



Physicochemical Characteristics and Levels of some Heavy Metals in Selected Waterholes in Old Oyo National Park, Oyo State, Nigeria

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ABSTRACT: Heavy metal contamination is a concern worldwide as it influences the functionality and integrity of ecosystems. The presence of heavy metals in the ecosystem above permissible limits is not desirable as they pose toxic effects to living organisms. Hence, the objective of this paper was to assess the physicochemical characteristics and levels of heavy metals such as cadmium, copper, lead, Chromium, Zinc, Nickel, Iron and manganese in selected waterholes in Old Oyo National Park, Oyo State, Nigeria using Agilent 240FS Flame Atomic Absorption Spectrophotometer (AAS). The mean concentrations of Chromium (0.19 ± 0.08), lead (0.27 ± 0.06), Nickel (0.10 ± 0.01), Cadmium (0.06 ± 0.04), Iron (10.57 ± 4.37) and Manganese (0.49 ± 0.28) were above the permissible limit for both National Safe Drinking Water and World Health Organization (WHO). Except for Copper (0.08 ± 0.03) and Zinc (0.17 ± 0.04) that is below the permissible limit. The study concludes that the sampled waterholes may not be potable and/or safe for drinking; thus, it is recommended that the management of Old Oyo National Park need to intensify efforts on a holistic conservation education and enlightenment programs for the surrounding communities of the park.

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Human environment is exposed to a number of pollutions. One of these is heavy metals Pollution. Although heavy metals occur naturally in the environment with a varying natural background concentrations in soils, rocks, sediments, water and living organisms, anthropogenic contribution results in higher concentrations of these metals relative to the normal background values (Zukal *et al.*, 2015). The pollution of aquatic ecosystems by heavy metals is an important environmental problem, as heavy metals constitute some of the most hazardous substances that can bioaccumulate in various biotic systems (Fernandez- Leborans and Olalla-Herrero,

2000). Bioaccumulation is a process in which a chemical pollutant enters into the body of an organism and is not excreted, but accumulated in the organism's tissues. Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage, while also posing a threat to human health. Cancer and damage of the nervous system have been documented in humans as a result of heavy metal consumption (Van den Broek *et al.*, 2002). Contamination with heavy metals is a serious threat because of their toxicity, bioaccumulation and biomagnification in the food chain. These pollutants often have direct

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physiological toxic effects because they are stored or incorporated in tissues, sometimes permanently (Abd EI-Salam *et al.* 2013). Heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organism and their accumulation over time in the bodies of animals and humans can cause serious ailments. Among all heavy metals, however, cadmium and lead are known as highly toxic (Binkowski 2012). The risk associated with the exposure to heavy metals present in food product have aroused widespread concern in human health. Cadmium is primarily toxic to kidney, especially to proximal tubular cells.

Bone demineralization is affected by cadmium toxicity directly by bone damage and indirectly as results of renal dysfunction (Solidum *et al.* 2013). Overexposure to lead affects the neurological, reproductive, renal, haematological systems. National parks and other conservations areas can be affected by contamination from outside their boundaries just as Old Oyo National Park is being particularly threatened by anthropogenic activities from outside the boundaries. This study therefore assessed the level of heavy metals in selected waters of Old Oyo National Park, Nigeria. Information on the concentration of heavy metal in aquatic environment is quite important. Moreover, the study provides

baseline information on the abundance of some heavy metal contents in rivers of our rural communities adjoining Old Oyo National Park. Hence, the objective of this paper is to assess the physicochemical characteristics and levels of heavy metals such as cadmium, copper, lead, Chromium, Zinc, Nickel, Iron and manganese in selected waterholes in Old Oyo National Park, Oyo State, Nigeria

MATERIALS AND METHODS

Study Area: The park lies between Latitude 8°15' and 9°00'N and Longitude 3° 35' and 4° 42' E. Old Oyo National Park is one of the oldest conservation areas in Nigeria and indeed the West African sub region having been designated upper Ogun Forest Reserve in 1936 and converted to Oyo-Ile Forest Reserve in 1941 and designated Game Reserve in 1952. The sources potentials and the rich cultural and biological diversities informed the Federal Government, decision to elevate the reserve to the status of a National Park by decree No 36 of 1991. It has a total land area of about 2,512 km² and average rainfall of 1,100mm/year. The vast guinea savannah ecotype with luxuriant grass, browse plants species and water supports grazing of ungulates.

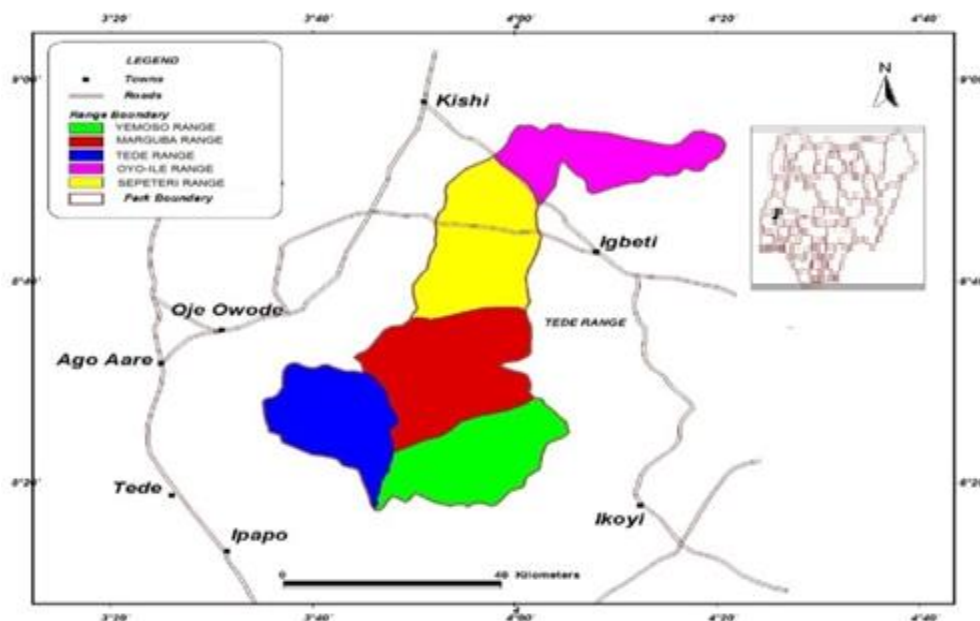


Fig. 1: Map showing Old Oyo National Park

Source: Ogunjimi *et al.*, 2016

Sample collection and treatment: Water samples were collected using the grab sampling technique. The samples were collected from river Ibuya, Oopo, Ayinta and Ogun into sample bottles from different

sampling points (upper, middle and lower course) along the rivers and were subsequently analyzed while the mean of the replicates was appropriately recorded.

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Sample analysis: Water samples were collected from four surface water bodies—Rivers Ibuya, Oopo, Ayinta, and Ogun—using the grab sampling technique, a standard method for field collection of water samples. Each sample was collected into a clean, 1.0 L polyethylene bottle, transported to the laboratory in cool box for digestion and analysis. A volume of 100 mL from each water sample was measured into a 250 mL acid-washed borosilicate glass beaker, and 10 mL of concentrated nitric acid (HNO_3) was added. The beakers were placed on a hot plate inside a fume hood and heated at a temperature of 85–95 °C. The digestion continued until the volume was reduced to approximately 20 mL, and the solution appeared light yellow or clear, indicating effective breakdown of organic materials.

After digestion, samples were allowed to cool to ambient temperature and filtered through filter paper into 100 mL volumetric flasks. The filtrates were made up to volume with deionised water and transferred into clean, labelled polyethylene bottles. The digested samples were stored at 4 °C before analysis. The determination of selected heavy metals: lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), iron (Fe), chromium (Cr), nickel (Ni), manganese (Mn) was carried out using Flame Atomic Absorption Spectrophotometry (FAAS). All measurements were carried out in triplicate, and concentrations were expressed in mg/L.

Statistical data analysis: Mean and standard deviation were calculated and the data were subjected to Analysis of Variance (ANOVA). Statistical significance was set at 0.05 with all the statistical analyses performed with Statistical Package for Social Sciences software (SPSS).

RESULTS AND DISCUSSION

The mean results for physicochemical parameters of the water samples collected during the study period are shown in Tables 2. The water quality observed during this study were compared with World Health Organization (WHO, 2011) and Nigerian Standard for Drinking Water Quality, (2015). The highest pH (8.09 ± 0.078) was observed in Oopo river, Ibuya river recorded highest Temperature (24.85 ± 0.13), The highest conductivity, Total dissolve solid and Hardness was recorded in Ogun river (901 ± 105.14 , 591 ± 69.24 and 198.57 ± 12.31 respectively), Ibuya river recorded highest dissolved oxygen and turbidity (5.25 ± 0.05 and 10.25 ± 0.43). Table 3 reveals the heavy metal concentration in the selected waterholes, the results indicated that the metals (Cr, Pb, Ni, Cd, Fe and Mn) are all above the permissible limit for both NSDQ and WHO. Except for Cu and Zn that is

below the permissible limit according to WHO. Pb recorded the highest concentration across the waterholes while Cu and Cd recorded the least. The concentrations are statistically significant $P > 0.05$. Water has a unique chemical property due to its polarity and hydrogen bonds which makes it able to dissolve, absorb, adsorb or suspend many different compounds. There is an increasing concern about heavy metals contamination in river systems (Ahmad *et al.*, 2009). Wastewaters carry toxic heavy metals that get introduced into the aquatic system through various processes. Sewage and industrial disposal have greatly increased the concentration of heavy metals in the aquatic ecosystems (Rai, 2008). Through rivers and streams, metals are transported as either dissolved species in water or as an integral part of suspended sediments (Duruibe *et al.*, 2007). The results obtained from this study showed that the mean concentration of Fe was highest across the waterholes.

This may be as a result of surface run-off into the water bodies with effluents and anthropogenic discharge of wastewaters from the surrounding communities. This finding is similar to that of Omonona *et al.*, (2018) who reported high level of Fe in River Omo of Omo Forest Reserve. Iron is regarded as one of the essential elements for humans. Approximately 3000 to 5000 mg of iron exists in the human body (Yu, 2000). Therefore, as long as the quantity of iron in the environment is not too large, it may not be harmful to the human body. However, iron can cause undesirable problems in industrial processes or ecosystems if its concentration in water is not managed properly. For example, the precipitates of iron hydroxide may block pipes, create turbidity problems, and iron deposits may act as a source material for an unpleasant taste or odor in water. Thus, excessive iron in water limits the usage of water for drinking or industrial processes. WHO, 2008 has recommended a value of 100mg.

Table 1: Water Sample Codes and Coordinates

River	Sample Code	LATITUDE /LONGITUDE
Ibuya	IW ₁	N08°27'7.316.2 E003°46'26.93
	IW ₂	N08°27'7.316.3 E003°46'26.92
	IW ₃	N08°27'7.316.5 E003°46'26.94
Ayinta	AW ₁	N08°58.321', E003°86.048'
	AW ₂	N08°58.324', E003°86.047'
	AW ₃	N08°58.326', E003°86.050'
Oopo	OW ₁	N008°27'28.3, E003°46.47'
	OW ₂	N008°27'28.5, E003°46.49'
	OW ₃	N008°27'28.6, E003°46.51'
Ogun	OGW ₁	N08°27'16.8, E003°46'35.2
	OGW ₂	N08°27'16.11, E003°46'35.4
	OGW ₃	N08°27'16.12, E003°46'35.5

W₁ – Upper River Courses W₂– Middle River Courses W₃– Lower River Courses

Table 2: Mean Results for Physicochemical Parameter of the Waterholes

Samples	pH	Temp (°C)	Conductivity (µS/cm)	TDS (mg/L)	DO (Mg/L)	Hardness (mg/L)	Turbidity (NTU)
Ibuya	7.91±0.12 ^b	24.85±0.13 ^a	392.55±99.66 ^a	258±69.26 ^b	5.25±0.05 ^{ab}	221.92±28.92 ^c	10.25±0.43 ^b
Ogun	7.12±0.11 ^a	24.50±0.14 ^a	901±105.14 ^b	591±69.24 ^c	5.05±0.11 ^{cd}	198.57±12.31 ^b	8.60±0.21 ^c
Oopo	8.09±0.078 ^b	24.45±0.14 ^a	180.50±38.34 ^a	337±4.63 ^a	5.15±0.09 ^{bc}	174.33±5.54 ^a	9.55±0.25 ^a
Ayinta	7.92±0.089 ^b	24.50±0.16 ^a	304.50±26.42 ^a	328±4.53 ^a	5.35±0.03 ^a	184.49±16.49 ^{bc}	6.90±0.26 ^c
Old Oyo National Park	7.76±0.39	24.57±0.16	444.88±286.65	378.25±132.17	5.20±0.11	194.82±18.64	8.75±1.44
NSDWQ	6.5-8.5	Ambient	1000	500	-	150	5.0
WHO	6.5-8.5	25-30	1000	500	2.0-5.0	—	5.0

Key: DO: Dissolved Oxygen, TDS: Total Dissolved Solid. Mean±SD

Superscripts with the same letters in each column are not significantly different ($P \geq 0.05$)

**World Health Organization, (2011). *Nigerian Standard for Drinking Water Quality, (2015)

Table 3: Heavy Metal Concentrations in Selected Waterholes in Old Oyo National Park

Heavy metals (mg/l)	Ibuya	Ogun	Oopo	Ayinta	Old Oyo National Park	NSDWQ (2015) Guideline for Drinking Water	WHO (2011) Guideline for Drinking Water
Cu	0.05±0.02 ^a	0.14±0.09 ^{ab}	0.07±0.03 ^b	0.08±0.03 ^b	0.085±0.03	1.0	1.5
Zn	0.12±0.05 ^a	0.17±0.07 ^b	0.24±0.13 ^b	0.15±0.07 ^c	0.17±0.04	3.0	5.0
Cr	0.08±0.6a	0.27±0.13 ^a	0.23±0.09 ^a	BDL	0.19±0.08	0.05	0.05
Pb	0.29±0.19 ^a	0.18±0.06 ^a	0.26±0.11 ^b	0.35±0.21 ^a	0.27±0.06	0.005	0.01
Ni	0.12±0.03 ^a	BDL	BDL	0.09±0.01 ^c	0.10±0.01	0.02	0.07
Cd	0.03±0.01 ^a	BDL	0.12±0.06 ^b	0.04±0.01 ^a	0.06±0.04	0.003	0.005
Fe	17.05±0.09 ^c	8.13±0.01 ^b	11.23±0.07 ^a	5.90±0.03 ^b	10.57±4.37	0.3	0.3
Mn	0.69±0.27 ^c	0.28±0.13 ^b	0.83±0.42 ^{ab}	0.17±0.11 ^a	0.49±0.28	0.4	0.4

Note: Mean values ± standard deviation in a row followed by similar superscripts are not significantly different at ($P > 0.05$) WHO: World Health Organization, NSDWQ: National Safe Drinking Water Quality; BDL: Below Detectable Limit

The iron transport capacity of a river has also been reported to be closely related to the vegetation types in its watershed. The mean concentration of Cr was discovered to be the lowest in the sampled rivers. This may be due to low industrial effluent discharge into most of the waterholes sampled. Chromium may catalyze diabetes-induced effects on kidneys. Kidney damage may further progress to end stage renal disease (ESRD) and death if exposure is high and prolonged. Recent investigations show that Cr may also play a role in the development of other cancers, such as testicular cancer, bladder cancer, pancreatic cancer and cancer of the gall bladder (Deng *et al.* 2019). The levels of Cr detected in all water samples however, pose no toxicological risk to consumers. The high concentration of heavy metals obtained in the study may be due to agricultural run-off, leaching of fertilizers and effluent discharge into the sample water from outside the boundaries of the park. Omonona *et al.*, (2018) reported similar findings in Omo Forest reserve.

Dominant anthropogenic activities like agriculture, charcoal production and illegal mining might contributed to mean level of the metals. The mean concentrations of the heavy metals were found to exceed the NSDWQ (2015) and WHO (2011) permissible limits. This implies that the sampled rivers are not portable or safe for drinking. It is

spread by air and water (sewage sludge) far over sea and land, but especially in the vicinity of heavy industrial plants and hence absorbed by many plants and sea organisms. When animal drink from these water bodies they possess bioaccumulation metals in their tissue and this could lead to disruptive behavior and reduction in disease resistance and affect other physiological processes (Dauwe *et al.*, 2006) posing threats to species perpetuation and decline in species population. Contamination with heavy metals is a serious threat to wildlife due to their toxicity, bioaccumulation and biomagnification within the food chain (Demirezen and Aksoy, 2004).

Conclusion: The trends of heavy metal levels in this study are a pointer to contamination of the ecosystem with possible health implication on game animal. The concentration of heavy metals analysed in the sample waterholes were above the permissible limits except for copper, as such the waterholes may not be potable or safe for drinking. It is therefore recommended that the management of Old Oyo National Park need to intensify efforts on a holistic conservation education and enlightenment programs for the surrounding communities of the park. The use of phytoremediation method to remediate heavy metals in the sampled waterholes is necessary.

Declaration of conflict of interest: The authors declare no conflict of interest.

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Data Availability: Data are available upon request from the second author (ALAYE, SA).

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