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Analysis of Stable Isotopic Composition of Precipitation in Katsina State In Nigeria As An Indication of Water Cycle

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ABSTRACT

The seasonal nature of precipitation in recent years had seriously affected the industrial and agricultural activities in Katsina state. Thus, stable isotopes composition of precipitation was used to check water cycle which delineated the nature of precipitation. The phase changing characteristic of water during successive cycle of evaporation and condensation (hydrological cycle) reveals the magnitude of isotope fractionation which reflect a wide range of δ^2H and δ^{18}O values in precipitation. The isotopic concentration changes, whenever condensation occurs to form precipitation. 19 precipitation samples were collected from different areas across Katsina state in Nigeria. The delta values for both deuterium and oxygen-18 of the samples were determined using Geo 20-20 Mass-Gas Spectrometer. Katsina State precipitation shows a wide range of stable isotopes variation; the δ^2H values range from -74‰ to -4.4‰ standard mean ocean water (SMOW) with weighted mean of -39.3‰ and the δ^{18}O values range from -10.20‰ to –1.88‰ (SMOW) with a weighted mean value of -6.1‰. Thus the delta values distribution for the State define a straight line on a cross-plot of δ^2H against δ^{18}O represented by approximate equation known as Local Meteoric Water Line (LMWL); $\delta^2H = 8.2\ \delta^{18}O + 11.5‰$. The slope in LMWL of the Katsina state indicates very minute or no evaporation effect during precipitation and thus confirms the continental nature of its precipitation (water form in the atmosphere which was raised from the land).

Keywords: *Fractionation, Stable isotope, Meteoric water, Deuterium, Oxygen-18*

INTRODUCTION

Precipitation is very crucial to the groundwater recharge which plays a significant role in the development of agricultural and industrial activities in Katsina state in particular and world at large. The intermittent nature of precipitation in recent years had frequently thwarted industrial and agricultural activities which lead to the closure of many industries and poor farming across the state. Therefore this research work intends to measure the stable isotopes composition of precipitation in Katsina state in order to determine its origin which could either be meteoric or continental type. In this research only precipitation samples was used. Chemical analysis of the sampled precipitation was not done. Adequate information about geology and hydrogeology data of the area was not available.

Knowledge of the factors that control the isotopic compositions of precipitation allowed the use of hydrogen and oxygen isotopes as tracers of water pathway and origin. On a regional scale, the distributions of isotopic compositions were controlled by several factors such as altitude effect, latitude effect, continental effect and amount effect [1].

Katsina state can be classified into two climatic zones; tropical continental and semi-arid: south of the state (from Dutsin-ma to Funtua) belong to the former with total annual rainfall figures ranging from over 800mm around Dusin-ma to around 1000mm in Funtua area. The north of state (from around Kankia to the extreme northeast i.e. Daura area) had total rainfall figures ranging from 700mm to 600mm annually. Generally, climate varied considerably according to months and seasons. There was a cool dry (harmattan) season from December to February; a hot dry season from March to May; a warm wet season from June to September; a less marked season after rain during the months of October and November, characterized by decreasing rainfall and a gradual lowering of temperature [2].

The natural processes that cause variation of isotopic composition of water were evaporation and condensation known as phase change. Thus the change in the isotopic composition of natural water occurred during its passage into the atmosphere or when it is subjected to a chemical reaction [1], [3]. The light molecules of water($H_2{}^{16}O$) are more volatile than the heavier ones, so on cooling of the atmospheric moisture the heavy molecules condense preferentially leaving a residual vapor more and more depleted in heavy isotopes (i.e. $D_2{}^{16}O$, $HD^{18}O$). Such sequential condensation occurred as air masses move inland from the sea or rise to higher altitude. Rivers might bring in water precipitated at high altitude, hence depleted in heavy isotopes. In ponds or lakes, the water might be considerably enriched in heavy isotopes through evaporation and they will deviate from a linear relationship between $\delta\,^2H$ and $\delta\,^{18}O$ usual for precipitation [1]. The linear relation between δ^2H and $\delta^{18}O$ is given by $\delta^2 D = 8\delta^{18}O + 10$[8]. It was referred to as the Global Meteoric Water Line (GMWL) upon which stable isotope interpretation of hydrological processes was based.

MATERIALS AND METHODS

The study area

The study area Katsina state covered an area of 23,938 sq. km and is a tropical savanna zone of Nigeria. Temperature remained high throughout the year (Dry Savanna). The mean annual maximum temperature was between 30-35^{0}C and the mean minimum annual temperature was between 23^{0}C-27^{0}C. The state was located between latitudes 11^{0}08' N and 13^{0}22'N and longitudes 6^{0}520'E and 9^{0}20'E with two broad seasons, the rainy season and dry Season. The rainy season began from late May or early June to mid-October with increasing rainfall from the southern part to the northern part of the state. Precipitation remained averagely 126 days with an unequal distribution of rainfall within the state in a given year [4].Annual rainfall wass closely related to latitudinal position with over 1000mm/a recorded in the southern part of the state and only about 600mm/a or less at its northern part. Evaporation was generally low in this area (i.e Daura area), especially in excess rainfall. Major rivers originated in or traverse the state include; the Koza, Sabke, Tagwai and Gada rivers in the northern half of the state (all flowing either north or northwestwards). Rivers in the south include the Karaduwa, Bunsuru, Gagare, Turamai, Sokoto, Tubo, Chalawa and Galma rivers (flowing either to Northwest, southeast or east). However, all these river systems contained water in their channels only during the rainy season and had little or no water in the dry season. Among them, river Gada, Karaduwa and sabke had been dammed mainly for irrigation purposes and the Dams were known as Jibiya, Zobe and Daberam dams respectively [2]. The hydrological map of the state is shown in figure 1 below.

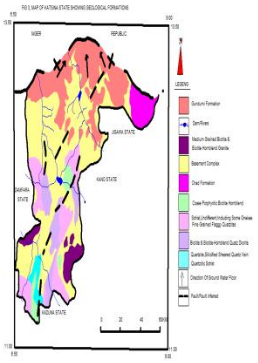

Fig:1 HYDROLOGICAL MAP OF KATSINA STATE

Theory

When water molecules change phase they do not keep the same isotopic composition. Heavier isotopes are less mobile (more difficult to shift). The kinetic energy of a molecule is solely determined by temperature

$$KT = \frac{1}{2}\,mv^2 \qquad (1)$$

Where K- Boltzmann constant, T- absolute temperature, m- molecular mass, v- average molecular velocity.

Therefore, molecules have the same $\frac{1}{2}\,mv^2$, regardless of their isotope content. This means that the molecules with lager mass necessarily have a smaller velocity [5].They need more energy this result in a change in isotopic composition of the two phase as physical process proceed. Also tiny differences are observed in chemical behavior of so-called isotopic molecules or isotopic compounds [10]. The phenomenon that these isotopic differences exist was called isotope fractionation. The natural processes that cause variations of the stable isotope in nature were temperature dependent.

The fractionation factor α expresses the magnitude of partitioning between two phases A and B as defined by [6], [7]

$$\alpha_{A-B} = \frac{R_A}{R_B} = \frac{1000 + \delta_A}{1000 + \delta_B} \qquad (2)$$

Where R is the isotope ratio of phase A and B respectively. The last term state the fractionation factor in terms of δ values for the phases A and B. Fractionation (ε) can be express interms of fractionation factor of the phases A and B.

$$\varepsilon_{A-B} = \left[\frac{R_A}{R_B} - 1\right] \times 1000 = (\alpha - 1) \times 1000 \qquad (3)$$

The last term gives the enrichment or depletion $(fractionation\ (\varepsilon))$ expressed by the fractionation factor (α). The enrichment (or depletion) factor may also be expressed in terms of δ values.

$$\varepsilon_{A-B} = \frac{1 + \delta_A}{1 + \delta_B} - 1 \approx \delta_A - \delta_B \qquad (4)$$

Delta value ratios related isotopic composition of a sample to that of a standard. Isotopes were generally reported in delta values (δ). Delta values were said to be either heavier (enriched) or lighter (depleted) than a standard. [6], [7]

$$\delta^A \ \ X_{sample/standard} = \frac{A_{R_{sample}-A_{R_{standard}}}}{A_{R_{standard}}} \qquad (5)$$

Where R reflects the isotope ratio of element X. δ values were dimensionless and were conventionally given in per mill (‰).

$$\delta\, {}^2H_{\ Sample}(‰) = \left[\frac{\left({}^2H / {}^1H\right)_{sample}}{\left({}^2H / {}^1H\right)_{Standard}} - 1\right] \times 1000 \qquad (6)$$

sampling and analysis

Nineteen precipitation samples were collected at various locations across the state, the samples were collected by attaching funnel to the high-density polyethylene bottle and kept in an open place for direct collection of rain water and immediately after the rain the bottle was unscrewed from the funnel and sealed with a plastic cone cap. The period in which the precipitation samples were collected covered the entire summer, ranging from 16th May 2010 to 25th October, 2011.

Stable isotopes analysis of the samples was performed using Geo 20-20 Mass-Gas Spectrometer at Environmental Isotope Group (EIG) iThemba Laboratories Gauteng, Johannesburg, South Africa. The water samples were equilibrated, at Water Equilibration System (WES) of Geo 20-20 Mass Gas Spectrometer, in order to prepare the samples for measurement. The standard side of the dual inlet system was connected to a tank of reference hydrogen (for deuterium) and reference carbon dioxide (for oxygen-18). The equilibration time of the water samples with hydrogen gas was just an hour (1hr) while on the other hand; the equilibration time of the water samples with carbon dioxide gas was eight hours (8hrs). The equilibration time depends on size and weight of the molecule.

The $^2H/^1H$ ratio measurement of sample water was done by means of the hydrogen-water isotopic equilibration reaction in the presence of platinum as a catalyst. The isotopic exchange between hydrogen gas and liquid water proceeded through two consecutive reactions [6], a reaction between hydrogen gas and water vapour in the present of platinum catalyst, and a reaction between water vapor and liquid water. The net reaction was summarized, thus:

$${}^1H \boxed{?}\, {}^2H_{(g)} + {}^1H_2\, 0_{(l)} \rightarrow {}^1H_{2(g)} + {}^1H\ {}^2HO_{(l)} \qquad (7)$$

Hence, the hydrogen isotope ratio of hydrogen gas ${}^{1}H \square {}^{2}H / {}^{1}H_{2}$, that was, (1 + 2)/(2) or 3/2 reflected the isotope ratio of the sampled water. After an equilibration time of 60 minutes, the analysis for hydrogen started when the sample gas was transferred via a liquid nitrogen cold temperature bath to the inlet system of the mass spectrometer. Thereafter the deviation of the deuterium content of sample water from that of the standard (or reference) used (SMOW) was determined by equation (9) below. After equilibration of the water sample with commercial dry CO_2 gas of known isotopic composition in the presence of platinum as a catalyst for about 480 minutes when isotopic information of the water had been transferred into the gas phase (CO_2) according to the following reactions [6]:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \qquad (8)$$

$$CO_{2(aq)} + H_2O \rightarrow HCO_3^- + H^+ \qquad (9)$$

$$C^{16}O_2 + H_2{}^{18}O \longrightarrow C^{16}O^{18}O + H_2{}^{16}O \qquad (10)$$

The gas was subsequently introduced into the inlet system down to mass spectrometer for comparison with a reference gas of known isotopic composition. The transfer line between WES and inlet system (SI) was immersed into a cold temperature bath (a mixture of acetone and liquid nitrogen at -70°C) to prevent water vapour from entering the inlet system. The spectrometer measured the $C^{16}O\,{}^{18}O / C^{16}O_2$ ratio, that was, the ratio of the mass (12 + 18 + 16)/(12 + 32) or 46/44. The value was corrected to be reported against the SMOW (Standard Mean Ocean Water) standard

$$\delta^{18}O_{Sample}(‰) = \left[\frac{\left({}^{18}O / {}^{16}O \right)_{Sample}}{\left({}^{18}O / {}^{16}O \right)_{Standard}} - 1 \right] \times 1000 \qquad (11)$$

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RESULT

The obtained results were presented in Table 1. The stable isotopes composition was express in part per thousand (per mill). The 19 rainwater samples collected from the study area have the respective $\delta^{18}O$ and $\delta^{2}H$ concentration ranged from −10.25‰ to −1.88‰ (average − 6.07‰)and−74.1‰ to−5.3‰ (average − 39.7‰) respectively. All of the rainwater samples were depleted in heavy isotopes with respect to the reference material (SMOW) except one rainwater sample with sample identification FRWS 18 showed a peculiar content of both $\delta^{18}O$ and $\delta^{2}H$ as +14.0‰ and +0.88‰ this happened because of the security checking at various point

Table1.The analytical result of the precipitation samples collected from the study area along sided with their locations and date of samples collection.

Date	Sample Identification	δ D (‰)	$\delta\ ^{18}O$ (‰)	Latitude	Longitude	Altitude
16/05/2010	FRWS1	-18.1	-3.72	N1131.256'	E00718.688'	2320
29/05/2010	FRWS2	-16.3	-3.84	N1131.718'	E00718.657'	2341
06/06/2010	FRWS3	-30.5	-4.83	N1131.296'	E00718.681	2210
15/06/2010	FRWS4	-28.4	- 4.40	N1131.871'	E00718.233'	2224
22/06/2010	FRWS5	-53.4	-8.02	N1131.629'	E00718.616'	2345
30/06/2010	FRWS6	-54.3	-8.05	N1131.233'	E00718.588'	2208
06/07/2010	FRWS7	-63.3	-8.77	N1130.113'	E00719.165'	2176
12/07/2010	FRWS8	- 8.8	-3.16	N1131.017'	E00718.521'	2319
19/07/2010	FRWS9	-48.6	-7.19	N1135.175'	E00714.199'	2216
28/07/2010	FRWS10	-65.5	-9.81	N1134.584'	E00712.366'	2130
05/08/2010	FRWS11	-74.1	-10.25	N1134.555'	E00712.467'	2107
12/08/2010	FRW12	-43.7	-6.76	N1131.787	E00718.364'	2013
19/08/2010	FRWS13	-25.1	-4.66	N1131.908'	E00719.275	2312
26/08/2010	FRWS14	-47.7	-7.09	N1130.016	E00718.324'	2200
07/09/2010	FRWS15	-8.2	-3.14	N1130.006	E00719.554'	2017
17/09/2010	FRWS16	-30.1	-4.91	N1131.162'	E00718.705	2260
11/10/2010	FRWS17	-4.4	-1.88	N1131.463'	E00718.163'	2314
21/10/2010	FRWS18	-14.0	-0.88	N1131.817	E00718.681'	2254
01/11/2010	FRWS19	-5.3	-1.93	N1131.233	E00719.055'	2317

DISCUSSION

The precipitation samples collected from the study area show a wide range of stable isotopes composition (table1); the δ^2H values range from -74.1‰ to -4.4‰ (SMOW) with a weighted mean value of -39.3‰ and the $\delta^{18}O$ values range from - 10.25‰ to -1.88‰ (SMOW) with a weighted mean value of -6.1‰.This indicate the extent of evapotranspiration in the area.

The δ^2H versus $\delta^{18}O$ relationship for rain water samples collected throughout the summer from the study area is defined by the following least square regression equation.

$$\delta^2H = 8.2\delta^{18}O + 11.5\text{‰ SMOW} \qquad (12)$$

With $R^2 = 0.985$ depicted in table 2 and R^2 is the coefficient of correlation. ''Eq. (12)'' shows the Local Meteoric Water Line (LMWL) of Katsina state and is illustrated in fig. 2.The slope of 8.2 in LMWL of Katsina state is close to the slope of the Global Meteoric Water Line (GMWL), given by $\delta^2H = 8\,\delta^{18}O + 10$ SMOW

[9]; this fact indicates very little or no evaporation effect during precipitation in the study area and confirms the continental nature of its precipitation. The intercept (11.5‰) is known as deuterium excess.

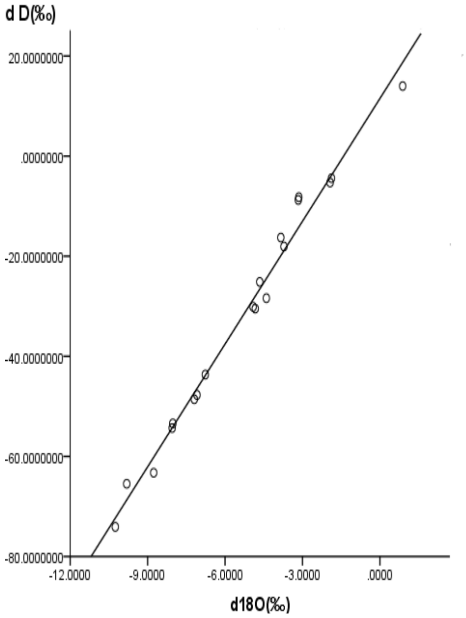

Fig. 2 : Local Meteoric Water Line (LMWL) of Katsina state.

The deuterium excess parameter (d) defined by

$$d = \delta^{2}H - 8\delta^{18}O \qquad (13)$$

relates position in (^{2}H, ^{18}O) space of water sampled from any location to the global meteoric water line [9]. The deuterium excess in LMWL of Katsina state is found to be 11.5‰ though the global average is about 10‰, it varies in space and time due to variations in wind speed, humidity and sea surface temperature.

CONCLUSION

The measured stable isotopes concentration (δD and δ^{18}O) in Katsina state precipitation samples were linearly related through $\delta D = 8.2\ \delta^{18}O + 11.5‰$, which is referred to Local Meteoric Water Line (LMWL). The slope of 8.2 in LMWL indicates no evaporation effect during the rainfall and further confirms the continental type of precipitation in Katsina state. The continental nature of the precipitation is an evidence of water cycle. The deuterium excess value (11.5‰) slightly differs from the Global Meteoric Water Line (GMWL) because of constant variation of some climatic element.

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