ABSTRACT

There are thirty-five (35) metals with public health implications due to occupational or residential exposure; twenty-three (23) of these are called heavy elements or metals. They are Antimony, Arsenic, Bismuth, Cadmium, Cerium, Chromium, Cobalt, Copper, Gallium, Gold, Iron, Lead, Manganese, Mercury, Nickel, Platinum, Silver, Tellurium, Thallium, Tin, Uranium, Vanadium, and Zinc. Interestingly, minute amount of these elements are common in our environment and diet and are actually necessary for a balanced health, but increased consumption may cause acute or chronic toxicity (poisoning). Allergies are not uncommon and repeated long-term exposure to these metals such as Zinc, Lead, Chromium, Selenium, Nickel, Cobalt and Cadmium may cause cancer. The alarming perceived increase of these pollutants around the south-western regions of Nigeria have necessitated the need to evaluate water and sediment samples of Osun river, popularly known for its cultural practices and activities. The physicochemical properties of samples such as pH, TDS EC, Total Dissolved Solid (TDS), Conductivity, Total Hardness, Sodium, Potassium, Phosphate, Nitrate, Chloride were analyzed and result showed compliance with recommended WHO standards. Trace and heavy metal composition in water using standard methods indicates the presence of Calcium (5.11±0.04ppm), Magnesium (0.54±0.004ppm), Potassium (1.28±0.01ppm) and Iron (0.05±0.00ppm) while sediment sample contained high composition of Zinc (21.99±2.67ppm), Iron (261.6±2.00ppm) and Manganese (105.6+0.50ppm). Results obtained from proximate analysis of both water and sediment samples, shows that there are no heavy metals presence in Osun River that could pose a threat to public health. Rather, there are more minerals and nutrients in availability which implies that water sample lacks considerable pollutants and can be certified healthy for moderate consumption and domestic uses which is within permissible value limits of WHO standards.

Keywords: heavy metal, pollutant, water, sediments, Osun river
INTRODUCTION

Heavy metal contamination has been a major challenge in every continent of the world. In Nigeria, due to the increasing number of industries and oil pumps, there has been constant assessment of water bodies per time in order to avoid diseases and illnesses caused by contamination of water bodies. Heavy metals have negative impacts on ecological stability of water ecosystems due to chronic environmental stress and bioaccumulation. They cause fish growth disturbances, reproduction failure, immune-suppression (Stave and Roberson 1985), histopathological changes in fish skin, gills, liver and kidneys and skeleton deformations (Sloof 1982; Hinton and Laurén 1990). Exposure of fish to heavy metals can cause metallothionein synthesis in the liver, kidneys and gills, and these metals can thus infiltrate the fish body directly by these non-alimentary routes (Hamilton and Mehrle 1986). In addition, copper and mercury slow down fish metabolism resulting from gill damage and enormous mucus secretion (Rice 1990). Heavy metal harmfulness in humans can bring about reduced mental and central nervous function, lower vitality levels, harm to blood synthesis, lungs, kidney, liver, and other essential organs. Long term accumulation may bring about progressive muscular and neurological degenerative cycles that impersonate Alzheimer's sickness, Parkinson's disease, strong dystrophy, and numerous sclerosis.

These metals may accumulate to a very high toxic levels causing acute impact on aquatic organisms without any immediate observable signs (Giguère et al., 2004). Presence of heavy metals is an indication of pollution in any aquatic environment and the toxicity of these metals’ stems are biologically non-degradable and have the tendency to percolate in water and bioaccumulate in fish bodies (Gale et al., 2004). Heavy metals are accumulated and biologically magnified in fish tissues (Ayas et al., 2007). The investigation of heavy metals in water and sediment might be used to assess the anthropogenic and industrial impacts and risks posed by waste discharges in riverine ecosystems. (Zheng et al., 2008).

The Oṣun River (sometimes, but rarely spelt Oshun) is a river that flows southwards through the central Yoruba land in southwestern Nigeria into the Lagos Lagoon and the Atlantic Gulf of Guinea. The number of fisheries, dockyards, shipyards and factories over the years have increased significantly across the country which possibly could contribute to contamination of aquatic life. The polluting industries such as chemical complexes, fish processing plants, steel and paper mills, rayon mill complexes, cement factories, paint and dye manufacturing plants, several soap and detergent factories and a number of light industrial units directly discharge untreated toxic effluent in to the water bodies. Besides, the release of untreated toxic effluents are the major sources of heavy metals in any aquatic ecosystem. Unfortunately, very little research has been conducted to assess the level of metal pollution of the Osun River mainly in Osogbo including its biotic resources, sediment and water quality. The site of study is at Osogbo where the mystic belief of Osun river goddess is proposed to have emerged and also celebrated yearly as the culture and heritage of indigenes till date. Therefore, the study was carried out with an objective to assess physico-chemical properties of samples, the necessary nutrients and presence of trace/heavy metals i.e. Lead (Pb), Cadmium (Cd), Chromium (Cr), Zinc (Zn), Cobalt (Co), Selenium (Se), Nickel (Ni), Copper (Cu), Iron (Fe), Magnesium (Mg), Manganese (Mn), Potassium (K), Sodium (Na), Calcium (Ca) in water and sediment of the Osun River which is traditionally known as a herb for the cure and treatment of diseases.
MATERIALS AND METHODS

SAMPLING AND SAMPLE PREPARATION
Water and sediment samples were obtained five (5) times (from July 2018 to April 2019) for every 2 months from five sites in the river. The sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface. About 0.5 L of the water samples were taken at each sampling site. Sediment samples were collected using grab sampler from five sites. Samples were transported to the laboratory and air-dried in the laboratory at room temperature. Once air-dried, sediment samples were powdered and passed through 160 µm sieve. The sieved samples were packed in polyethylene bags and stored below −20°C prior to analysis. Sediments samples were weighed, placed into the digestion bombs with 10 mL of HNO₃/HCl (1:3 v/v) and digested in a microwave digestion system. Sediments analysis was carried out according to the procedure described earlier.

The samples gathered were preserved and the analysis of various physico-chemical parameters was performed in the laboratory. pH, total dissolved solid (TDS), conductivity, salinity, total hardness, Alkalinity sodium, potassium, phosphate, nitrate, and exchangeable acidity of surface water and sediments were determined using IITA analytical standard methods. Organic matter in sediment was determined by measuring weight loss after burning in a preheated muffle furnace at 450°C for 4hrs. Sediment pH was measured in a suspension of 10g of sediment in 25mL deionized water after shaking for 2hrs using a digital pH meter.

Instrumental calibration was carried out prior to metal determination by using standard solutions of metal ion prepared from salts. Commercial annular grade 1000ppm stock solutions of Zn, Cr, Pb Fe, Ni, Co, Cd were diluted in 25cm³ standard flask and made up to the mark with deionized water to obtain working standard solutions of 2.0ppm, 3.0ppm and 4.0ppm of each metal ion using atomic absorption spectrophotometer. The essence of the digestion before analysis was to reduce organic matter interference and convert metal to a form that can be analyzed by AAS.

RESULTS AND DISCUSSION
The physico-chemical parameters of water and sediments such as pH, electric conductivity, alkalinity, dissolved oxygen, total dissolve solid, calcium, magnesium, chloride, nitrate and phosphate, sodium, potassium, and organic matter, were analyzed for the water and sediments samples collected from the Osun River. The samples were taken from five different sites during different months of the year. All parameters with the mean value of the data with standard error were calculated as shown in the Tables below. Correlation of matrix of physico-chemical characteristics of water and sediment samples shows positive variance.

As shown in figure 1, sediments with grain size dominates, sediment is said to be sandy with 84%, less silky and clayey with no organic carbon present. pH is one of the most important factors that serve as an index of pollution. Sediment pH in sampling is in acidic condition which makes it good and based on texture and composition, could be used as a raw material for constructions. Figure 3 show the high concentration of Magnesium and Calcium needed for the nutritious value of the aquatic life according to WHO standard. High level of Iron 261.6±2.00 and Manganese
105.6+0.50 is of no exemption which contributes to why edible foods in water bodies are more nutritious in Osun River. Ammonia, nitrate was not detected and can be said to be absent in Osun River sediment composition.

Table 1: Sediment Composition in Osun River

| SAMPLES       | PH(H2O) 1:1 | PH(KCl) 1:1 | %OC    | %N     | %SAND | %SILK | %CLAY |
|---------------|-------------|-------------|--------|--------|-------|-------|-------|
| MEAN/S. D.    | 6.70±0.07   | 6.06±0.20   | 0.60±0.20 | 0.06±0.03 | 84±1.00 | 6±1.73 | 10±0.94 |

Table 2a: Proximate analysis of Mineral/Heavy metals in Sediments of Osun River

| SAMPLES       | Ca (ppm)   | Mg (ppm)   | K (ppm)  | Na (ppm) | Exch. Acidity | ECEC |
|---------------|------------|------------|----------|----------|---------------|------|
| MEAN/S. D.    | 21.99±2.67 | 1.00±0.20  | 105.6+0.50 | 261.6±2.00 | 1.43±0.07     | 0.13±0.02 | 2.55±0.02 |

Table 2b: Proximate analysis of Mineral/Heavy metals in Sediments of Osun River (Contd.)

| SAMPLES       | Zn (ppm) | Cu (ppm) | Mn (ppm) | Fe (ppm) | NO₃-N | NH₄-N | Michelle P |
|---------------|----------|----------|----------|----------|-------|-------|------------|
| MEAN/S. D.    | 2.07±1.10 | 0.73±0.40 | 0.15±0.01 | 0.1±0.004 | 0.00  | 3.07±1.67 |            |

Figure 1: Physico-chemical Properties of Sediments in Osun River
Figure 2: Proximate Composition of Exchangeable Cations

Figure 3: Trace/Heavy Metal Composition of Sediments in Osun River
Table 3: Chemical Analysis of Water

| SAMPLES | pH   | Elec. Cond. | T | TDS | TH | NO$_3$-N (ppm) | NH$_4$-N (ppm) | PO$_4$-P (ppm) |
|---------|------|-------------|---|-----|----|----------------|----------------|----------------|
| MEAN/S. D. | 7.08±0.04 | 91.6±0.01 | 0.00 | 122.60 | 14.96±0.02 | 0.83±0.03 | 0.12±0.01 | 0.73±0.01 |

Table 4a: Trace/ Heavy Metal Composition

| SAMPLES | Ca | Mg | K | Na | Fe | Cu |
|---------|----|----|----|----|----|----|
| MEAN/S. D. (ppm) | 5.11±0.04 | 0.54±0.004 | 1.28±0.01 | ND | 0.05±0.00 | ND |

Table 4b: Trace/ Heavy Metal Composition Contd.

| SAMPLES | Zn | Pb | Cr | Se | Co | Cd |
|---------|----|----|----|----|----|----|
| MEAN/S.D. (ppm) | 0.01±0.00 | ND | ND | 0.03±0.00 | ND | 0.01±0.00 |

Figure 4: Proximate Analysis of Minerals/Heavy Metals in Water Bodies
The hardness of the water and sediments is not a direct pollution indicator but indicates the quality of the water and sediments in terms of calcium and magnesium. The hardness is governed by the carbonates and bicarbonates of calcium and magnesium and other ions. Calcium and magnesium accounted for most of the hardness in the river. Water samples indicates the presence of calcium 5.11±0.04 and Magnesium 0.54±0.004. Potassium occurs naturally in ground water by weathering of rocks and is very essential mineral for the plants and human health. The maximum potassium content in water was observed to be 1.28±0.01. With the result above, it was made evident that no trace of heavy metal is present in Osun river. So, it could be concluded that the water is free from industrial waste and effluent discharge. All results are within standards of the WHO (1993), EPA (2002), EC (1998), WPCL (2004), and NOAA (2009) quality control value-limits.

CONCLUSION

From the results of proximate analysis of both water and sediment samples, there are no heavy metals presence in Osun River that could pose a threat to public health. Rather, there are more minerals and nutrients available which implies that water sample could be considered healthy for moderate consumption and domestic activities. Sediments in Osun River is very sandy and can be best used for construction which also contributes to the wellbeing of its aquatic life. Based on the research, Osun River and its aquatic food is free of toxicity and can be recommended for adequate consumption. Further work and analysis should be carried out on Osun River to support these postulates. Effective and efficient study will make River Osun not just a centre of cultural attraction but a means to reduce and cure human numerous diseases due to its available nutrients/minerals in aquatic foods and plants.
REFERENCES

Ayas Z., Ekmekci G., Yerli S.V. and Ozmen M. (2007). Heavy metal accumulation in water, sediments and fishes of Nallihan Bird Paradise, Turkey. Journal of Environmental Biology. 28: 545-549.

Gale N.L., Adams C.D., Wixson B.G., Loftin K.A. and Huang Y.W. (2004). Lead, zinc, copper, and cadmium in fish and sediments from the Big River and Flat River Creek of Missouri's Old Lead Belt. Environmental Geochemistry and Health. 26: 37-49.

Giguère A.P.G., Campbell L., Hare D., McDonald G. and Rasmussen J.B. (2004). Influence of lake chemistry and fish age on cadmium, copper, and zinc concentrations in various organs of indigenous yellow perch (Perca flavescens). Canadian Journal of Fisheries and Aquatic Sciences. 61(9), 1702-1716.

Hamilton S.J. and Mehrle P.M. (1986). Metallothionein in fish: review of its importance in assessing stress from metal contaminants. Transactions of the American Fishery Society 115: 596-609.

NOAA (National Oceanic and Atmospheric Administration), (2009). SQUIRT, Screening Quick Reference Tables for in Sediment, Retrieved on 23rd March 2009 from http://response.restoration.noaa.gov/bookshelf/122_NEW-SQuiRTs.pdf

Rice J. A. (1990). Bioenergetics modeling approaches to evaluation of stress in fish. Biological indicators of stress in fish 8. American Fisheries Society Symposium, Maryland. 80-92

Sloof W. (1982). Skeletal anomalies in fish from polluted surface waters. Aquatic Toxicology. 2: 157-173

Stave J.W. and Roberson, B.S. (1985). Hydrocortisone suppresses the chemiluminescent response of striped bass phagocytes. Developmental and Comparative Immunology, 9: 77-84.

World Health Organization (1993). Guidelines for drinking water quality. Recommendations, vol. 1, Chemical Aspects (2nd ed., pp. 40-57). Geneva.

WPCL (Water Pollution Control Legislation), (2004). Land Based Water Quality Classification, Official Journal, 25687, Turkey.

Zheng N.A., Wang Q., Liang Z. and Zheng D. (2008). Characterization of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. Environmental Pollution. 154: 135-142.