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Chemical Examination of Ikogosi Warm Spring in South Western Nigeria

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Abstract: The chemistry of the Ikogosi Warm Spring in South West Nigeria has been studied. Four out of the six warm spring primary sources show close similarity in temperature, pH, dissolved solids, suspended solid, alkalinity, hardness, SO_4^{2-}, Cl^- and trace metals. All measured values are within classification as fresh water and WHO standards. Further study of the warm spring flow reveal a time (distance) dependent atmospheric environmental induced variations. These variations were made manifest through the optimization of AAS machine parameters such as observation height, PMT voltage, hollow cathode lamp current and optical beam wavelength. A comparison has also been made between the warm spring, a cold stream and the normal ground water of the area through direct and simultaneous measurement of the hiked parameters. Major differences in T, hardness, SO_4^{2-}, Ca, Mg, Na, K, Fe, Zn, Pb and Cd contents imply the existence of unexplored processes on the spring water.

Key words: Warm spring, trace metals, alkalinity, hardness, Ikogosi

INTRODUCTION

The potential of the warm spring water source on the outskirts of the agrarian town of Ikogosi-Ekiti in South-Western Nigeria for recreational, culinary and drinking purposes had been a major source of interest in the past four decades[1]. The Baptist Mission developed the spring for domestic use and constructed a swimming pool there. The Ekiti State Government built a modern conference centre and guest chalets around the spring to encourage tourism. Several proposals on the establishment of a water bottling company to package the water for drinking purposes had been put forward. The stream resulting from the mixing of the warm spring and a cold stream, tributary of the Owena River, is the major source of the cooking and drinking water needs of the over 30,000 inhabitants of Ikogosi-Ekiti town.

Despite its much-vaunted potentials, the quantity of published scientific work on the characteristics and biochemical integrity of the spring water could be described as scanty at best. An attempt was made earlier to determine the physical and chemical properties of the water from the source by Rogers *et al.*[1]. They concluded by attributing its ordinariness and the measured water temperature to the normal geothermal gradient of the area. This finding could be corroborated by geological/radiochemical studies on the abundance and potentials of Hot Dry Rocks (HDR) around the spring area[2,3]. In fact the measured average temperature of the water (38°C) was attributed to the circulation of the normal groundwater to a depth of one to several thousand feet[1]. While such circulation of groundwater has a potential filtering effect, it also offers the possibility of water pollution through weathering of the basement rocks. Chemical species such as CO_3^{2-}, Ca, Mg, Na, K, Fe which have some salutary health effects as well as toxin such as Pb, Cd, SO_4^{2-} and as could easily be introduced into the water through leaching[4].

Before any useful step towards commercialization of the spring source is taken, it is imperative to establish a comprehensive and detailed database of these and other substances to serve as baseline for future environmental impact assessment of such projects in the area. Atomic Absorption Spectrometry (AAS) is particularly suited for analysis of most metals in sample solutions due to its high sensitivity, rapidity and reproducibility. Samples from various points around the spring area have been analysed by this method and some wet chemistry techniques. The procedures adopted and the results obtained are presented in this paper.

MATERIALS AND METHODS

Sampling: The sampling points are presented in Fig. 1. One litre samples were collected in clean white plastic bottles from six points within the site of the warm spring

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Table 1 : AAS analysis conditions for metals in Ikogosi water samples

	Ca	Mg	Na	K	Fe	Zn	Pb	Cd
Wavelength (nm)	423.40	285.70	589.60	767.20	248.80	214.40	217.40	229.30
Slit size (mm)	0.05	0.05	0.25	0.25	0.02	0.05	0.10	0.10
Lamp current (nm)	6.00	3.00	5.00	5.00	8.00	4.00	4.00	2.00
Burner height (a.u)	6.00	7.00	7.00	7.00	6.00	7.00	6.00	7.00
Flame type	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2

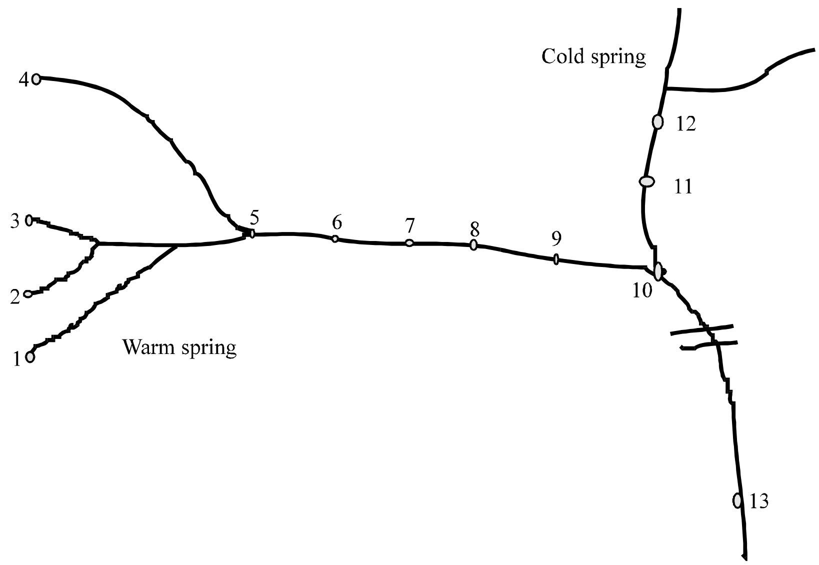

Fig. 1: Schematic representation of the sampling points at the site of the Ikogosi spring source (Not shown in scale)

and one point in the town of Ikogosi. The points are as follows:

- Oozing points of 4 of the active sources.
- Meeting point of all the sources.
- Varying points along the course of the warm stream.
- Two points on the cold stream.
- The mixing point of warm and cold streams
- Two hundred meters downstream the mixing point. (water fetching point for the inhabitants).
- A shallow well downtown Ikogosi.

Sample temperature, was taken immediately on collection using a thermistor while the pH value was also measured using pH_{ep} 3 (Hanna Instruments). The samples were then acidified by addition of 10 mL of conc. HNO_3 (69%) so as to prevent the metals from accumulating on the container walls. All samples were kept at 4°C prior to analysis.

Analysis: The Alpha 4 Atomic Absorption Spectrophotometer (ChemTech Analyticals) of the Centre for Energy Research and Development, Ile-Ife, Nigeria, was used to analyze for Na, Mg, K, Ca, Fe, Zn, Cd and Pb in the samples by flame atomization. The major operating conditions for each element are listed in Table 1. The analytical protocol for these elements in fresh water by AAS is well documented[5,6] and will not be discussed in details here. For this newly acquired instruments however, it is pertinent to note a few machine parameters capable of influencing the quality of results. These are the observation height in the flame, the hollow cathode lamp current, wavelength of the incident optical beam and the applied voltage on the photomultiplier tube. They were adjusted to give the uptima conditions for achieving best results.

Analysis of water samples for Total Dissolved Solid TDS) and Suspended Solid (SS) was done by gravimetric method. Alkalinity, Hardness, Cl^- and SO_4^{2-} concentrations were determined according to the standard procedures[7,8].

RESULTS AND DISCUSSION

Inter-source variation: Analysis of samples from the four designated spring sources out of the six active sources is shown in Table 2 for Ca, Mg, K, Na, Fe, Zn, Cd, Pb, Cl^-, SO_4^{2-}, Hardness (as mg L^{-1} $CaCO_3$), Alkalinity (as mg l^{-1} $CaCO_3$), Total Dissolved solids (TDS) and Suspended Solids (SS). Also presented are Temperature and pH values as measured *in situ*. Generally, the values are comparable for all the four sources with pH varying from 6.1 to 7.0 and Temperature from 35.2 to 37.0°C. The average temperature is 35.9°C while the average pH is 6.6.

Table 2: Measured values of chemical species in warm spring sources 1, 2, 3 and 4

Parameters / Sources	1	2	3	4	Average
T°C	35.80	35.20	35.50	37.00	35.90
pH	6.10	6.80	6.60	7.00	6.60
DS (ppm)	170.00	375.00	178.00	514.00	309.00
SS (ppm)	30.00	25.00	22.00	86.00	41.00
Alkalinity (ppm $CaCO_3$)	49.50	40.00	35.00	51.50	42.70
Hardness (ppm $CaCO_3$)	7.20	6.80	8.60	10.60	8.30
Cl^- (ppm)	10.90	9.00	6.40	5.30	7.90
SO_4^{2-} (ppm)	50.10	30.10	70.00	181.10	84.80
Ca (ppm)	2.67	2.06	2.10	2.28	2.28
Mg (ppm)	4.41	4.32	4.22	4.28	4.31
K (ppm)	0.84	0.73	0.69	0.67	0.73
Na (ppm)	0.71	0.70	0.67	0.69	0.69
Fe (ppm)	0.17	0.13	0.10	0.08	0.12
Zn (ppm)	0.05	0.28	0.09	0.11	0.13
Pb (ppm)	0.017	0.010	0.00	0.000	0.007
Cl (ppm)	0.002	0.004	0.00	0.002	0.003

Table 3: Variation of measured parameters with distance on the course of the warm stream

Parameter / Distance	0 m	10 m	25 m	40 m	50 m
T°C	34.50	34.00	32.00	31.00	30.50
PH	6.60	7.30	7.70	7.80	7.70
DS (ppm)	158.00	186.00	362.00	344.00	354.00
SS (ppm)	42.00	32.00	38.00	56.00	46.00
Alkalinity (ppm $CaCO_3$)	44.00	50.00	40.00	50.00	40.00
Hardness (ppm $CaCO_3$)	8.00	7.60	8.00	7.00	11.20
Cl^- (ppm)	8.15	8.32	8.86	8.61	10.64
SO_4^{2-} (ppm)	82.30	111.10	123.50	161.10	177.00
Ca (ppm)	2.38	2.15	2.44	2.67	2.21
Mg (ppm)	4.41	4.27	4.49	4.71	4.28
K (ppm)	0.68	0.64	0.68	0.68	0.76
Na (ppm)	0.70	0.67	0.68	0.69	0.66
Fe (ppm)	0.17	0.19	0.26	0.59	0.77
Zn (ppm)	1.43	0.72	0.52	0.05	0.05
Pb (ppm)	0.012	0.004	0.005	0.005	0.006
Cd (ppm)	0.003	0.005	0.004	0.008	0.007

Table 4: Comparison of warm spring, with cold stream and groundwater (GW) chemistry from Ikogosi

Parameter	Warm spring	Cold stream	Ground water	Warm/cold	Warm/GW
T. °C	35.90	25.00	28.00	1.44	1.28
PH	6.60	6.90	6.90	0.96	0.96
DS	309.00	91.00	560.00	3.40	0.55
SS	41.00	322.00	40.00	0.13	1.03
Alkalinity	42.70	35.30	30.00	1.21	1.42
Hardness	8.30	6.50	348.80	1.28	0.02
Cl^-	7.90	4.40	3.50	1.80	2.26
SO_4^{2-} X 10^{-2}	84.80	109.80	296.30	0.77	0.29
Ca	2.28	1.81	96.50	1.26	0.01
Mg	4.31	3.02	9.04	1.43	0.48
K	0.73	0.08	39.96	9.13	0.02
Na	0.69	0.67	0.43	1.03	0.07
Fe	0.12	7.63	0.41	0.02	0.29
Zn	0.13	0.04	0.55	3.25	0.24
Pb	0.007	0.014	0.024	0.50	0.29
Cd	0.003	0.003	0.028	1.00	0.11

However, an interesting feature of the results is the observation that measured values of T, pH, DS, SS, Alkalinity, Hardness and SO_4^{2-} are systematically highest in source 4 than the three other studied sources. A visual observation of the sources also shows that source 4 contributes more volume of water to the pool of all the sources. The temperature of this source is 37°C. This is 1.1°C higher than the average Temperature. The difference in temperature between the water from different sources might be due to the different pathways the water took inside the rock to reach the surface[1]. Higher TDS obtained for source 4 might be due to higher temperature as solubility of most salts tend to increase with temperature.

Chemical variations with stream flow: The channeling of the different sources into a single point of warm water over time has created a crater designated as point number

5 in Fig. 1. From this point the warm stream flows eastward at an estimated speed of 2 ft/s. After following this course for a distance of about 60 m, the warm stream joins the cold stream and the resulting stream flows southward. This lukewarm mixture forms the major source of drinking water need of the inhabitants of Ikogosi at a fetching point located at a distance of about 200 m from the warm spring source. The levels of T, pH, TDS, TSS, Alkalinity, Hardness, Cl^-, SO_4^{2-}, Ca, Mg, K, Na, Fe, Zn, Pb and Cd were determined in samples collected from varying points along the course of the warm spring between the pool and the confluence of the warm and cold streams. The results obtained are shown on Table 3 in which certain trends become apparent:

- There is a clear decrease in the values of Temperature and also in the concentrations of Zn and to some extent Pb as the streams flow downhill.
- Obvious increases with distance are observed for pH, TDS, Cl^-, SO_4^{2-}, Fe and to a certain extent Cd.
- Values of TSS, Alkalinity, Hardness, Ca, Mg, K and Na do not vary significantly.

The variation in the chemical composition of the water as it flows downhill could result from the various chemical reactions that take place in water. For example, there is decrease in the concentration of heavy metals such as Zn and Pb which may be as a result of double decomposition reaction which can result in the precipitation of insoluble salts of those metals. Whereas, the concentration of Ca, Mg, K and Na (which are alkali and alkaline earth metals) do not vary significantly as most of their salts are water-soluble.

Comparing the water chemistry of the warm spring, cold stream with groundwater samples: Average values of measured parameters of samples from the 4 warm spring sources, 2 samples collected at 2 points located 20 m apart on the cold stream and 2 replicate samples of groundwater collected from a shallow well (10 m deep) in the middle of Ikogosi town are presented on Table 4. Also presented are the mathematical ratios of the parameters for warm/cold and warm/groundwater for ease of comparison.

A direct comparison of the figures in columns 5 and 6 shows the relationship between the cold, surface stream and the groundwater that recharges the stream during the raining season. Naturally, the level of closeness of the figures to value of 1 is a measure of similarity between the Warm Spring and the cold stream (column 5) and groundwater (column 6). Major similarities between Warm and Cold are noted with respect to pH, Alkalinity, Hardness SO_4^{2-}, Ca, Mg, Na and Cd. Significant variation are observed for T, DS, Cl, K, Zn and particularly Fe and suspended solids. Between the warm spring and the groundwater a close relationship is observed for T, pH, suspended solids and to a lesser extent Dissolved Solids. Major differences are noted for Cl^-, SO_4^{2-}, Mg, Fe, Zn, Pb, Cd and especially Na, K and Ca. The most significant differences between the Cold stream and the Groundwater were measured for dissolved solids suspended solids, Hardness, SO_4^{2-}, Ca, K, Na, Fe and Cd.

Warm water whose average temperature is measured to be about 36°C oozes out of six active sources in the rain forest of Ikogosi town and is thought to result from groundwater finding its way through faults in the bedrock of the area. This high temperature could be explained not only by the normal geothermal gradient expected from such deep circulation but also enhanced by the abundance of Hot-Dry-Rock in the basement[2].

The four studied sources have similar water chemistry and comparable temperature. Measured levels of alkali and alkaline earth metals, trace element (Pb, Zn, Cd) other chemical species (Cl^- and SO_4^{2-}) as well as Dissolved Solids are consistent with what is expected from fresh groundwater[9]. Levels of all the measured chemical species are well below WHO maximum levels for drinking water[10].

The effect of environmental vagaries on the chemical integrity of the spring water could be seen in the evolution of the species with stream flow. The notable increases in values of the pH, TDS, SO_4^{2-}, Fe, Cl^- and Cd could be attributed to environmental contributions to water quality degradation.

Comparing the water chemistry of the warm spring on one hand with those of the cold stream and groundwater from the area on the other shows a number of similarities that tend to support the conclusion of Roger *et al.*[1] on the ordinariness of this spring source. A number of major differences between warm and cold such as those observed for dissolved solids, suspended solids, K and Fe are quite significant and could be attributed to what could normally be expected between rock filtered groundwater (Warm) and ordinary surface water. However, the differences observed between the Warm Spring and the Groundwater are quite interesting. Of particular importance are the differences in Hardness, SO_4^{2-}, Ca, Mg, K, Na, Fe, Pb and Cd. These differences are just too important to be ignored and are at variance with the conclusion of Rogers *et al.*[1] on the sameness of the warm spring and the normal groundwater of the area.

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