

## Hydro-chemical studies for pollution assessment: A case study

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### Abstract

Water is the most abundant liquid on earth which runs steadily to the ocean along vast network of rivers. Rivers are natural courses of water flowing along a bed on the earth towards the ocean and as rivers flow into the ocean, it drains about 60% of the earth's land surface, and transports concentrated minerals and wastes. Water samples taken from ten sites in Oshun River covering the wet and dry seasons were analyzed to understand the seasonal variability of the physico-chemical and heavy metal contents of the river water. Collected water samples were analyzed using Atomic Absorption Spectro-photometer (AAS), Digital Meters and Titration methods. Results of the analyses indicated that all the physico-chemical variables in the River are within the maximum permissible limit set by World Health Organization (WHO) and Nigerian Standard for Drinking Water (NSDW) except turbidity which recorded high values. Oshun river basin exhibited an overall ionic dominance pattern of Na>K>Ca>Mg and HCO<sub>3</sub>>Cl>SO<sub>4</sub>, a pattern which is an intermediate between fresh and sea water systems. Mean concentrations of analyzed ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>) were 14.32, 7.97, 41.73, 14.44, 22.53, 4.31, 10.45 and 57.80 mg/l, respectively.

Characterization of Oshun River water followed the trend:  $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$  and  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . The Pollution Index (PI) value of the River was 0.76.

### **Keywords**

Seasonal variability; Ionic dominance pattern; Pollution Index

## **Introduction**

Rivers are the most important freshwater resource available for man but unfortunately, river waters are being polluted by indiscriminate disposal of sewage, industrial waste and plethora of human activities, which affects their physico-chemical characteristics and microbiological quality [1]. The usual source of drinking water is the streams, rivers, wells and boreholes which are mostly untreated and associated with various health risks [2]. Presently, the menace of water-borne diseases and epidemics still looms large on the horizon of developing countries as a result of lack of accessibility to good quality water. Polluted water has been the cause of all such cases, in which the major sources of pollution are domestic and municipal wastes from urban and industrial activities, runoff from farmland, etc. [3]. Thus, this study deals with the assessment and characterisation of Oshun River Basin water in the south-western part of Nigeria. Student T-test between hydro-chemical parameters has been done with the objective of indicating the nature and the sources of the polluting substances of the River.

Urban runoff worsens the water quality in rivers and lakes by increasing the concentrations of nutrients (phosphorus and nitrogen), sediments, animal wastes (fecal coliform and pathogens), petroleum products, and road salts. Industrial, farming, mining, and forestry activities also significantly affect the quality of rivers as farming can increase the concentration of nutrients, pesticides, and suspended sediments while industrial activities can increase concentrations of metals and toxic chemicals, add suspended sediment, increase temperature, and lower dissolved oxygen in the water [4]. Each of these effects can have a negative impact on the river and make water unsuitable for established or potential uses.

A better representation of the potential problems arising from pollution sources is given by the degree of environmental damage revealed from water quality studies, and it has been remarked that unplanned development has resulted in severe environmental damage and

declining quality of life for many people [5]. Therefore, constant groundwater monitoring of a river system is required to evaluate the effects of environmental factors on water quality for proper utilization and sustainable development of the resource.

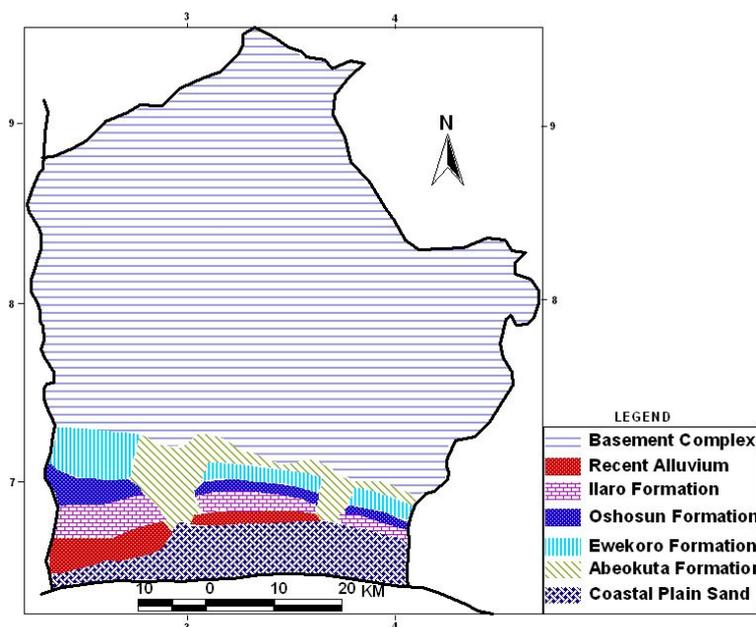
Several studies in Nigeria had identified anthropogenic activities as easy source of water pollution [6-8], this implies that though water is important to life, it is one of the most poorly managed resources in the world. It has also been observed that scarcity of supply of clean water and heavy pollution of fresh water led to a situation in which one-fifth of the developing countries urban dwellers and three quarters of their rural dwelling population do not have access to reasonably safe water supplies [9], while 75% of the population in developing countries lack adequate sanitary facilities thereby dumping most of their waste in the flowing river which resulted to the pollution of the river. Consequently, water related diseases such as cholera, typhoid fever, hepatitis and dysentery are rampant. Therefore, assessment of water is very crucial to safeguard public health and the environment. The main purpose of assessment is to be able to determine the levels of pollutants present in the water.

### **Material and method**

The Oshun River Basin covers an area in Osun, Ogun and Lagos state of Nigeria, it is located between latitudes 6°30'N and 8°20'N and longitudes 3°23'E and 5°10'E. The major drainage system is Oshun River, which rises in the Oke-Mesi ridge about 5 km north of Effon Alaiye on the border between Oyo and Ondo States and flows through the Itawure gap to latitude 7°53'30"N before winding its way first westward through Oshogbo and Ede and then southward to enter the Lagos Lagoon about 8 km east of Epe in Lagos state. The Oshun River is of strategic importance because it is abstracted for water supplies in Ogun, Oshun, and Oyo State. The main tributaries of the river are the Oba, which rises about 15 km north of Ogbomosho in Oyo State, and the Erinle, which rises just south of Offa in Kwara state. The Ona system is located west of the Oshun and comprises the Owa, the Ona, the Ibu and the Omi River systems [10].

The geology of the basin (Figure 1) in the southern part is underlain by sedimentary rocks of cretaceous and later deposits whilst the remainder of the Basin composed of crystalline rocks of the basement Complex that form part of the African Crystalline shield.

The areal distribution of outcrops of the Crystalline Basement varies considerably, as influenced by differential resistance to weathering of the various rock types, presence of laterite or drift from the sedimentary rocks and presence or absence of erosion by streams. Outcrops are variously identified as isolated boulders, large exfoliated domes and inselbergs, and low smooth areas, Fig. 1 shows the geology of the project area.



*Figure 1. Geological map of Ogun-Oshun river basin*

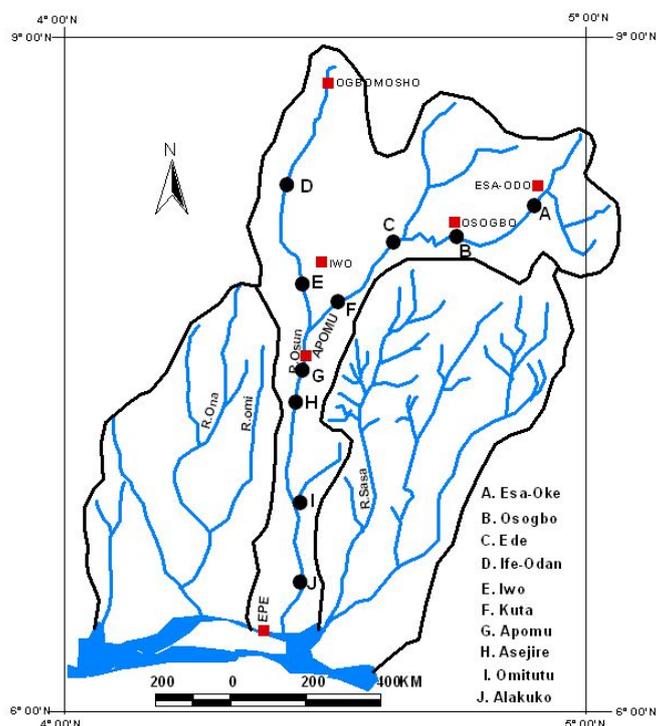
The topography of the Oshun River Basin reflects the contrast between the hummocky terrain underlain by the crystalline rocks to the north with its compact drainage pattern, and the thickly forested undulating hills and swampy lowlands of the sediments to the south. The topography of the Basin overlying the crystalline basement is characterized by a gradually rising elevation from about 30m in the south to about 600m in the north. The relief is moderate with low, forested hills and occasional hog's back quartzite ridges which can be traced for several kilometres.

The larger, older granite masses, and in some places the gneisses and migmatites, create a rugged topography with inselbergs rising abruptly above the surrounding country. The lower basin topography is characterized by two main features, the Ewekoro Depression and the alluvial flood plains. The Ewekoro depression may be described as a low-lying marshy belt, which runs east-southeast across the lower basin about 30m above sea level. The alluvial plain is flanked by the northern and southern uplands lying north and south of the Ewekoro depression, respectively.

The northern uplands consist of plateaux whose surfaces are shaped by the underlying cretaceous sandstones, sloping gently to the south. The southern uplands are characterized by rounded hills separated by deeply incised gullies. In general the wet season occurs from April through October, while a dry season with little or no rainfall occurred between November and March. Seasonal changes in the rainfall of the drainage basin results in alternation of the hydrological regimes of the river. The high water level of the river that arose as a result of the rains made the water flowed unidirectional from July through December.

### *Sample collection and analysis*

Plastic bottles with hard plastic screw caps were used for sample collection. The sampling containers were properly cleaned before use and rinsed with the water to be sampled before sampling. The actual samplings were done in midstream by projecting the mouth of the containers upstream against the flow direction. Three (3) water samples were taken from each selected ten (10) locations repeated five (5) times during the dry and wet season, sample location is on Figure 2.



**Figure 2.** Oshun river basin showing the sampling locations

A thermometer was used for monitoring temperature, while Hatch Camlab pH was used to measure pH, Hanna H198703 Turbidimeter was used to determine turbidity on-site. Other physico-chemical parameters were analyzed in the laboratory using methods prescribed

by APHA. Heavy metals in the water samples were analysed using Atomic Absorption Spectrophotometer (AAS) after pre- concentration [11]. Data generated from the monitoring programme were statistically tested for seasonal variation using the student's t-test.

### ***Determination of the pollution indices of the river***

Mean concentrations of pH, Total Dissolved Solids (TDS), Total Hardness, Magnesium, Sulphate and Chloride in milligram/litre were used to determine the Mean Pollution Index (PI) of the river. This was done using the method developed by [12].

$$PI = \sqrt{(\text{MAXIMUM } C/L)^2 + (\text{MEAN } C/L)^2} / 2$$

where: C = Mean Concentration of the Constituents listed above and L = WHO (2008) permissible levels.

## **Results and discussion**

The results of the physicochemical characteristics of water from the river for dry and wet seasons and statistical analysis of the River water parameters compared with standard recommended water quality criteria are shown in Table 1 while the heavy metal concentrations are presented in Table 2 and their significance in Table 3.

**Table 2.** Heavy metals concentrations (mg/l) in Oshun River water

Sample	Season	Pb	Cd	Cu	Fe	Mn	Zn
Esa- Oke	Wet	0.003	0.003	0.064	2.1	0.076	0.040
	Dry	0.015	0.010	0.075	2.3	1.088	0.094
Osogbo	Wet	0.009	0.003	0.101	2.6	0.200	0.030
	Dry	0.045	0.012	0.342	0.9	0.445	0.020
Ede	Wet	0.035	0.032	0.056	2.4	0.062	0.010
	Dry	0.084	0.018	0.045	1.2	0.210	1.062
Ife Odan	Wet	0.005	0.010	0.027	2.8	0.120	0.025
	Dry	0.026	0.002	0.060	1.3	0.195	0.135
Iwo	Wet	0.025	0.006	0.034	3.2	0.240	0.069
	Dry	0.005	0.014	0.017	2.1	0.165	0.102
Kuta	Wet	0.010	0.003	0.040	2.4	0.076	0.145
	Dry	0.050	0.010	0.066	2.9	1.602	0.015
Apomu	Wet	0.018	0.009	0.040	2.2	0.043	0.018
	Dry	0.134	0.003	0.073	2.2	0.127	0.074
Asejire	Wet	0.009	0.020	0.012	2.9	0.102	0.020
	Dry	0.012	0.001	0.045	1.3	0.080	0.074
Omitutu	Wet	0.010	0.010	0.010	2.2	0.060	0.021
	Dry	0.016	0.003	0.062	1.1	0.123	0.287
Alakuko	Wet	0.003	0.007	0.026	2.1	0.082	0.020
	Dry	0.042	0.010	0.083	1.7	0.106	0.072

**Table 1.** Statistical analysis of Oshun River water parameters compared with standard recommended water quality criteria

Parameters	Range	G.Mean	Std Dev.	CV	T cal	Desirable Limit	Permissible Limit	Organization
Temp°C	27.0-31.50	28.92	1.55	5.37	5.762	30	34	NSDW
Colour (H.U)	1.45-5.68	3.99	1.52	38.14	7.446			
Turbidity (NTU)	6.30-13.90	10.70	2.28	21.33	-2.626	<1	5	WHO, NSDW
Ph	6.10-6.92	6.52	0.29	4.43	9.631	7 – 8.5	6.5 – 9.2	WHO, NSDW
TH (mg/dm <sup>3</sup> )	8.67-20.00	13.22	2.66	20.29	-0.646*	100	500	FEPA, ICMR
DO (mg/dm <sup>3</sup> )	6.50-12.30	10.02	1.62	16.19	0.025*			
TDS (mg/dm <sup>3</sup> )	76.00-123.00	98.83	15.07	15.25	5.024*	500	1500	ICMR
Cl <sup>-</sup> (mg/dm <sup>3</sup> )	13.00-37.00	22.53	8.36	37.11	3.343*	250	600	WHO, NSDW
Po <sub>4</sub> <sup>2-</sup> (mg/dm <sup>3</sup> )	1.30-6.60	4.31	1.17	27.06	0.880*	3.5	6.1	EC
Ca <sup>2+</sup> (mg/dm <sup>3</sup> )	10.08-21.40	14.32	3.65	25.48	2.470*	75	200	ICMR NSDW
K <sup>+</sup> (mg/dm <sup>3</sup> )	11.46-18.34	14.44	9.53	15.68	0.724			
Mg <sup>2+</sup> (mg/dm <sup>3</sup> )	3.47-14.78	7.97	3.05	38.29	-0.529*	30	150	WHO, NSDW
So <sub>4</sub> <sup>2-</sup> (mg/dm <sup>3</sup> )	4.00-18.02	10.45	4.48	42.89	4.818*	-	500	FEPA
Na <sup>+</sup> (mg/dm <sup>3</sup> )	6.76-65.90	41.73	17.53	42.01	-3.958	50	175	WHO
HCO <sub>3</sub> <sup>-</sup>	20.00-100.0	57.80	22.40	38.40	0.666*			
Pb	0.00-0.13	0.028	0.032		-0.380*		0.01	NSDW
Cd	0.00-0.03	0.009	0.008		1.516*		0.05	WHO
Fe	0.90-3.20	2.095	0.069		1.304		0.3	NSDW
Mn	0.04-1.60	0.269	0.656		-0.046		0.05	WHO
Zn	0.01-1.06	0.116	0.391		0.579		3.0	NSDW
Cu	0.01-0.34	0.063	0.232		0.818		0.05	WHO

G. Mean = Grand mean; SD = Standard Deviation; CV = Coefficient of Variation; t cal = t values calculated for test of significant difference between dry and wet season; \*Significant  $p < 0.05$ . WHO: World Health Organization; ISI: Indian Standard Institution; ICMR: Indian council of Medical Research; EC: European Community; EPA: Environmental Protection Agency; FEPA: Federal Environmental Protection Agency; NSDW: Nigerian Standard for Drinking Water

The mean concentrations of pH, Total Dissolved Solids (TDS), Turbidity and Dissolved Solid (DO) of the Oshun River water were 6.52, 98.83, 10.70 and 10.02 mg/l, respectively. All the physico-chemical variables of the River are within the maximum permissible limit set by World Health Organization (WHO) and Nigerian Standard for Drinking Water (NSDW) except turbidity which recorded high values. It is however, noted that the reduced rate of increase in the mean concentrations of all the parameters and a lowering of the pH of the Oshun River Water is a potential hazard if the trend is not checked.

**Table 3.** Statistical analysis of Oshun River water heavy metal parameters

Parameters	Range	Mean	Std Dev.	T cal	NSDW/ WHO
<b>Pb</b>	0.00 - 0.13	0.028	0.032	-0.380*	0.01/NSDW
<b>Cd</b>	0.00 - 0.03	0.009	0.008	1.516*	0.05/WHO
<b>Cu</b>	0.01 - 0.34	0.063	0.069	1.304	0.05/WHO
<b>Fe</b>	0.90 - 3.20	2.095	0.656	-0.046	0.3/NSDW
<b>Mn</b>	0.04 - 1.60	0.269	0.391	0.579	0.05/WHO
<b>Zn</b>	0.01 - 1.06	0.116	0.232	0.818	3.0/NSDW

G. Mean = Grand mean; CV = Coefficient of variation; SD = Standard Deviation;

T cal = t values calculated for test of significant difference between dry and wet season;

\*Significant  $p < 0.05$ , NSDW = Nigerian Standard for Drinking Water, WHO = World Health Organization

### ***Ionic dominance pattern***

The estimated means and standard deviations of major elements (both cations and anions) for the river basins were calculated to examine the overall ionic dominance pattern of the rivers in order to predict the nature and the sources of polluting substances. The Oshun river basin exhibited an overall ionic dominance pattern of Na>K>Ca>Mg and HCO<sub>3</sub>>Cl>SO<sub>4</sub>, the ionic dominance of this river basin was in contrast with the ionic dominance pattern of Ca>Mg>Na>K and HCO<sub>3</sub>>SO<sub>4</sub>>Cl for fresh water and Na>Mg>Ca>K and Cl>SO<sub>4</sub>>HCO<sub>3</sub> for sea water. Thus, like most tropical fresh waters there is a dominance of Na and HCO<sub>3</sub> in the cationic and anionic components, respectively [13].

### ***Major cations and anions***

The mean concentrations of the major cations and anions of the river conform to World Health Organizations standard for safe drinking water. The overall mean values of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> the River were 14.32, 7.97, 14.44 and 41.73 mg/l, respectively while the mean values of HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were 57.70, 22.53, and 10.45 mg/l respectively. Characterization of Oshun river water followed the trend: Na<sup>+</sup>>K<sup>+</sup>>Ca<sup>2+</sup>>Mg<sup>2+</sup> (for the cations) and HCO<sub>3</sub>>Cl>SO<sub>4</sub> (for anions), also showing that the Oshun River water is NaHCO<sub>3</sub> water. The results indicate that the concentrations of the constituent major cations and anions of the river water is generally moderate; this is typical of most tropical African lakes [13]. The nutrient level of the river indicated by the concentrations of phosphates is very low in some of the observed sites; which shows that the river has moderately low eutrophication level.

### ***Pollution index***

The mean Pollution Indices (PI) of Oshun River is 0.76 ( Tables 4 and 5). It has been noted that the critical value of Pollution Index is 1; hence, pollution index of more than 1 indicates very high degree of pollution [12]. However, there is need to monitor the PI value since it is already tending to the critical value of 1. The observed pollution trends in the Oshun River necessitates appropriate monitoring procedures for pollution control and mitigation for a sustainable development of the resource.

### ***Water uses of the rivers***

There are both consumptive and non-consumptive water uses within the study area.

Consumptive water uses include withdrawals of raw water for domestic water supplies, irrigation, and livestock watering. Non consumptive water uses include in stream uses by fish and aquatic life, and recreation and aesthetics.

**Table 4.** Parameters used in calculating Pollution Index

S/No	Parameters Considered	WHO Lower Limit (L)	OShun mean constituent (C2)	OShun (C2/L)
1	pH	6.50	6.52	1.003
2	TDS (mg/l)	500	98.83	0.198
3	Total Hardness(mg/l)	50	13.22	0.264
4	SO <sub>4</sub> <sup>2-</sup> (mg/l)	400	10.45	0.026
5	Cl <sup>-</sup>	250	22.53	0.090
6	Na <sup>+</sup> (mg/l)	50	41.73	0.835
7	Mg <sup>2+</sup> (mg/l)	30	7.97	0.266

**Table 5.** Pollution Index of Oshun River

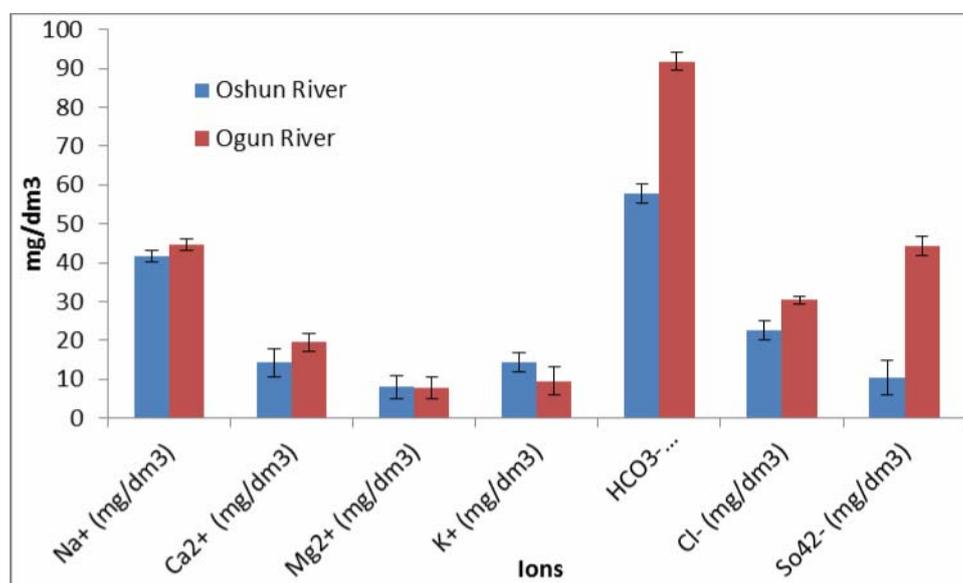
S/No	Parameter	Value
1	Maximum (C/L)	1.003
2	Mean (C/L)	0.383
3	PI Value	0.76

The Rivers and their tributaries provide habitats for a number of important fish species. Aquatic habitats within the watershed also support a variety of resident fish species, aquatic invertebrates, amphibians, reptiles, birds, and mammals. The rivers are also becoming increasingly important for recreational water uses, including swimming, canoeing and bird watching.

#### *Ionic dominance pattern within two basins (Oshun and Ogun river basin)*

The estimated means and standard deviations (Figure 3) of major elements (both cations and anions) for Oshun river basins were calculated to examine the overall ionic dominance pattern of the rivers in order to predict the nature and the sources of polluting substances. The Oshun river basin exhibited an overall ionic dominance pattern of Na>K>Ca>Mg and HCO<sub>3</sub>>Cl>SO<sub>4</sub> while Ogun river basin exhibited an overall ionic dominance pattern of Na>Ca>K> Mg and HCO<sub>3</sub>>SO<sub>4</sub>>Cl, the ionic dominance of these river basins were in contrast with the ionic dominance pattern of Ca>Mg>Na>K and HCO<sub>3</sub>>SO<sub>4</sub>>Cl for fresh water and Na>Mg>Ca>K and Cl>SO<sub>4</sub>>HCO<sub>3</sub> for sea water [13]. Thus, like most tropical fresh waters there is a dominance of Ca and HCO<sub>3</sub> in the cationic and anionic components, respectively [14]. It is apparent that the dominance of chloride over sulphate in Oshun basin could be due to the large amount of domestic wastes being discharged into the river waters. Sodium showed the highest variation within the sampling

period. The high threshold value was due to the high level of domestic activities in the catchment.



**Figure 3.** Mean  $\pm$  standard deviation of ion (mg/dm<sup>3</sup>) in Ogun and Oshun river basin

### Conclusion

Our results indicated that most of the physico-chemical variables of the River are within the maximum permissible limit set by World Health Organization (WHO) and Nigerian Standard for Drinking Water (NSDW). The high turbidity observed in the basin is attributable to poor farming practices which result to large quantities of top soil ending up in the river after heavy rains. Turbidity indicates the presence of organic suspended material which promotes the growth of microorganisms. Nutrient loads in the Oshun River were mainly from domestic, agricultural and commercial activities. The Oshun basin exhibited a general ionic dominance pattern of  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  and  $\text{HCO}_3 > \text{Cl} > \text{SO}_4$ . Both cationic and anionic patterns were intermediate between those of fresh and sea water but the dominance of chloride over sulphate could probably be due to domestic activities resulting from household effluents, fertilizer use and anthropogenic point sources. The observed pollution trends in the Oshun River necessitates appropriate monitoring procedures for pollution control and mitigation for a sustainable development of the resource.

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