



Use of stable isotopes (^2H and ^{18}O) to identify the source of dissolved ions in groundwaters in parts of the Ayensu basin in the central region, Ghana

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ABSTRACT

Stable isotopes of ^2H and ^{18}O and physico-chemical data of groundwater and surface water from parts of the Ayensu Basin have been used to assess the origin of groundwater and the possible source of salinity in the groundwater. The pH of groundwaters ranges from 5.53-7.21; the groundwaters are between mildly acidic and slightly alkaline. Chloride concentration of the boreholes ranges between 49.985-399.876mg/L. The conductivity of groundwater samples also varied between 382-2140 $\mu\text{S}/\text{cm}$ while their total dissolved solids (TDS) varied between 164.9-913mg/L. The isotopic compositions of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ of the groundwaters plotted along the local meteoric water line indicating that the groundwaters do not undergo significant evaporation before recharge. The plot of $\delta^{18}\text{O}$ versus chloride indicates that processes for the increasing salinity could be due to enrichment by evaporation and possibly dissolution of soil salts. The study has also shown that the aquifers could be discontinuous.

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Introduction

Stable isotopic composition of water is modified by meteoric processes, so the recharge waters in a particular environment will have a characteristic isotopic signature. This signature then serves as a natural tracer for the provenance of groundwater (Clark and Fritz, 1997). Stable hydrogen ($\delta^2\text{H}$) and oxygen isotope (primarily $\delta^{18}\text{O}$) ratios in water are ideal conservative tracers of water sources, because they are part of the water molecule (Fritz, 1983).

A wide variety of combinations between oxygen and hydrogen isotopes is possible but only three are of practical interest: $^1\text{H}_2^{16}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$, and $^1\text{H}_2^{18}\text{O}$ (Fritz, 1983); these three occur in nature in easily detectable concentrations.

Of special interest to hydrogeologists are the ratios of the main isotopes that comprise the water. It is analytically difficult to determine absolute isotope abundances but relative measurements based on the comparisons of the sample with a standard can be done easily and economically (Craig, 1957). The internationally accepted standard for reporting the hydrogen and oxygen isotopic ratios of water is Vienna Standard Mean Ocean Water, V-SMOW (Coplen, 1996) and results are expressed as parts per thousand (permil, ‰) difference from the reference (Fritz, 1983).

The isotope ratios are expressed in delta units (δ) differences relative to an arbitrary standard:

$$\delta\text{‰} = \left(\frac{R - R_{\text{std}}}{R_{\text{std}}} \right) * 1000$$

where R and Rstd are the isotope ratios of the sample and the standard respectively.

The process by which the isotope content of water changes as a result of evaporation, condensation, freezing, melting, chemical reactions or biological processes is known as isotope

fractionation. Evaporation of water results in isotope fractionation of hydrogen and oxygen such that ^{16}O and ^1H preferentially enter the vapour phase, while ^{18}O and ^2H are concentrated in the liquid phase (Freeze and Cherry, 1979).

The rate of evaporation at a given temperature is a function of the vapour pressure of H_2O , which is a function of the hydrogen bond strength between water molecules. Since an ^{18}O -H bond between molecules is stronger than a ^{16}O -H bond, the H_2^{18}O has a lower vapour pressure than H_2^{16}O . The greater vapour pressure or flux of H_2^{16}O leads to an enrichment of ^{16}O in the vapour phase. Conversely, heavier H_2^{18}O accumulates in the liquid phase. When the system has reached isotopic equilibrium, the greater vapour pressure of ^{16}O causes an overall enrichment in the vapour, and depletion for ^{18}O (Clark and Fritz, 1997).

A relationship of great importance compares the ^{18}O and ^2H values in precipitation. It has been found that on a global basis,

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$$

On an ^{18}O vs. ^2H plot this is a straight line which is called the Global Meteoric Water Line (GMWL). (Fritz, 1983)

For most of the communities along the Ayensu River serves as their main source of domestic water and for others it complements water from wells and/or boreholes. The main problems encountered in the area are a decrease of the surface water resource due to irregular rainfall patterns drying of boreholes and an increase in water salinity in the coastal area.

Authors such as Akiti, T.T. (1986), Banoeng-Yakubu, K.B. (2000), Gibrilla, A. et al (2010), and Acheampong, S.Y. (2000), Pelig-Ba, K.B. (2009), Kortatsi, B.K. (1992) and others have used environmental isotopes especially of ^2H and ^{18}O in groundwater as a complementary analytical tool to conventional

hydrological and hydrochemical assessment procedures in various parts of the country.

This paper makes use of stable isotopes (^2H and ^{18}O) to investigate the origin of the groundwater and the possible source of the ions as well as the relationship between the surface water and the groundwater.

Study area

The Ayensu River is about 103 km in length drains southerly into the Atlantic Ocean at the Gulf of Guinea near Winneba about 56 km west from the national capital - Accra. It lies between latitude $5^{\circ} 20' \text{N}$ to $6^{\circ} 10' \text{N}$ and $0^{\circ} 30' \text{W}$ to $0^{\circ} 50' \text{W}$.

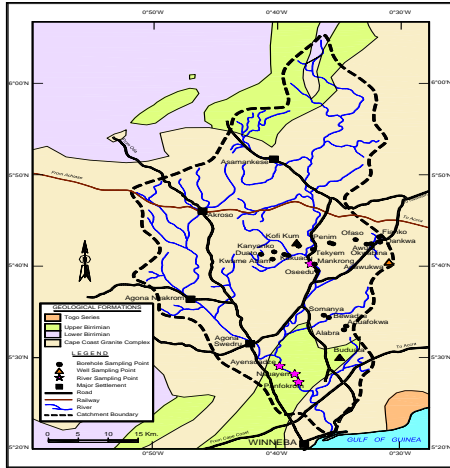


Figure 1 Map of the Ayensu Basin showing the Geology and Sampling points

The Ayensu Basin is underlain by rocks of the Precambrian age (the Cape Coast granitoids and the Birimian System). The Cape Coast granitoids are well foliated, often migmatitic, potash rich granitoids and come in the form of muscovite biotite granite and granodiorite, porphyroplastic biotite gneiss, aplites and pegmatites. They are often characterized by the presence of many enclaves of schist and gneisses. These granitoids are quoted to be enriched in such lithophile elements as Li, Be, Sn and Th. They also have a relatively high alkaline content. (Kesse, 1985) The Birimian System consists of sandstones, tuffs, grit, quartzites and some breccias (Gibrilla, A et al, 2010).

The hydrogeological conditions prevailing are governed by the geological and tectonic structures of the area. The crystalline rocks or granitoids do not possess any primary porosity, but have acquired secondary porosity and permeability through jointing, fracturing and shearing which are the main storage and transport of groundwater (BASH, 2008). The presence of these porosities affects the weathering in the rocks. It is therefore expected the depth to bedrock within the sediments should be larger than that in the granites. (BASH, 2008)

The basin is located in two climatic regions: the wet Semi-Equatorial in the northern part and the dry Equatorial in the south. The two climatic regions have two rainfall maxima. However, the dry Equatorial has mean annual rainfall less than 900mm while the wet Equatorial has mean annual rainfall between 1200mm and 2000mm (WARM, 1998).

The area experiences high temperatures during the major part of the year. The hottest months are January to May, just before the main rainy season (BASH, 2008).

Figure 2 is a graph of the monthly average maximum and minimum temperatures in degree Celsius for 10 years (1996-2005).

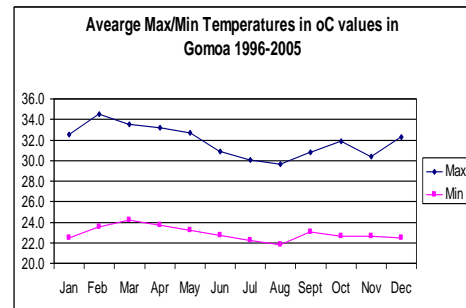


Figure 2 Average Maximum/Minimum Temperatures in $^{\circ}\text{C}$ values of Winneba Climatologic Station. Data from Central Region Ghana Meteorological Agency

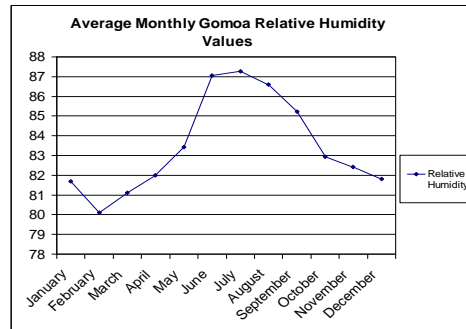


Figure 3 Average Monthly Relative Humidity for ten years (1996 – 2006) of Winneba Climatologic Station in the districts from Central Region Ghana Meteorological Agency

Methodology
Water samples were collected from 25 boreholes and 4 river (surface water) points. Samples were collected untreated in 80mL polyethylene bottles and tightly capped to prevent evaporation.

Deuterium and oxygen-18 were analyzed using the liquid water isotope analyzer. The samples were shaken to equilibrate and then pipetted into vials making sure that the samples and standards were pipetted into the correct vials. The tray was placed on the auto sampler and the run configured on the laser instrument. When the run was completed the run results were transferred, archived and post processed. All stable isotope data are reported in the usual δ notation, where $\delta = (R/RSTD - 1)1000$, R represents either the $^{18}\text{O}/^{16}\text{O}$ or D/H ratio of the sample, and $RSTD$ is the isotope ratio of the VSMOW, a reference standard.

Results and discussion

Physico-chemical

The pH of groundwaters ranges from 5.53-7.21; the groundwaters are between mildly acidic and slightly alkaline. Chloride concentration of the boreholes ranges between 49.985-399.876mg/L. The occurrence of chloride is proposed to be probably from the dissolution of soluble salts in the soil horizon and aerosol spray. The conductivity of groundwater samples also ranges between 382-2140 $\mu\text{S}/\text{cm}$ while their total dissolved solids (TDS) ranges between 164.9-913mg/L. The groundwater in the area can be classified as freshwater based on TDS and conductivity values.

Stable Isotopes

Isotopic composition of Groundwater

The $\delta^{18}\text{O}$ values of the groundwater samples vary from -3.26‰ to -2.01‰ vs VSMOW, with a mean composition of -2.63‰ vs VSMOW. The $\delta^2\text{H}$ values range from -12.59 to -5.05‰ vs VSMOW, with a mean composition of -8.93‰ vs VSMOW.

A plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ of the analyzed samples is shown in Fig. 4. The Local Meteoric Water Line [LMWL, $\delta^2\text{H} = 7.86\delta^{18}\text{O} + 13.61$ (Akiti, 1980)] is used as a reference line. Figure 4 shows that most of the groundwater samples clustered along the LMWL indicating that the groundwaters do not undergo significant evaporation before recharge; they are recharged by direct rainfall (isotopic composition of the original rainfall is not altered before recharge).

Some of the groundwater samples also plot along the evaporative water line suggesting that these samples belong to groundwater that had undergone evaporation on the land surface and in the unsaturated zone before recharge.

Isotopic composition of the River

For the river samples, the $\delta^{18}\text{O}$ values range from -2.27 to -1.31‰ VSMOW, with a mean of -1.69‰ and the $\delta^2\text{H}$ values ranges from -6.18 to -3.18‰ vs VSMOW, with a mean of -4.83‰. These values are more depleted than those of seawater ($\delta^2\text{H} = 0$ and $\delta^{18}\text{O} = 0$ ‰). Some of the river samples plot close to the evaporation line; they are isotopically enriched indicating evaporation effect (Fig. 4).

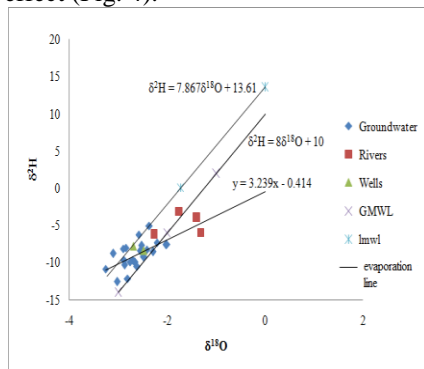


Figure 4 Plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$

In order to evaluate the sources of groundwater salinity, the chloride concentration is plotted against $\delta^{18}\text{O}$ values (Fig. 5). The plot indicates that processes for the increasing salinity could be due to: enrichment by evaporation; this is the case for the river samples, and an increase in conductivity is not related to evaporation in the groundwaters and this suggests dissolution (possibly of soil salts), this is the case for the groundwaters. The dissolution band therefore indicates that there could be dissolution of soluble salts in the soil horizons.

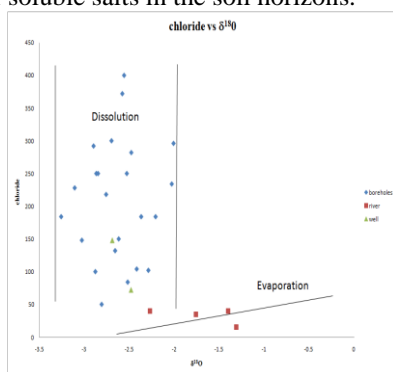


Figure 5 Plot of chloride versus $\delta^{18}\text{O}$

It is observed from Figure 6 that there was no correlation between the two (isotope composition remains the same with increasing conductivity along a flow path). The broad dissolution band observed in the figure suggests that the groundwaters are recharged by different episodes of rainfall/surface water events or are not connected; they could be discontinuous aquifers. Further work will have to be done to find out the exact mechanism operating in the area.

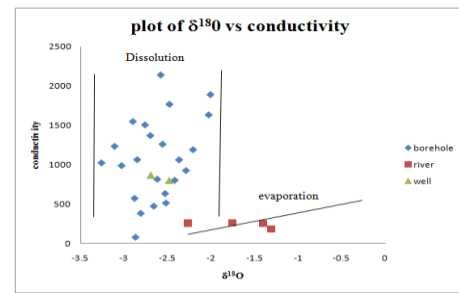


Figure 6 Plot of conductivity versus $\delta^{18}\text{O}$

Relation between the River and Groundwater

From Figure 4 some of the groundwater samples plot along the evaporative water line suggesting that these samples belong to groundwater that had undergone evaporation on the land surface and in the unsaturated zone before recharge; this is indicative of the presence of surface water. Again from Fig. 4 some of the river samples plot close to the LMWL; these could possibly be capable of recharging groundwaters.

Conclusion

The distribution of $\delta^{18}\text{O}$, Cl⁻ and electrical conductivity indicates that the source of the groundwater salinity is possibly the dissolution of soluble salts.

The isotopic compositions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of groundwater from the study area show that the origin of recharge is by direct rainfall infiltration as well as infiltration from surface water.

The plots of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ also indicate that the river water is capable of recharging the groundwater. Plot of conductivity versus $\delta^{18}\text{O}$ indicates that the aquifers could be discontinuous aquifers.

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Table 1.0 Reportable values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$

sample no	sample ID	Location	pH	Temp	cond	Cl	$\delta^2\text{H}$ (permil)	$\delta^{18}\text{O}$ (permil)
1	ADT	Duato	6.7	26	474	131.96	-10	-2.66
2	AOS	Oseedu	6.69	29.4	1371	299.91	-9.7	-2.7
3	ADW	Adawukwa	6.66	26.9	382	49.99	-12.18	-2.81
4	AKK	Kukuado	6.66	28.6	633	149.92	-7.74	-2.53
5	AKK2	Kukuado	6.68	27.5	78.6	249.92	-10.35	-2.87
6	AKM	Kwame Abam	6.68	25.3	1260	399.88	-8.43	-2.56
7	AKN	Kanyanko	6.66	27.8	513	83.97	-8.5	-2.52
8	AMA	Mankrong	6.65	28.5	1064	149.92	-8.05	-2.85
9	A1	Pamfokrom	6.71	26.7	252	39.99	-6.18	-2.27
10	A2	Nsuayem	6.69	27.8	255	14.99	-3.18	-1.76
11	A3	Ayensuadze	6.68	27	250	39.99	-3.94	-1.4
12	A4	Mankrong	6.71	27.8	176.6	6.00	-6.02	-1.31
13	GBD	Buduata	6.71	26.9	926	101.97	-8.56	-2.29
14	GBD2	Buduata	6.7	26.7	796	51.98	-8.38	-2.48
15	BEW	Bewadze	6.83	25.9	1890	195.91	-7.54	-2.01
16	SOM	Somanya	5.99	25.7	1549	291.91	-8.15	-2.9
17	AOK1	Awutu Okwabina	6.51	25.6	1190	183.94	-7.33	-2.21
18	AOK2	Awutu Okwabina	6.45	25.6	1768	281.91	-9.26	-2.48
19	OFA	Ofaso	7.17	25.8	1506	217.93	-9.91	-2.76
20	DAN	Dankwa	6.08	26.1	816	109.95	-10.53	-2.62
21	TEK	Tekyem	6.11	25.8	802	103.97	-8.28	-2.42
22	PEN2	Penim	7.05	25.7	1633	233.93	-7.62	-2.03
23	PEN1	Penim	6.77	25.9	988	147.95	-12.59	-3.03
24	FIA	Fianko	6.34	26.9	1234	227.93	-8.79	-3.11
25	KOK1	Kofi Kum	6.2	27.1	573	99.97	-9.65	-2.88
26	KOK2	Kofi Kum	6.09	27.1	862	147.95	-7.81	-2.69
27	KOK3	Kofi Kum	5.53	26.1	1062	103.94	-5.05	-2.37
28	ADU	Aduafokwa	7.21	27	2140	371.89	-6.28	-2.58
29	ALA	Alabra	6.65	27.2	1023	183.94	-10.88	-3.26