two sites have the same value for the mean soil water content. However, the Potroase profile showed significantly higher values for both total porosity and soil water content as compared to the Teacher Mante and Ayikai Doblo. Teacher Mante (TM) and Ayikai Doblo (AD) are located in the same climatic zone; this explains why the distribution of the soil water along the cores of TM and AD has approximately the same pattern. However, between the depths of 1.5 to 3.75 m, the water content showed some degree of inconsistency; these observations are likely due to localized rainfall events or comparatively higher rainfall recharging the soil. Other factors, such as evaporation and root uptake, might also lead to the observed trend. The POT profile consistently showed higher water content throughout the profile as compared to TM and AD. The plotting of the POT profile on the right side of the TM and AD implies that the POT profile is receiving a

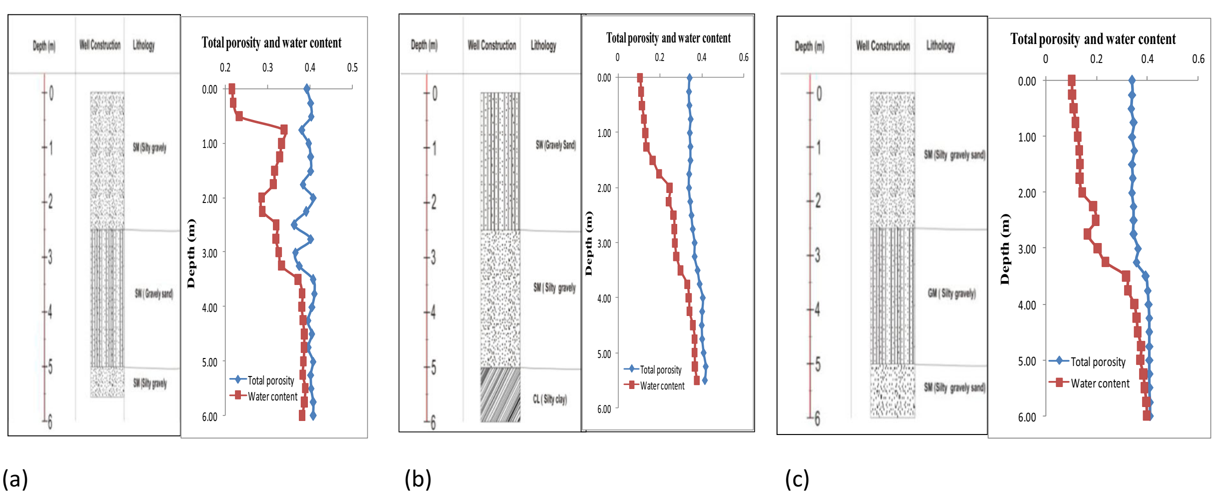



Fig. 5 Variation of depth with total porosity and water content along the profiles at **a** Potroase, **b** Teacher Mante and **c** Ayikai Doblo

higher amount of recharge and annual rainfall as compared to TM and AD profiles.

## Origin of the soil water using stable isotopes

Soil water is the link between precipitation and groundwater; hence, the dynamics of isotopic composition in soil water are indicative of the processes of precipitation infiltration, evaporation of soil water and recharge to groundwater (Li et al. 2007). The major source of soil water is precipitation. Other sources such as surface water and irrigated water can also contribute to soil water. The variation of stable isotopes of soil water is also influenced by evaporation, different rainfall events and root uptake/vegetative cover. The $\delta^{18}O$ and $\delta^{2}H$ of the soil water at POT site range from −5.72 to −2.89 and −38.2 to −18.9‰ with a mean value of −4.89 and −30.6 ‰, respectively. The $\delta^{18}O$ and $\delta^{2}H$ of soil water in the TM and AD profiles show similar characteristics. $\delta^{18}O$ ranges from −4.85 to −1.98‰ with a mean value of −4.11‰ while the $\delta^{2}H$ ranged from −30.2 to −16.3‰ with a mean value of −26.0‰ for TM. The AD $\delta^{18}O$ and $\delta^{2}H$ ranged from −4.42 to −1.83 and −32.3 to −11.5 ‰ with mean values of −3.88 and −27.5‰, respectively. By comparing the soil water isotopic composition and rain water isotopic composition on a $\delta^{2}H$ and $\delta^{18}O$ diagram in Fig. 3b, the trend of the isotope values of the soil profiles suggests that the soil water originated from rain water. The POT profile shows little effect of evaporation suggesting a fast movement of the water. However, the AD and TM profiles plot parallel to the GMWL suggesting some degree of evaporation. This deviation may be due to the fractionation controlled by evaporation during the infiltration or the contribution from an enriched source such as Densu River and its tributaries. Generally, the extent of deviation from the GMWL increases from POT in the north to AD in the south.

## Infiltration mechanism of the soil water

The vertical distributions of the $\delta^{18}O$ with lithology of the three profiles of the three sites are shown in (Fig. 6a–c) while Fig. 7 shows the comparison of the three profiles. The three profiles exhibited the following characteristics: (1) the isotope values decrease with depth, (2) the shallow depths (0 to 2.5 m) $\delta^{18}O$ varied widely with a prominent isotopic peaks at 2.75 m in all the sites, (3) the $\delta^{18}O$ values remain virtually constant beyond 3 m at TM and AD with POT decreasing

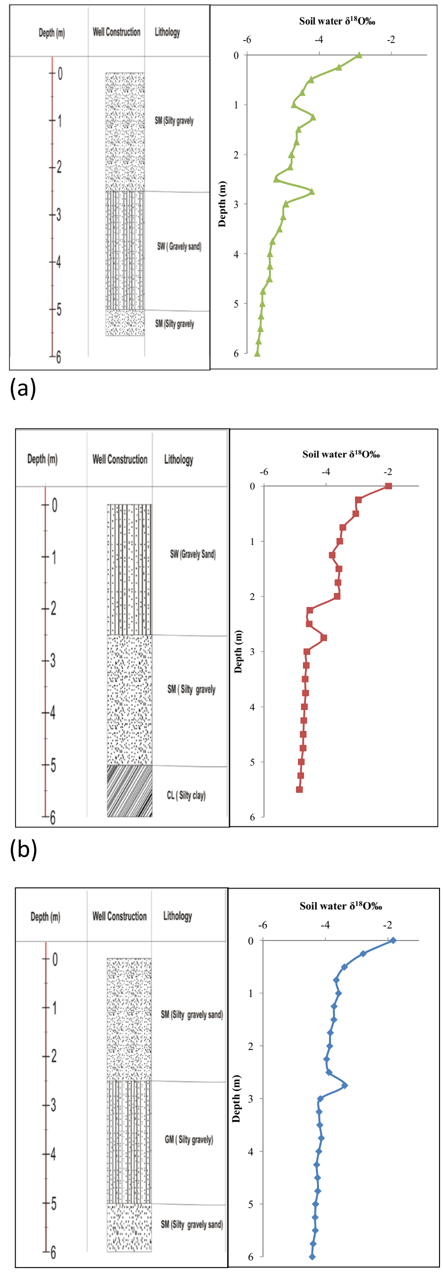



**Fig. 6** Variation of depth with $\delta^{18}O$ along the profiles at **a** Potroase, **b** Teacher Mante and **c** Ayikai Doblo

slightly, and (4) the POT profile showed a depleted $\delta^{18}O$ as compared to the TM and AD. These observations could be interpreted as follows: the process of rainwater infiltration was a uniform process controlled by the homogeneous nature of the soils at the sampling site. This can also be explained by groundwater fluctuation, upward fluxes due to evapotranspiration or

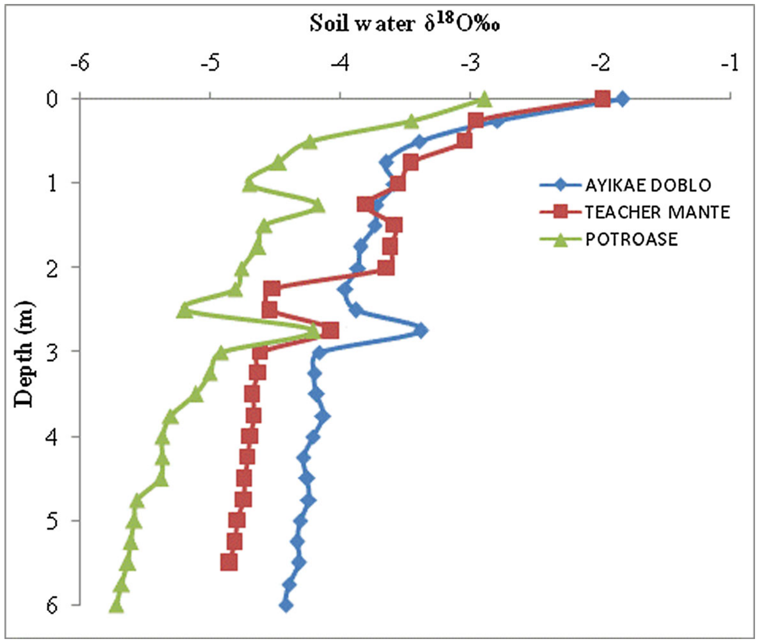



**Fig. 7** Vertical distributions of the $\delta^{18}O$ with depth in the three profiles of the study area

capillary rise where the deeper soil water with the lighter isotopic composition came from the accumulation of the preferentially risen depleted groundwater into the unsaturated zone.

The second observation suggests that the shallow depths (0 to 2.5 m) are the most affected by evaporation which led to the isotopic enrichment and subsequent anomaly. This soil water is likely to be lost, hence unlikely to contribute to groundwater recharge. This enrichment process may occur as a result of several processes such as evaporation, differences in isotopic composition of different rainfall events, mixing effect, evapotranspiration and preferential root uptake. In theory, the soil water isotope signal of every rainfall event recorded on the soil layer will not change until the soil layer accepted the 'new' water that had different isotopic composition (Zimmermann et al. 1967). Figure 7 shows that along the vertical profile, the change range of $^{18}O$ in the soil in the three sites becomes narrower and narrower with depth. While admitting the widely postulated view of evaporation being responsible for the upper soil enrichment, our results suggest that the mixing effect, evapotranspiration and preferential root uptake significantly contribute to the isotopic variation and enrichment.

The relatively constant $\delta^{18}O$ beyond 3 m supports the assumption that soil water reaching 3 m in the three sites can contribute to local groundwater recharge. This observation also leads to the inference that the groundwater recharge mechanism is by downward diffusion or piston flow, and in this case, the old water is push downward and replaced by the newer water.

Many researchers have demonstrated that vegetative cover of soil could have a dramatic effect on the soil physical environment near the soil surface, especially in the range of 0 to 4 m (Bristow and Horton 1996; Chung and Horton 1987). Under vegetative cover, due to the significant decline in net radiation, soil surface temperature decreases. Consequently, thick vegetative cover suppresses the soil water evaporation to a large extent compared to less vegetative or bare soil. Therefore, the difference in evaporation trend between POT and AD and TM with distinct vegetative cover could be explained by the influence of vegetative cover on the stable isotope composition from the top soil. The relatively depleted $^{18}O$ in the POT profile also suggests a recharge area with high infiltration rate.

## Comparison of $\delta^{18}O$ and $\delta^{2}H$ of rain water, soil water, groundwater and groundwater recharge process

The isotope compositions ($^{18}O$ and $^{2}H$) in rain water, surface water, soil water and groundwater at Potroase, TM and AD with the local meteoric water line (LMWL) and global meteoric water line (GMWL) are given in Fig. 3b. The rain water isotopic compositions from both sites (Accra and Koforidua) plotted close to the GMWL ($\delta^2H=8\delta^{18}O+10$; Clark and Fritz 1997). The soil water samples at POT define a regression line of $\delta^2H=8.351\delta^{18}O+10.27$, TM is $\delta^2H=4.821\delta^{18}O-6.125$, and AD is $\delta^2H=8.899\delta^{18}O+7.072$. Most of the samples in the three sites plotted below both the LMWL and GMWL. The differences in the regression indicate the differences in water isotope transport at these three sites. Generally, the ratios at the Potroase site were more depleted and have a slope 8.31 and intercept of 10.27 which is close to the GMWL. This suggests greater contribution of direct rainfall to replenishment compared to the other sites. The regression lines from the Potroase, TM and AD sites deviate slightly from the LMWL, which is attributed to enrichment due to evaporation. The slope of $\delta^2H$ and $\delta^{18}O$ relationship of TM is distinct and lower than that of POT and AD. Fonte (1980) postulated that a low slope for the $\delta^2H$ and $\delta^{18}O$ relationship reflected the mixing of waters from both above and below the evaporation front of infiltrating events with a subsequent effect of decreasing the slope of $\delta^2H-\delta^{18}O$. The TM falls within the extensive commercial agricultural zone in the basin, hence, greatly affected by mixing of rainfall and irrigation water leading to a wide variation in the stable isotopes. The trend in all the profiles suggests that the process of evaporation and infiltration occurs simultaneously at the shallow depth; however, as the soil water moves downward, the effect of evaporation decreases and soil water is replaced by new recharged and enriched water.

From Fig. 3b, the following observations can be deduced: (1) there is a gradual shift in stable isotopes from the GMWL from POT to TM to AD. (2) The groundwater showed relatively enriched values in stable isotopes as compared to the rain and soil water in the three profiles. (3) Some of the surface waters (River Densu) have similar isotopic characteristics as the groundwater. The above observations can be explained as follows: the gradual shift of the stable isotopes from POT to TM to AD suggests groundwater flow from POT to AD with POT being the recharge area. The second observation could lead to the following inferences: (1) the infiltrated rain undergoes mixing or dilution with a large aquifer, (2) there is a significant contribution of an enriched source (Densu River) to the groundwater, and (3) it could also be due to capillary rise, where there could be preferential rise of the depleted water to the unsaturated zone. The third observation signifies the possibility of surface water–groundwater interaction (Densu River groundwater). Figure 8 shows a simplified conceptual diagram of groundwater recharge processes in the basin. Despite the limited current understanding of recharge and unsaturated zone processes and limited data on seasonal stable isotope profiles in the basin, based on the preliminary data and the findings, we propose the tentative hypothesis that groundwater flow in the basin is topographically driven from north to south.

## Implication for groundwater recharge and utilization in the basin

Groundwater resources currently play an important role in providing sustainable drinking water sources in the basin and will continue to do so in the near future. Several climate models exist in literature predicting the

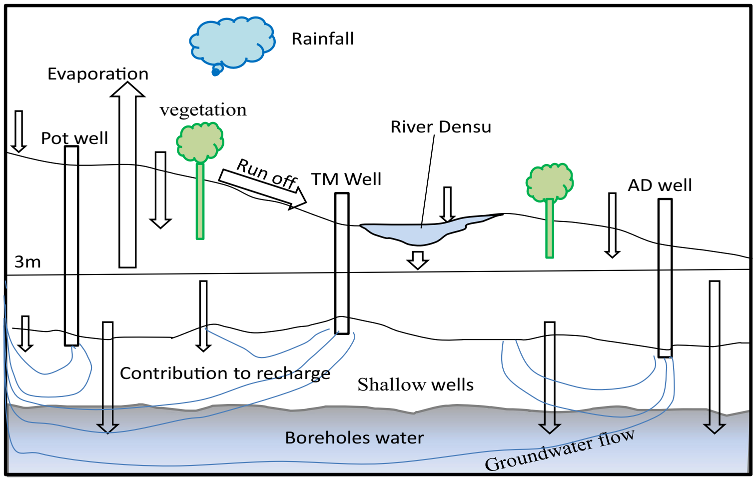



**Fig. 8** Conceptual diagram of the groundwater recharge processes and groundwater flow in the Densu River basin

impact of climate variability on groundwater. Despite the major uncertainties in these models, there is a general agreement that there will be an intensifications of past climate variability in the future (Parry et al. 2007). The groundwater utilization in the basin is mainly through the use of boreholes with hand pumps for domestic, industrial and agricultural purposes; however, several shallow groundwaters mainly by open hand-dug wells and hand-dug wells fitted with pumps exist. The generally unfractionated stable isotope values of the groundwater suggest rapid recharge mechanism probably dominated by diffuse recharge. Earlier studies by Adomako et al. (2010b) in the basin using tritium suggest a strong evidence of modern recharge in the basin.

The observed deviation from the GMWL by some of the groundwater could be likely due to focused recharge from the Densu River and other tributaries of the river while that of the soil water could be due several factors such as evaporation, urbanizations, vegetative cover, different rainfall events and some biological activities in the unsaturated zone. This could lead to water quality implications for the shallow hand-dug wells and the groundwater in the near future. This potential risk may include microbiological contaminations from poorly designed sewage systems. Pesticides and nitrates due to shift towards intensive crop production and improper domestic waste disposal (Lapworth et al. 2012).

There is also a growing evidence of more variability in rainfall and intense land use changes in the basin which could lead to periodic recharge coupled with high population density leading to increasing demand for groundwater for irrigation, therefore, further increase in the insecurity of the rural water supply (Anornu et al. 2012; Fianko et al. 2009).

## Deuterium excess

The deuterium excess (*d* excess) defined as *d* excess=$\delta^2H-8\delta^{18}O$, Dansgaard 1964 is the intercept of the GMWL. The *d* value is close to 10 for meteoric waters on the global scale. This is due to slower diffusion of $H_2{}^{18}O$ relative to $H_2{}^{16}O$ ($D(H_2{}^{18}O)/D(H_2{}^{16}O)=0.9691$) than $HD^{16}O$ relative to $H_2{}^{16}O$ ($D(HD^{16}O)/D(H_2{}^{16}O)=0.9839$) during evaporation occurring at the air–sea interface (Cappa et al. 2003). The mean *d* excess obtained for groundwater in the DRB during this study is 11.35‰ with a range from 7.01 to 14.08‰. The surface water and rain water *d* excess value had maximum values of 11.22 and 14.12‰ and minimum values of 5.58 and 4.28‰, respectively. The respective mean values are 9.50 and 10.91‰. The AD and TM soil water showed a relatively low *d* excess values ranging from 2.34 to 8.72 with mean values of 3.58 and −0.46 to 9.48 with mean value of 6.95, respectively. The POT soil water has *d* excess values ranging from 4.22 to 13.22 with mean value of 8.55‰. These values compare relatively well with the groundwater and the surface water. The wide variation in the rain water *d* excess value suggests a contribution of local isolated moist air masses resulting in uncharacteristic low *d* excess values.

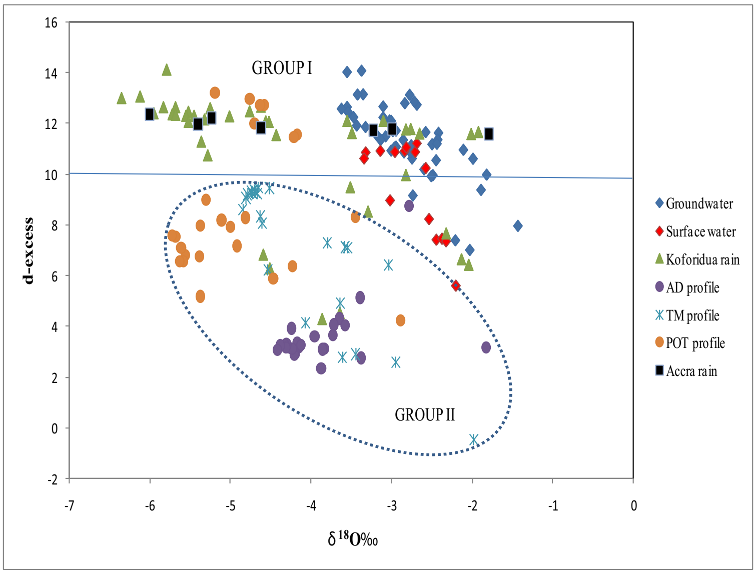



**Fig. 9** The relationship between $\delta^{18}O$ and *d* excess in the study area

Several studies have shown that *d* excess value of water vapour is a function of humidity, surface temperature, isotopic compositions of ambient water vapour and evaporating water (Al-Gamal 2011). Figure 9 shows the relationship between $\delta^{18}O$ and *d* excess. In this plot, two distinct groups were observed. Group I consists of high *d* excess values (>10‰) which are largely from the rain water, some groundwater, surface water and POT soil water. The association of group I with the rain water suggests their meteoric origin. Group II consists of low *d* excess values (<10‰) which includes soil water at AD and TM with few soil waters from POT, groundwater and the surface water. The low *d* excess values (all soil water at AD and TM and few soil water at POT, surface water and groundwater) suggest that there is significant evaporation of rainwater leaving the residual groundwater and soil water with lower values of *d* excess.

## Conclusion

The study gave an insight into the water movement in the unsaturated zone and the process of rain water infiltration and subsequent transformation of rain water to soil water to groundwater. The groundwaters in the study area are mainly meteoric recharged by soil water below 3 m with piston flow mechanism. The fact that the isotope contents are slightly decreasing with depth suggests that some of the pore water was exchanged with more depleted groundwater. This could be caused by capillary rise, groundwater table fluctuations, upward fluxes due to evapotranspiration or lateral water flow of more depleted water. The study also revealed that the groundwaters in the area are likely recharged from an enriched source leading to the dilution of the infiltrating soil water. This could lead to water quality degradation in the near future. However, since stable isotopes alone are not sufficient for a complete scientific understanding of the processes involved coupled with lack of conventional hydrologic data on the profiles, such processes remain unsolved as periodic and long-term monitoring of $\delta^{18}O$ depth profiles in Ghana is lacking. This study will, therefore, serve as a baseline study for future work in the country.

**Acknowledgments** The authors are very grateful to the Director of National Nuclear Research Institute, Ghana Atomic Energy Commission (GAEC) and International Atomic Energy Agency (IAEA) for making funds available for this work. We also thank all the Technicians of the Chemistry Department, GAEC, and Institute of Groundwater Ecology, Munich, Germany, for helping us during the sampling campaigns as well as the analysis. Finally, to our anonymous reviewers, we wish to thank you for making time to review our work and offering valuable suggestions.

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