

# Hydrogeochemistry and Stable Isotopes ( $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ) Assessment of Ikogosi Spring Waters

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**Abstract** Ikogosi warm spring is a unique tourist centre where warm and cold spring waters flow together. Consequently, understanding the hydrochemical processes and recharge source are critical to the sustainability and management of the warm spring. Hence, stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and hydrochemical study of Ikogosi spring waters was carried out to conceptualize the recharge source and the extent of water-rock interaction on the hydrochemical evolution of the waters. The study approach involved field sampling and in-situ measurements of physico-chemical parameters followed by laboratory hydrochemical and stable isotope analyses of the spring water samples. The hydrochemical analysis revealed that Ikogosi spring water is alkaline in nature with values ranging between 7.4 and 9.0. The TDS ranges from 14.3 to 66.8 mg/L with mean value of 49.2mg/L while the TH is from 6.3 to 39.0mg/L with mean value of 27.61mg/L. All EC values for the sampled spring waters were below 1000 $\mu\text{S}/\text{cm}$  indicating fresh water.  $\text{Ca}^{2+}$  was the dominant cation with value ranging from 2.2-9.6mg/L while Cl- was the dominant anion with value ranging from 88.6-144.0mg/L. The spring water is low mineralized and hydrochemically potable. Rock-water interactions were the dominant processes controlling the major ion composition of the spring while the dominant water was Ca (Mg)-Cl type. Stable isotopes analysis revealed recharge from recent precipitation. Conclusively, Ikogosi spring waters have low EC and TDS along with low total hardness (TH) values suggesting a low mineralized soft fresh water system recharged from recent precipitation with limited residence time.

**Keywords:** hydrochemical processes, recharge source, stable isotopes, potable, low mineralized

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## 1. Introduction

Spring arises where groundwater naturally emerges from the earth's subsurface in a defined flow and in amount to form a pool or stream-like flow [1]. Freshwater from the spring could be directly discharged onto the ground surface, directly into the beds of rivers or streams or into the ocean below sea level.

Spring water was associated in the public mind with exceptional quality. As a matter of fact, bottling of spring water has become a prominent business across the world. The importance of springs have gone beyond just being sources of domestic and municipal water supply but also sources for foreign exchange earnings as they serve as places for tourist attraction and industrial establishment where safe drinking water could be bottled [2]. However, the water bearing strata of the spring called aquifers could contain unconsolidated materials like sand, gravels, glacial drift or consolidated materials like sandstones and limestone that could affect the hydrochemistry of the spring water. Treatment of spring's water is therefore necessary to guide against outbreak of water borne diseases.

Ikogosi spring waters have been known for ages. The waters comprise of a warm spring that runs down a hilly

landscape and a cold spring from an adjoining hill. The two springs (warm and cold) merged down slope into one continuous flowing stream. The evergreen tall trees surrounding the spring provide coverage and reduce evaporation of the spring waters. Ikogosi town has been catapulted to national and international limelight because of the presence of the warm and cold springs flowing side by side in the town. The spring is very useful to the people of Ikogosi town as it provides not only sources of potable water, sites of recreational and cultural value but a source of employment. In view of the economic activities in the area, human activities have increased contributing to possible anthropogenic contamination in addition to geogenic contamination resulting from dissolution of mineral constituents of the bedrocks hoisting the spring. Thus there is need for chemical characterization of Ikogosi spring waters with a view to having a better understanding of the hydrochemical processes in relation to water-rock interactions.

There are many unscientific mysterious tales with respect to the origin of the springs that need to be redressed. Also, scientific postulates focused on one of two alternatives of whether the waters rise from hot magmas at depth similar to Rafin Rewa warm spring of Nigeria that flows from Precambrian rocks (migmatite – gneiss) [3] or are they originally rainwater which has

percolated down deep into the earth's crust, thereby heated by some unknown process [4]. These few insufficiently addressed questions necessitate stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) evaluation to unravel the source(s) of Ikogosi spring waters. The water of the warm springs, like all water, is made up of the elements hydrogen and oxygen in the form,  $\text{H}_2\text{O}$ . Each of these two elements has closely similar forms known as isotopes. Isotopes are atoms of the same element that have different numbers of neutrons (i.e. different masses). In many cases, the elements constituting the water molecule hydrogen and oxygen, undergo changes in the various phases of hydrologic environments; atmosphere, hydrosphere, biosphere and the upper part of the earth's crust. These changes result in isotopic fractionation to give isotopic "fingerprints" due to different physicochemical, biochemical, kinetic and thermodynamic effects [5]. Furthermore, the spatial changes of the stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in the hydrologic environments can be evaluated and used to trace the recharge source(s) to the spring waters. In particular,  $^{18}\text{O}$ ,  $^2\text{H}$ , and  $^3\text{H}$  are integral parts of natural water molecules that fall as rain or snow (meteoric water) each year over a watershed and consequently, are ideal tracers of water [6].

Previous works in the study area have been limited to geological, hydrochemical and geophysical appraisal of the geologic structure beneath the Ikogosi warm spring [7,8,9,10]. The previous studies did not fully address the provenance of the waters. Moreover, geological and hydrogeochemical processes are dynamic and required constant re-evaluation. Hence, this study presents the

chemical and stable isotopic compositions ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) of Ikogosi spring waters with the aim of providing an overall assessment on the origin of the waters and hydrogeochemical processes that modified their chemical evolution.

## 2. Location and Geology

Ikogosi is a small town in Ekiti West Local Government area of Ekiti State, about fifty-five kilometres from Akure, the state capital of Ondo State (Figure 1). Ikogosi warm spring lies about 2km west of Ikogosi town on longitude  $4^\circ 56.46'\text{E}$  and latitude  $7^\circ 36.88'\text{N}$ . The topographical elevation determined from topographic map varies from less than 473 m in the valleys to 549 m on the hills [10]. The spring is a low enthalpy system, its temperature being around  $36^\circ\text{C}$  [9]. Reference [7] identified six indigenous tributaries encompassed by two dry valleys trending approximately north-south of the fractured basement rocks of the area. The study area falls within tropical rain forest of Nigeria with two distinct seasons; rainy and dry seasons signifying the climatic system. The wet season is as a result of the prevailing moisture laden winds emanating from the Atlantic Ocean while the dry season is from the North-East dry, hot and dusty winds from the Sahara desert. The area is characterized by annual rainfall of 1500mm, high relative humidity of between 70 – 85% with average annual temperature of  $28^\circ\text{C}$ .

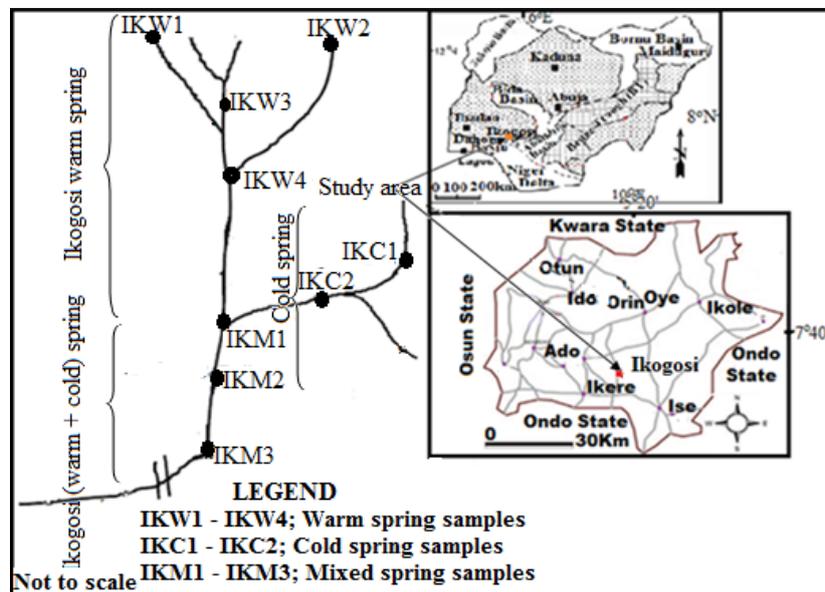


Figure 1. Location of Study

The warm spring is within massive quartzite and fissile quartzite bedrocks that form part of the Okemesi quartzite, member of the Effon psammite formation in the Ilesha schist belt of Nigerian Basement Complex (Figure 2). The Okemesi quartzite is characterized by a North-South trending ridge overlain by quartz mica schist and underlain by quartz sillimanite schist [7]. Thus the study area is characterized by undulating land forms with the quartzite forming the highland and the river channels indicating valleys. The quartzite constitutes the residual

hills covered with gently sloping sediment that post erosion threat to the environment. Reference [10] reported that magnetic study of the area revealed fractured quartzite/faulted areas within fresh massive quartzite at varying depths while the geoelectrical sections developed from Vertical Electrical Sounding (VES) interpretation results also delineated a subsurface sequence consisting of a topsoil/weathered layer, fresh quartzite, fractured/faulted quartzite and fresh quartzite bedrock.

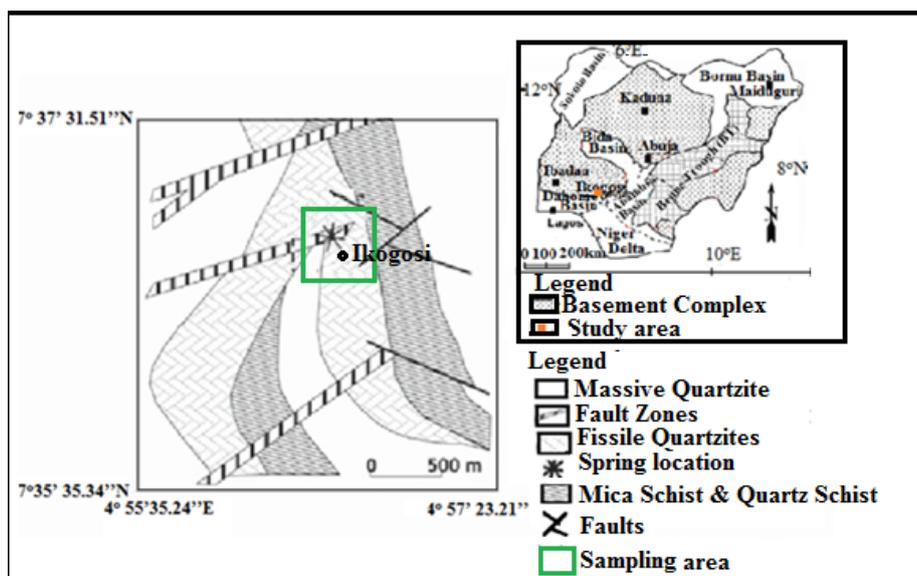


Figure 2. Local geological map of the study area (modified after Adegbuyi et al., 1996)

### 3. Methods

Field operations were carried out between 14<sup>th</sup> and 15<sup>th</sup> January, 2013 during which spring water sample for cations at each location was collected carefully in 100ml polystyrene bottle and preserved with Conc. HNO<sub>3</sub> while the sample for anions was collected using 500ml bottle. The sampling points are as follows: Discharge point (IKW1 and IKW2) representing warm part of Ikogosi spring, 2 varying points along the course of the warm stream (IKW3 and IKW4), 2 varying points along the course of the cold stream (IKC1 and IKC2), meeting point of warm and cold streams (IKM1) and 2 varying points along the warm and cold stream mixture (IKM2 and IKM3). Water samples for Isotope analysis comprising of 2 samples of the warm spring stream, 2 samples of the cold spring stream, 2 samples of the mixture of warm and cold spring (stream section) and 1 borehole sample from Ikogosi town to serve as control were filtered using 4mm membrane and collected in 100ml polystyrene bottle and stored in a refrigerator at 4°C before analysed in the Laboratory. Field insitu measurement (temperature, electric conductivity (EC) and pH) were measured using a multiparameter portable meter (model Testr-35) while cations and anions hydrochemical parameters were subsequently determined at the Laboratory of the Department of Agronomy, University of Ibadan, Nigeria employing colorimetric and atomic absorption spectrometry methods for anions and cations respectively. Stable isotopes (<sup>18</sup>O and <sup>2</sup>H) measurements were carried out using Isotope ratio mass spectrometry (IRMS) at Hydroisotop Laboratory, Schweitenkirchen in Germany. Results were reported in  $\delta$  (‰) values compared to VSMOW standard values. Results were presented in  $\delta \pm 0.15$  ‰ for Oxygen-18 ( $\delta^{18}\text{O}$ ) and  $\delta \pm 1.5$  ‰ for Deuterium ( $\delta^2\text{H}$ ) while Deuterium-excess was calculated using  $d\text{-excess} = \delta^2\text{H} - 8\delta^{18}\text{O}$ . Result of the hydrochemical data were subjected to graphical evaluation using [11] and [12] to define the various chemical evolution of the spring and borehole waters sampled in the study area. Furthermore, scatter plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  with respect

to Global Meteoric Water Line (GMWL) was employed to determine the source of groundwater in the stud area.

### 4. Results and Discussion

The results of the physico-chemical analysis of Ikogosi water samples are represented in Table 1. In Table 2, results of average values of some parameters [temp (°C), pH, Cl<sup>-</sup>(mg/L), Ca<sup>2+</sup>(mg/L), Mg<sup>2+</sup>(mg/L), K<sup>+</sup>(mg/L), Na<sup>+</sup>(mg/L), Fe<sup>2+</sup>(mg/L) and Zn<sup>4+</sup>(mg/L)] selected from the research of chemical examination of Ikogosi spring by [9] compared to results of the present research along with [13] and [14] are tabulated. The differences observed in the two data sets are reflections of hydrogeochemical processes dynamism requiring continuous reevaluation. Both data indicate low dissolved ions in the spring waters.

### 5. Hydrogeochemistry

The temperature of Ikogosi spring waters range between 22.1 and 34.8°C with the maximum temperature occurring close to the point where the warm spring discharged/seeped out from the fractured quartzitic bedrock. The WHO does not recommend any limit values as regards water temperature. However, reference [15] revealed that temperature higher than 15°C facilitates the development of microorganisms and in the same time intensify the organoleptical parameters such as odours and taste and activates chemical reactions. In the study area, the warm temperature have probably aided chemical reactions. From the result obtained, the pH lies between 7.4 and 9.0 (mean 8.30). The spring waters are alkaline with some of the values exceeding [13] and [14] recommended standards (6.5 – 8.5) for drinking water. Actually, the cold spring displays higher pH values compared to the warm spring indicating more hydrogen ion (H<sup>+</sup>) availability (activity) in the warm spring. The hydrogen ion is very small and is able to enter and dissolve mineral structures so that they contribute dissolved constituents to the spring waters. Consequently, the greater the availability of H<sup>+</sup> ions, the lower the pH,

the higher the EC and TDS in the water. This observation to some extent is observed by the hydrochemical result presented in (Table 1) with EC value ranging from 19 to 90  $\mu\text{S}/\text{cm}$ . The warm spring has TDS range of 33.90 – 66.8mg/L compare to the cold spring with TDS of 14.3 –

33.8mg/L. The mixed spring have relatively higher TDS values due to increased residence time of the water in the aquifer allowing longer contact with the minerals, the greater the extent of its reaction with those minerals and the higher will be the content of dissolved minerals.

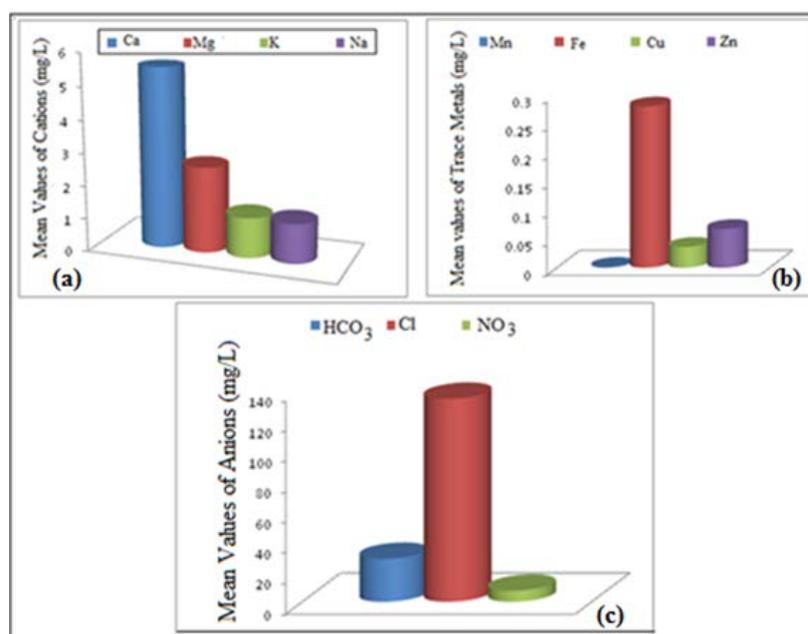
**Table 1. HYDROCHEMICAL RESULT OF IKOGOSI SPRING WATERS**

Parameters	IKW 1	IKW 2	IKW 3	IKW 4	Mean (Warm spring)	IKC 1	IKC 2	Mean (Cold spring)	IKM 1	IKM 2	IKM 3	Mean (Warm+Cold spring)
Temp (°C)	34.5	34.4	34.8	34.1	34.45	22.1	22.4	22.25	32.9	31.9	32	32.27
pH	7.4	8.3	7.6	7.5	7.7	8.7	8.6	8.65	8.4	8.8	9	8.73
EC ( $\mu\text{S}/\text{cm}$ )	88	89	90	90	89.25	19	45	32	88	85	86	86.33
TDS (mg/L)	66	66.8	34.1	33.9	50.2	14.3	33.8	24.05	66	63.8	64.5	64.77
TH (mg/L)	31.3	33.9	39	37.41	35.4025	6.3	12.5	9.4	30.9	23.9	33.3	29.37
HCO <sub>3</sub> <sup>-</sup> (mg/L)	45.8	15.3	38.5	44.8	36.1	45.8	50.2	48	30.5	15.3	30.5	25.43
Cl <sup>-</sup> (mg/L)	126	126	125	126.2	125.9	90	88.6	89.3	90	90	144	108.00
NO <sub>3</sub> <sup>-</sup> (mg/L)	7.8	7.4	7.2	8	7.6	5.5	5.2	5.35	6	6.7	8.8	7.17
Ca (mg/L)	7.2	7.1	9.6	8.3	8.05	2.2	3.7	2.95	6.8	5.2	6.4	6.13
Mg (mg/L)	3.3	3.9	3.6	4	3.7	0.2	0.8	0.5	3.4	2.7	4.2	3.43
K (mg/L)	1.9	1.4	1.9	1.7	1.725	0.6	0.8	0.7	1.6	1.2	1.2	1.33
Na (mg/L)	2	1	1.9	1.9	1.7	1.1	1.1	1.1	1.1	1	1.1	1.07
Fe (mg/L)	0.1	0.1	0.2	0.1	0.125	1	0.4	0.7	0.1	0	0.2	0.10
Cu (mg/L)	0.1	0	0.1	0.1	0.075	0	0	0	0	0	0.1	0.03
Zn (mg/L)	0.1	0.1	0.1	0.1	0.1	0	0.1	0.05	0.1	0.1	0.1	0.10

IKW1 – IKW4; Ikogosi warm spring, IKC1 – IKC2; Ikogosi cold spring and IKM1 – IKM3; Ikogosi mixed spring (cold + warm)

**Table 2. COMPARISON OF AVERAGE VALUES OF SELECTED CHEMICAL PARAMETERS FROM [13] WITH PRESENT RESEARCH**

Parameters	Data from [13]		Data from present research		NSDWQ (2007)	WHO (2004)
	Warm spring	Cold spring	Warm spring	Cold spring		
Temp (°C)	35.90	25.00	34.45	22.25	-	-
pH	6.60	6.90	7.70	8.70	6.50 – 8.50	6.50 – 8.50
Cl <sup>-</sup> (mg/L)	7.90	4.40	125.90	89.30	250.00	250.00
Ca (mg/L)	2.28	1.81	8.05	2.95	-	75.00
Mg (mg/L)	4.31	3.02	3.70	0.50	0.20	50.00
K (mg/L)	0.73	0.08	1.73	0.70	-	-
Na (mg/L)	0.69	0.67	1.70	1.10	200.00	200.00
Fe (mg/L)	0.12	7.63	0.13	0.70	0.30	0.30
Zn (mg/L)	0.13	0.04	0.10	0.05	3.00	3.00



**Figure 3.** Comparison of Mean ionic concentrations of Ikogosi spring waters

As per the TDS classification [16], all the water samples are fresh water (TDS < 1,000 mg/L) type.

In the study area, TH as  $\text{CaCO}_3$  range from 6.3 – 39mg/L with a mean of 27.61mg/L. According to [17], all samples from Ikogosi spring are with};in the soft water category with TH as  $\text{CaCO}_3$  less than 60mg/L. The low EC and TDS values along with low total hardness (TH) values suggest a low mineralized soft fresh groundwater system with limited residence time. The total concentration of alkaline earth metal ions, such as calcium and magnesium, in water determine the hardness of water. This is reflected in the cross plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  (mg/L) versus TH (mg/L) with correlation coefficient of 0.997 (Figure 4A). Possible source of hardness in the spring waters could be as a result of geogenic introduction of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions into water by leaching from minerals within the aquifer of the water. There is no health based standard for the hardness of drinking water. Reference [14] has identified that water with a hardness of 200 mg/l or higher (measured as calcium carbonate) will produce scale and soft water with a value of 100 mg/l (as calcium carbonate) or less will have a low buffering capacity and be more corrosive to pipes. A minimum total hardness of 150 mg/L (as calcium carbonate) is recommended by [14] because there is some limited evidence of a relationship between water hardness and cardiovascular health which may be related to the beneficial properties of magnesium and calcium in the diet. Water hardness is of no consequence in the study area. However, wherever water hardness is a concern, water softening is commonly used to reduce hard water's adverse effects. The concentrations of the major cations for the spring waters (warm, cold and mixed) appear in the order of  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$  (Figure 3a) with concentrations ranges of 2.2 – 9.6, 0.2 – 4.2, 1.0 – 2.0 and 0.6 – 1.9 mg/L, respectively, while that of the anions vary with  $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^-$  (Figure 3b). The other of trace metal concentrations is  $\text{Fe}^{2+} > \text{Zn}^{4+} > \text{Cu}^{2+} > \text{Mn}^{4+}$  (Figure 3b).  $\text{SO}_4^{2-}$  anion concentrations

in the area were not detected by the colorimetric analytical method employed for the analysis.

In Ikogosi spring waters, variability in chemical compositions were observed in the warm, cold and mixed (cold + warm) portion of the spring/stream. More dissolved ions were in the warm and mixed sections compared to the cold portion (Table 1). The variability observed is as a result of the effects of combination of factors such as temperature, chemical reactions/migratory residence time of the waters as well as their degree of mixing. These factors are reflected in the EC ( $\mu\text{S}/\text{cm}$ ) values (Table 1) as EC of water samples from the warm spring/stream are relatively high compare to the samples from the cold stream section. Increased temperature aids dissolution of the minerals in the bedrocks and thus more solutes are contributed to the warm spring/stream section of the study area. The effects of mixing and longer migratory history are reflected in the downstream section where warm and cold stream water mixed together reflecting moderate solute input from the bedrocks. All ionic concentrations are within [13] and [14] approved standard for drinking water except for pH in few locations.  $\text{Na}^+$  plays significant role in human metabolic system as is related with the function of nervous system, membrane system and excretory system. According to reference [14] guideline, the maximum admissible limit  $\text{Na}^+$  concentration is 200 mg/L. Excess sodium causes high pressure, nervous disorder, etc. In the study area, the  $\text{Na}^+$  concentration (1.0 – 2.0 mg/L) in the spring waters constitute no risk to human health.

As presented in Figure 4, the cross plots provide insight into the source of ionic input to the spring waters at Ikogosi. Figure 4B with low correlation coefficient (0.28) compared to Figure 4C with correlation coefficient of 0.46 are clear indication that the TDS values are most likely to be consequent of anthropogenic activities. However, positive correlation of 0.72 for the cross plot of  $\text{Ca} + \text{Mg}$  (mg/L) versus  $\text{Cl}^-$  (mg/L) Figure 4D is indicative of geogenic  $\text{Cl}^-$  input into Ikogosi spring waters.

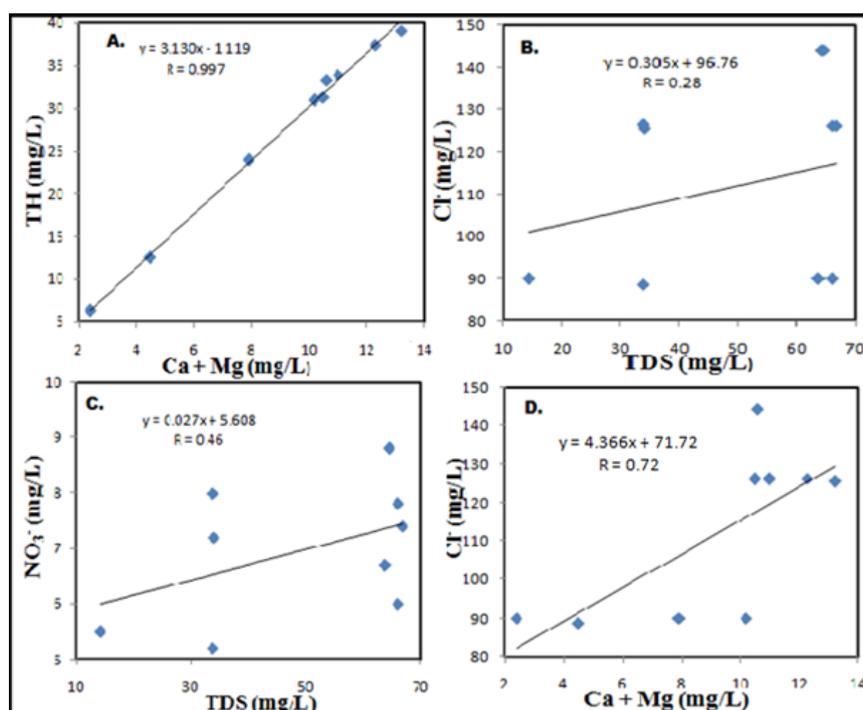


Figure 4. Cross plots of some ions in the study area

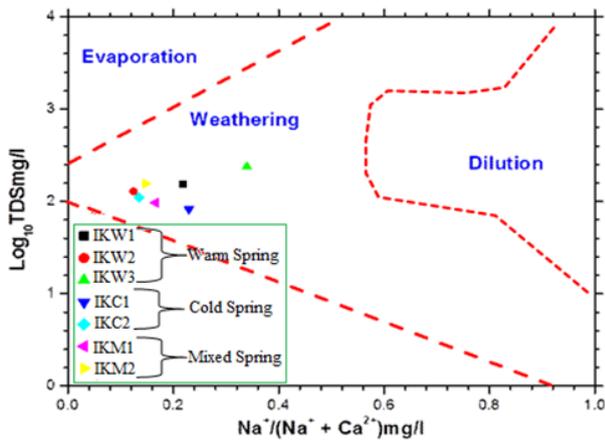


Figure 5. Gibb's Plot

Generally, low values of ions in the spring water are reflection of meteoric source water with limited migratory history. Field observation revealed the bedrock of the study area to be quartzite and mica schist. The dominant mineral is quartz ( $\text{SiO}_2$ ) with minor muscovite and feldspar. Some of the observed ions are most likely to have been leached from the quartzitic rock. Some quartzites are very pure in mineral composition, others have in greater or less abundance other minerals representing in parts remains of original mineral grains, such as feldspar mixed with those of quartz, or new ones which have resulted from the metamorphism of the clay or lime cement, which formerly filled the interstices between the grains of the sandstone. Such are muscovite, chlorite, kyanite and epidote etc. [18] from which ionic components of the spring waters were leached out. The concentration of dissolved ions in groundwater samples are generally governed by lithology, nature of geochemical reactions and solubility of interaction rocks [19]. The functional sources of dissolved ions can be broadly assessed by plotting the samples, according to the variation in the ratio of  $\text{Na}/(\text{Na}+\text{Ca})$  as a function of

$\text{Log}_{10}\text{TDS}$  (mg/L) [12]. The Gibb's plot of data from study area (Figure 5) indicates rock-water interactions as the dominant process controlling the major ion composition of Ikogosi spring waters.

### 5.1. Hydrochemical Facies

The relative ionic composition of Ikogosi spring waters were plotted on a Piper Trilinear diagram as presented in Figure 6 [11]. This diagram provides a convenient method to classify and compare water types based on the ionic composition of different water samples [20]. Cation and anion concentrations for the spring waters (Ikogosi warm spring, Ikogosi cold spring and Ikogosi mixed spring) were converted to meq/L and plotted as percentages of their respective totals in two triangles (Figure 6). Subsequently, the cation and anion relative percentages in each triangle were then projected into a quadrilateral polygon that describes the water type or hydrochemical facies. The values obtained from the analyzed Ikogosi spring waters samples and their plot on the Piper's diagram [11], revealed  $\text{Ca}^{2+}$  as the dominant cation while  $\text{Cl}^-$  is the dominant anion. In the study area, the major spring water type is Ca (Mg)-Cl (Figure 6) based on [21]. The plausible explanation as to the evolved water type was from weathering induced through high precipitation that characterized the study area. However, anthropogenic contributions cannot be ruled out in view of increase in the number of tourists visiting the spring site. Furthermore, the Schoeller semi-logarithmic diagram [22] allows the major ions of many samples to be represented on a single graph, in which samples with similar patterns can be easily discriminated. The Schoeller diagram shows the total concentration of major ions in log-scale. Results of the Schoeller plots (Figure 7) revealed  $\text{Ca}^{2+}$  as dominant cation and  $\text{Cl}^-$  as dominant anions corroborating the classification from Piper Trilinear diagram.

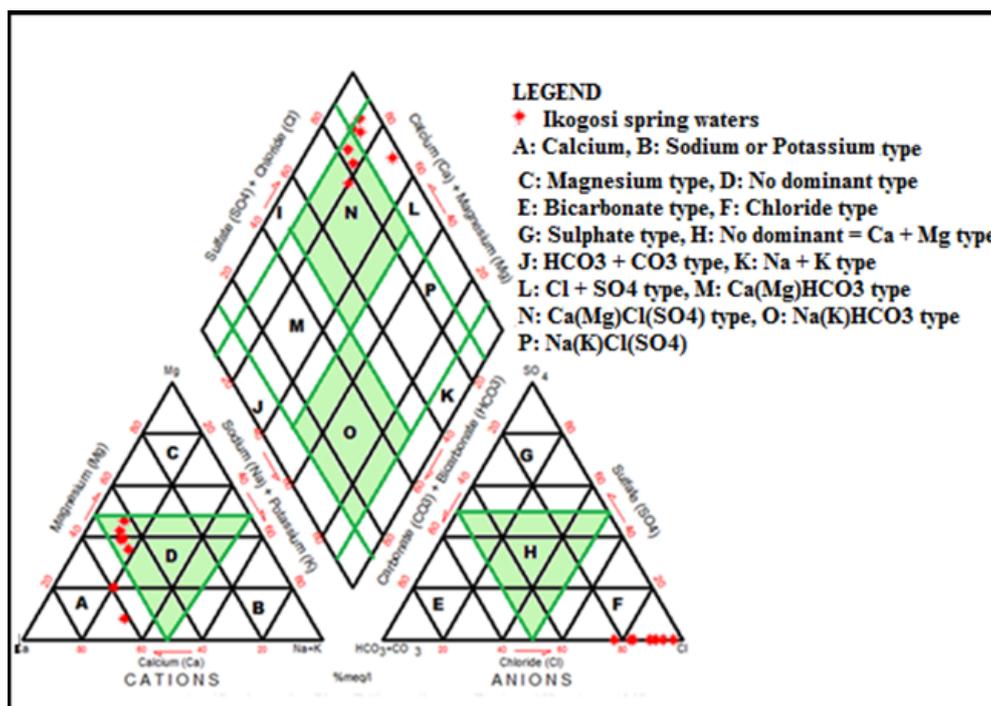


Figure 6. Water type classification using Piper Trilinear diagram (Back and Hanshaw, 1965)

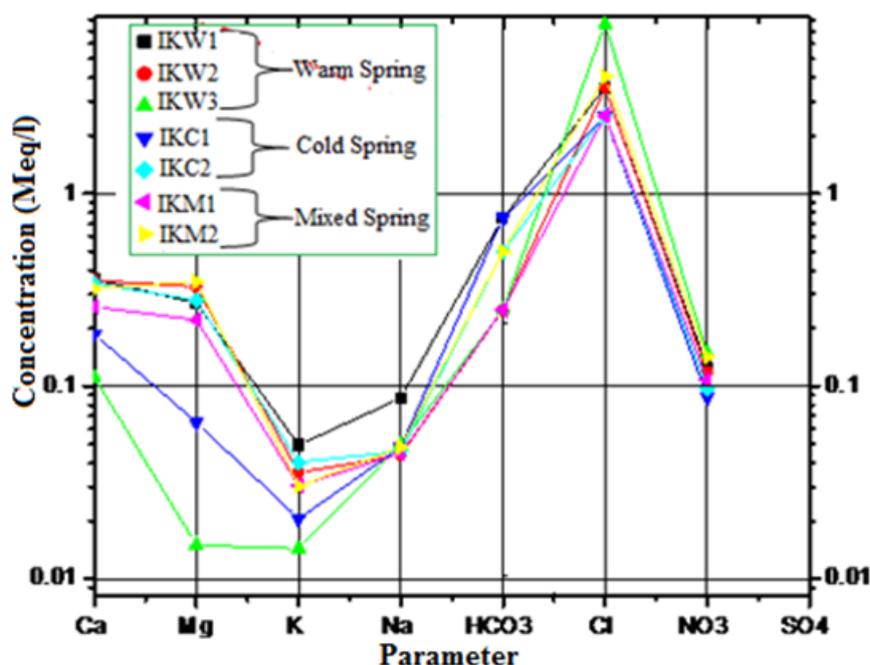


Figure 7. Schoeller Diagram

## 6. Stable Isotopes of Oxygen and Hydrogen

Hydrochemical and isotope studies are frequently included in basement aquifer investigations and give valuable additional information on the structure of the aquifer system i.e. to the aquifer hydrodynamics/groundwater flow regime [23]. In regional studies, hydrochemical and isotope data can be used to distinguish between shallow and deep aquifers [24,25]. They are useful for identifying zones of interaction (mixing) and recharge processes [26,27]. Deuterium and oxygen-18 are influenced by processes affecting the water, rather than the solutes, and can help identify waters that have undergone evaporation, recharge under different climatic conditions than the present, and mixing of waters from different sources. The

isotopic composition of Ikogosi spring waters can be helpful in understanding sources of water and solutes and identifying geochemical reactions of the spring. In this study, ratios of the stable isotopes of oxygen (oxygen-18/oxygen-16, or 18O/16O) and hydrogen (deuterium/hydrogen, or 2H/1H) of Ikogosi spring water samples were investigated. The isotopic composition of oxygen and hydrogen are reported in terms of differences of 18O/16O and D/H (2H/1H) ratios relative to a standard called Standard Mean Ocean Water (SMOW) [28].

$$\delta^{18}\text{O} = \frac{(^{18}\text{O}/^{16}\text{O} - ^{18}\text{O}/^{16}\text{O}_{\text{SMOW}}) \times 10^3}{^{18}\text{O}/^{16}\text{O}_{\text{SMOW}}} \quad (1)$$

$$\delta^2\text{H or } \delta\text{D} = \frac{(^2\text{H}/^1\text{H} - ^2\text{H}/^1\text{H}_{\text{SMOW}}) \times 10^3}{^2\text{H}/^1\text{H}_{\text{SMOW}}} \quad (2)$$

Table 3. Result of Stable Isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) analysis

Code	Location	$\delta^{18}\text{O}$ (‰VSMOW)	$\delta^2\text{H}$ (‰VSMOW)	d-excess
IKW1	Ikogosi	-3.91	-19.56	11.50
IKW2	Ikogosi	-3.87	-19.60	11.40
IKC1	Ikogosi	-3.68	-17.97	11.20
IKC2	Ikogosi	-3.66	-18.00	11.30
IKM1	Ikogosi	-3.81	-18.70	11.80
IKM2	Ikogosi	-4.16	-22.3	11.00
IKBH	Ikogosi	-2.56	-10.8	9.70
	Min	-4.16	-22.30	9.70
	Max	-3.66	-17.97	11.80
	Mean	-3.85	-19.36	11.37
	Median	-3.84	-19.13	11.35
	Stdev	0.18	1.61	0.27

IKW1 – IKW2; Ikogosi warm spring, IKC1 – IKC2; Ikogosi cold spring, IKM1 – IKM2; Ikogosi mixed spring (cold + warm) and IKBH; Ikogosi borehole (not considered for statistical summary).

While positive values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  indicate enrichment when compared to SMOW, the negative values imply depletion of these samples relative to the standard. On the basis of large numbers of meteoric water collected at different latitudes, it has been shown that  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of meteoric water are linearly related as represented by the equation:  $\delta\text{D} = 8\delta^{18}\text{O} + 10$  [28,29]. Data plotted on the meteoric water line suggests that such water is derived from the meteoric origin. Large deviations signify evaporative effects or recharge from other sources. In this study, 7 samples comprising of six (6) water samples from Ikogosi spring and one (1) borehole water sample from the centre of Ikogosi town were analyzed for Oxygen-18 and Deuterium. The results of the stable isotopes compositions, in  $\delta$ -notation along with their statistical summary are presented in Table 4 with all values reported in per mille (‰) with reference to Vienna-SMOW and measurement accuracy of  $\pm 0.15$  for  $\delta^{18}\text{O}$  and  $\pm 1.5$  ‰ for  $\delta^2\text{H}$ . The relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in the classical  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  plot alongside with the global meteoric water line (GMWL) defined by [28] is presented in Figure 8. Such plot usually reveals indications about origin and recharge source(s) of groundwater system as well as possible evaporation effect [30]. The measured  $\delta^2\text{H}$  values of the analysed Ikogosi

spring waters range from -22.30 to -17.97‰ with an average value of -19.36‰ while that of  $\delta^{18}\text{O}$  range from -4.16 to -3.66‰ with an average value of -3.85‰ (Table 3). The result thus presented revealed that Ikogosi spring waters are isotopically depleted. However, the borehole water was equally isotopically depleted but relatively enriched compared with Ikogosi spring. All sampled waters do not only show depletion compared to that of the sea water ( $\delta^2\text{H} = 0$  ‰;  $\delta^{18}\text{O} = 0$  ‰) but also plotted along the GMWL as defined by the equation  $\delta\text{D} = 8\delta^{18}\text{O} + 10$  (Figure 8). The general implication of this is that the origin of waters in the study area can be related to meteoric source i.e. recent precipitation water recharging the associated shallow basement aquifer, with little or no imprint of kinetic evaporation. The result is further supported by the fact that deuterium excess (d-values) are generally in the range of  $10 \pm 2$  i.e. close to 10 which support the observation of recent precipitation with little or no imprint of kinetic evaporation. However, changes in gradient of the straight line of GMWL to a value  $< 8$  as reflected in the Local Meteoric Water line (LMWL) of N'Djamena in Northern part of Nigeria (Figure 8) with  $\delta^2\text{H} = 6.3\delta^{18}\text{O} + 4.4$  [31] which was essentially caused by evaporation during precipitation.

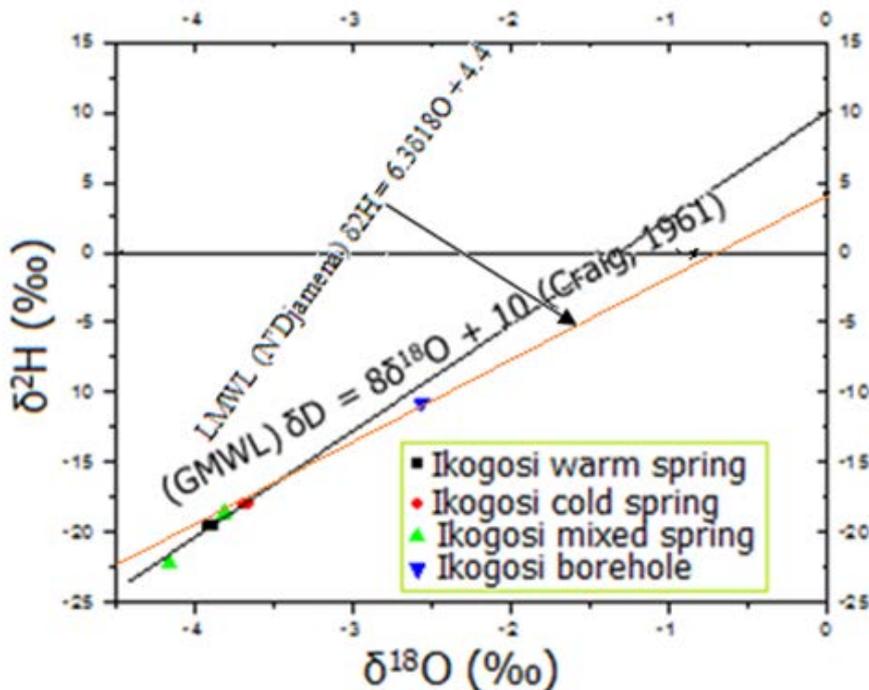


Figure 8.  $\delta^{18}\text{O}$  (‰) vs  $\delta^2\text{H}$  (‰)

## 7. Conclusion

Ikogosi spring has been assessed for hydrochemical and stable isotopes (Oxygen-18 and Deuterium) compositions. The spring is soft, fresh alkaline water with  $\text{TDS} < 1000 \text{ mg/L}$ . The concentration of physiochemical constituents in the spring water samples are within [13] and [14] recommended standards for drinking water quality except in few locations where pH exceeded the value. The concentrations of the major cations for the spring waters (warm, cold and mixed) appear in the order of  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$  while that of the anions vary

with  $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^-$ . The other of trace metal concentrations is  $\text{Fe}^{2+} > \text{Zn}^{4+} > \text{Cu}^{2+} > \text{Mn}^{4+}$ . Rock-water interactions are the dominant processes controlling the major ion composition of Ikogosi spring while the dominant water is Ca (Mg)-Cl type. Stable isotopes analysis revealed that all sampled spring waters are depleted compared to the standard mean ocean water while the cross plot of  $\delta^{18}\text{O}$  (‰) versus  $\delta^2\text{H}$  (‰) plotted on the GMWL signifying recharge from recent precipitation. Conclusively, Ikogosi spring waters have low EC and TDS along with low total hardness (TH) values suggesting a low mineralized soft fresh water system with limited residence time. The stable isotopes analysis revealed

recharge from recent precipitation with no effect of kinematic evaporation.

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