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Evaluation of Heavy Metals Level and their Potential Effects to Water, Sediment, and Water Hyacinth Plants in Opa Reservoir, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria

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ABSTRACT: The contamination of the aquatic ecosystem with heavy metals has become a rising global concern due to their possible adverse health effects on human beings and the environment. Hence, the objective of this paper was to evaluate the levels of Fe, Cu, Cd, Zn, Pb, As, and Cr and their potential effects on water, sediment, and water hyacinth plants in Opa Reservoir, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria using Atomic Absorption Spectrometry. The concentration of heavy metals in the hyacinth samples varied from 0.002 ± 0.000ppm to 0.5 ± 0.000ppm exceeding permissible limit except for Cu, Zn, and Fe. The metals in water samples ranged between 0.003 ± 0.001ppm to 0.5 ± 0.000ppm also surpassing the concentration limit established by WHO with only Cu, Zn, and Fe having lower concentrations. Sediment samples revealed a high concentration, varying from 0.005 ± 0.000ppm to 4.150 ± 0.002ppm. The values obtained were far above the permissible values set by WHO with only Zn, Fe, and As having lower concentrations. The contamination factor analysis indicated generally low contamination factor with the exception of Fe and Cr which showed moderate contamination. Although the pollution load index and geo accumulation index revealed that all metals were within the range of unpolluted geo-accumulation index, enrichment factor indicated varying degrees of contamination. While some metals exhibited depletion to minimal enrichment, others revealed significant or even extremely high enrichment pollution index. Considering the pollution status of the Opa reservoir, it is therefore recommended that regular monitoring of the reservoir be put in place to ensure the safety of human and aquatic ecosystems in general.

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One of the focal research areas of study at present time is water pollution. Water is an extremely important resource, particularly surface water like rivers, for meeting the needs of humans, industries, and animals (Nnamonu *et al*., 2015). The importance of water to human being and other biological systems cannot be over-emphasized, and there are several scientific and economic realities that, shortage of water or its pollution can result to a severe reduction in productivity and deaths of living species (Galadima *et*

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al., 2011). The presence of metal pollution in an aquatic environment can be assessed by analyzing both the abiotic components (water and sediment) and biotic components (plants and animals) of the ecosystem (Hamed and Emara, 2006). Monitoring metal concentrations in water is essential, especially considering that humans consume fish which can accumulate these metals. In the same vein, studying the metal concentration in sediment is important because sediment serves as a source or storage of chemicals in the water, often containing higher metal concentrations than the water column itself (Ndimele and Owodeinde, 2021). Pollutants are being discharged into aquatic ecosystems and finally leaching into the soil calling for serious attention due to its hazardous effect on the environment and human health. The contamination of heavy metals is a significant environmental subject of research because of its bioaccumulation possibility (Ebol *et al*., 2020). When municipal, agricultural, and industrial wastes enter the water, they bring biological and chemical contaminants, including heavy metals (Nnamonu *et al*., 2015). The contamination of aquatic ecosystems with heavy metals has become a rising concern globally owing to their probable adverse effects on human health and the environment. Pollution of the aquatic eco-system occurs when harmful substances find their ways into water bodies, threatening human health and the natural ecosystem (Galadima *et al*., 2011). Hence, the idea of incessant monitoring of water quality receives global attention (Butu and Iguisi, 2012). The quality of water differs from source to source which is mainly influenced by natural and human factors (Khatri *et al*., 2015). One such factor is the various concentrations of heavy metal present in water which could be a result of variations in geological and geographical factors. Sediments are vital constituents of the aquatic ecosystem and play crucial part in maintaining the trophic status of aquatic bodies (Singh *et al*., 1997). Sediments located around urban areas often contain high concentration of contaminants due to runoff from roads, industries and sewage systems posing a significant environmental challenge for anthropogenically impacted aquatic environments (Magalhaes *et al*., 2007). In addition to influencing pollution, sediments in rivers also serve as historical records of pollution events. They are known to be carriers and sources of contaminants in the aquatic body (Shuhaimi, 2008). The pollution of sediments with heavy metals can lead to severe environmental hazards (Loizidou *et al*., 1992). Heavy metals can either adsorb onto sediments or accumulate in benthic organisms and their bioavailability and harmful nature is subject to the different forms and quantities bound to the sediment matrices (Chukwujindu *et a*l., 2007).

Water hyacinth is a fast growing, perennial aquatic plant and persists throughout the year. It is considered a harmful freshwater weed due to its vigorous root system and is recognized as one of the major aquatic problems worldwide (Malik, 2007; Gichuki *et al*., 2012). The plant is notorious for its rapid reproduction, doubling its population every twelve days (Lissy and Madhu, 2010). Aquatic hyacinths are plant that contains important nutrients and a significant amount of fermentable materials, making it potentially valuable. However, it is also recognized for its ability to accumulate substantial concentrations of heavy metals from polluted water sources (Matindi, 2016). Therefore, the objective of this paper was to evaluate the levels of Fe, Cu, Cd, Zn, Pb, As, and Cr and their potential effects on water, sediment, and water hyacinths in Opa Reservoir, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria.

MATERIALS AND METHOD

Brief Description of Study Area: Opa Reservoir is located within the Obafemi Awolowo University, Ile-Ife, Nigeria. According to Akinbuwa and Adeniyi, (1996) as described by Adedeji *et al*., (2020) was established in 1978 by the impoundment of the Opa River, which has its source in Oke-Opa, a series of hills on the eastern side of the Ife-Ilesha road. Several streams unite to form the Opa River, the major ones being the Rivers Amuta, Obudu, and Esinmirin. The surface area of the Reservoir is about 0.95 km^2 while the maximum capacity is about $675{,}000m^3$. The minimum depth is 1.01m while the maximum depth is 6.01m; at this level storage is about $389{,}000m^3$. The reservoir was primarily created to supply potable water to the University community hence fishing activities are permitted only for recreational and research purposes. It has a catchment area of about $116km^2$ extending in width from longitude 004˚31 to 004˚ 39΄E, and in length from latitude 07˚21 to 7˚35΄N.

Sample Collection: Samples of water, sediment, and hyacinth samples were collected from six sampling points along the river (Figure 1) into plastic bottles, and polyethylene bags respectively. They were properly labeled to prevent sample mix-up. Each plastic sample container was first rinsed with the sampled water to avoid any external contamination. The water samples were acidified with 5ml of conc. HNO_3 to prevent ionic changes and upsurge of organic materials as well as to ensure that the individual metallic ions remain in solution pending analysis. The samples were transferred to the laboratory at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife.

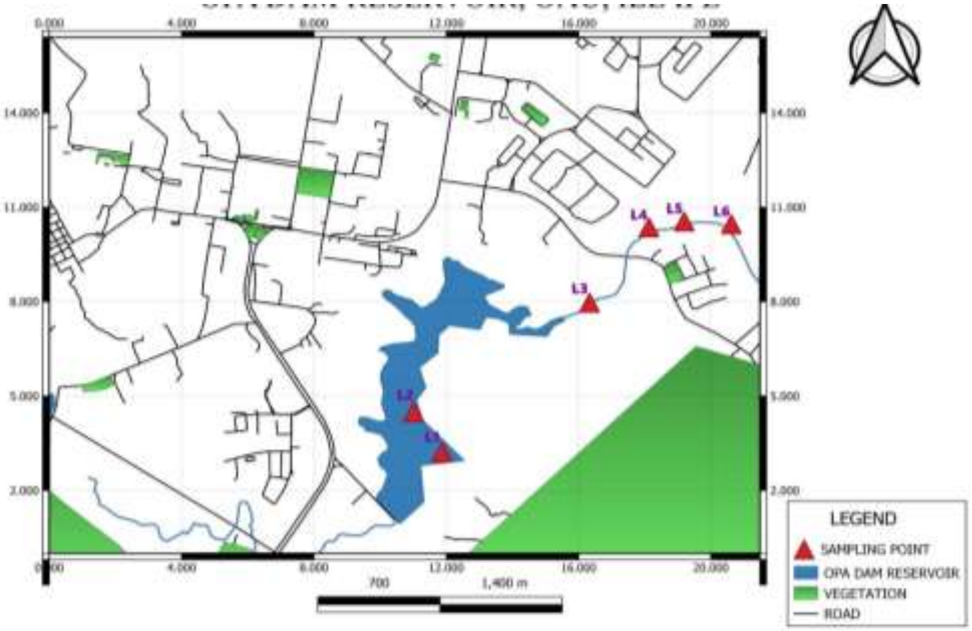

Fig 1: Map showing the sampling points on the Reservoir

Digestion of water sample for AAS analysis: The water samples were digested using standard methods by APHA *et al.* (1992). A 100 mL sample was measured and transferred into a beaker. For the metals to be analyzed, 5 mL of concentrated HNO_3 was added. The sample was heated on a hot plate at a temperature of 90 to 95 ^oC until the volume was reduced to 15-20 ml. The solution was allowed to cool and the beaker walls were rinsed with water. The final volume was adjusted to 100 mL with distilled water. The metal concentration in the digested water samples was determined using a Perkin Elmer 400 Atomic Absorption Spectrophotometer (AAS). This machine operated based on instrumental conditions for the determination of seven (7) heavy metals viz: Cu, Zn, Fe, Cr, Cd, As and Pb by flame atomization, using air-acetylene flame and single element hollow cathode lamp.

Digestion of plant samples for AAS Analysis: The digestion method employed in this study was wet digestion (HNO_3 /H_2O_2). About 0.5 g of each ground plant sample was placed in a 250ml dry flask with the addition of about 5ml of HNO_3 making the material wet. Afterward, about 4ml of 33% H_2O_2 was carefully added in a well-ventilated hood and slightly stirred. This mixture was heated on a hot plate for 10 minutes till a strong effervescence occurred. Then, the solution was allowed to cool, a slightly yellow and small white solid quantity in suspension remained. The solution was filtered, using a Whatman filter paper and diluted up to mark in a 25ml standard flask with distilled water. The prepared solution was transferred into well-cleaned labeled sample bottles for heavy metal determination using the Atomic Absorption Spectrophotometer (AAS).

Sediment sample preparation for AAS: The wet sediment samples were air dried in the laboratory, large lumps and rocky granules were removed and the remainder was ground into finer particles. Two (2) grams of the sediment sample were placed in a beaker with the addition of 5ml HNO_3, 2ml of $HClO_4$, and 5ml HF. The solution was heated for one hour on a hot-plate at 160^{o}C. After proper digestion, the sample was allowed to cool and then, filtered. The filtrate was transferred into a 100ml volumetric flask and made up to 50ml mark with distilled water. The prepared sample solution was transferred into pre-cleaned labeled sample bottles for Atomic Absorption Spectrometer (AAS) analysis.

Sediment Pollution Analysis: The metal concentrations in the sediment samples were subjected to pollution indices such as contamination factor, geo-accumulation index, enrichment factor, and pollution load index.

Assessment According to Contamination Factor (C_f): The contamination factor (C_f) was used to determine the contamination status of sediment in the present study. Contamination factor values for describing the contamination level are described below. The contamination factor was calculated using the relationship;

$$Cf = Cmetal \,/\, Cbackground \;\ldots\ldots (1)$$

Where the background value of the metal was supplied by Turekian and Wedepohl (1961). C_f is defined according to four categories as follows:

$C_f < 1$ = low contamination factor, $1 < C_f < 3$ =moderate contamination factor; $3 < C_f < 6$ = considerate contamination factor, $C_f > 6$ = very high contamination factor (Ata *et al.,* 2009)

Geo-Accumulation Index (I_{geo}): I_{geo} was introduced by Muller (1981) to measure the degree of metal pollution in aquatic sediment studies. The I_{geo} is a qualitative measure of pollution intensity of the samples and is categorized as unpolluted (< 0), unpolluted to moderately polluted ($0 \leq I_{geo} \leq 1$), moderately polluted ($1 \leq I_{geo} \leq 2$), moderately to strongly polluted ($2 \leq I_{geo} \leq 3$), strongly polluted ($3 \leq I_{geo} \leq 4$), strongly to extremely polluted ($4 \leq I_{geo} \leq 5$) and extremely polluted ($I_{geo} \geq 5$).

The I-geo formula used for the calculation is:

$$I - geo = log2\ [Cs/\ 1.5\ x\ CB] \qquad (2)$$

C_s is the calculated concentration of an element in the sample and $C_{B,}$ is the geochemical background value in average shale (Turekian and Wedepohl, 1961) of element n. The concentration used as background is multiplied by a factor of 1.5 which takes care of natural fluctuations of the metal in the environment as well as other influences. The calculated I_{geo} values were compared with I-geo classification for sediment quality to know the extent of pollution on the sampled areas.

Enrichment Factor: Enrichment factor (EF) was used to assess the degree of contamination and the possible anthropogenic impact on the sediment. In this study, Cu was used as a conservative tracer to differentiate natural components from anthropogenic ones. Enrichment Factor was calculated using:

$$EF = \left(\frac{M}{Cu}\right) sample - \left(\frac{M}{Cu}\right) background \quad (3)$$

Where $(M/Cu)_{sample}$ is the ratio of metal and Cu concentration of the sample, $(M/Cu)_{background}$ is the ratio of metal and Cu concentration of a background

The background concentrations of the heavy metal study were taken from Turekian and Wedepohl (1961). There are five contamination categories recognized based on the EFs; EF < 2 indicating depletion to minimal enrichment; EF = 2–5 indicating moderate enrichment; EF = 5–20 indicating significant enrichment; EF = 20–40 indicating very high enrichment; EF >40 indicating extremely high enrichment.

Pollution Load Index: The pollution load index of a single site is the root number (n) of multiplied together contamination factor (C_f) values. Pollution load index (PLI) was used in evaluating the pollution level in an environment

$$PLI = (CF1 \times CF2 \times CFn \ldots \times CFn)1/n \ldots. (4)$$

Where n is the number of metals and C_f is the contamination factor.

PLI > 1 means polluted while PLI < 1 shows no pollution

RESULT AND DISCUSSION

The concentration of heavy metals (ppm) as obtained from the atomic absorption spectrometry (AAS) is presented in Table 1. Seven (7) metals were determined in each of the hyacinth, water, and sediment samples namely; Cu, Zn, Fe, Cr, Cd, As, and Pb. The concentrations of copper in the hyacinth samples were observed between 0.050 ± 0.000ppm to 0.084 ± 0.000ppm (Table 1). The value obtained is significantly low when compared to the W.H.O (2017) and NSDWQ (2007) standards of 2.0 and 1.0 respectively. The lowest metal concentration was recorded at sampling point L5, while the highest concentration was sampling point L6. The result indicates minimal human impact such as mining. In the water samples, the concentrations of copper ranged from 0.087 ± 0.001ppm to 0.117 ± 0.002ppm (Table 1), this is significantly low compared to the WHO (2017) and USEPA (2019) standards of 1.50ppm and 1.30ppm respectively. The concentration of copper in the sediment samples ranged from 2.550 ± 0.002ppm to 3.700 ± 0.002ppm. The highest concentration of copper contamination was observed in L 6. The values were observed to be a little above the permissible values set by WHO (2017) except for L1 and L2. Copper is a major environmental pollutant that poses significant health risks to human being and it is one of the commonest heavy metals found in aquatic bodies (Abioye, 2011). Sources of Copper in river water include industrial discharges, agricultural runoff, domestic sewage, and atmospheric deposition. Copper is widely used in industrial processes, and its discharge into water bodies contributes significantly to the pollution of river water. The use of copper-based pesticides and fertilizers are also a significant source of copper pollution in river water (Abioye, 2011). Domestic sewage and wastewater discharge also contribute to the pollution of river water with copper. Atmospheric deposition of copper particles from industrial and natural sources is also a significant contributor to copper pollution in river water. Copper is an essential nutrient required by the human body in small quantities, but excessive exposure to copper can lead to various health hazards (Mahurpawar, 2015). Acute exposure to high concentrations of copper in river water may result to vomiting, nausea, and diarrhea. Long-term exposure to copper pollution in river water can cause liver and kidney damage, anemia, and neurological disorders (Obasi and Akudinobi, 2020). Copper pollution in river water can also lead to the accumulation of copper in fish, which can then be consumed by humans, leading to health problems.

Table 1: Level of concentration (ppm) of Heavy Metals at different sampling points

Location	Medium	Cu	Zn	Fe	Cr	Cd	As	Pb
L1	Water	0.100 ± 0.001	0.006 ± 0.000	0.086 ± 0.001	0.006 ± 0.000	0.013 ± 0.000	0.012 ± 0.000	0.010 ± 0.000
	Sediment	2.750 ±0.001	1.925 ±0.001	3.775 ± 0.001	1.125 ± 0.001	0.825 ± 0.001	0.375 ± 0.000	0.500 ± 0.000
	Hyacinth	0.071 ± 0.001	0.039 ± 0.001	0.086 ±0.001	0.061 ± 0.002	0.019 ± 0.000	0.006 ± 0.000	0.008 ± 0.000
L2	Water	0.117 ±0.002	0.008 ±0.000	0.071 ±0.001	0.007 ±0.000	0.013 ± 0.000	0.012 ±0.000	0.012 ±0.000
	Sediment	2.550 ± 0.002	2.075 ± .0110	3.300 ± 0.001	1.100 ±0.001	0.750 ±0.0001	0.475 ± 0.000	0.500 ± 0.000
	Hyacinth	0.077 ± 0.001	0.033 ± 0.001	0.088 ± 0.001	0.065 ± 0.002	0.017 ± 0.0004	0.008± 0.0002	0.011 ± 0.000
L3	Water	0.087 ±0.001	0.013 ±0.000	0.070 ±0.009	0.010 ±0.000	0.015 ±0.000	0.023 ±0.000	0.015 ±0.000
	Sediment	3.150 ± 0.001	2.500 ±0.002	4.150 ±0.002	0.800 ±0.001	0.875 ±0.001	0.475 ±0.0004	0.425 ±0.0004
	Hyacinth	0.062 ± 0.000	0.040 ± 0.001	0.100 ± 0.001	0.045 ± 0.002	0.020 ± 0.001	0.008 ± 0.000	0.014 ± 0.000
L4	Water	0.129 ± 0.002	0.010 ± 0.000	0.084 ± 0.001	0.005 ± 0.000	0.012 ± 0.000	0.022 ± 0.000	0.012 ± 0.000
	Sediment	3.500 ±0.001	2.075 ±0.001	3.050 ±0.001	1.275 ±0.001	0.675 ±0.000	0.525± 0.000	0.425 ±0.000
	Hyacinth	0.066 ± 0.000	0.028 ± 0.000	0.105 ± 0.002	0.096 ± 0.001	0.018 ± 0.000	0.005 ± 0.000	0.009 ± 0.000
L5	Water	0.092 ± 0.001	0.077 ± 0.001	0.092 ± 0.001	0.025 ± 0.001	0.020 ± 0.001	0.018 ± 0.000	0.009 ± 0.000
	Sediment	3.025 ± 0.001	1.775 ± 0.001	3.500 ± 0.002	1.375 ± 0.001	0.725 ± 0.000	0.500 ± 0.000	0.400 ±0.000
	Hyacinth	0.050 ± 0.000	0.040 ± 0.001	0.074 ± 0.001	0.079 ± 0.002	0.002 ± 0.000	0.006 ± 0.000	0.007 ± 0.000
L6	Water	0.103 ± 0.001	0.010 ± 0.000	0.098 ± 0.001	0.005 ± 0.000	0.003 ± 0.001	0.012 ± 0.000	0.012 ± 0.000
	Sediment	3.700 ± 0.002	2.300 ± 0.001	3.550 ± 0.001	1.075 ± 0.001	0.725 ± 0.001	0.600 ± 0.001	0.500 ± 0.000
	Hyacinth	0.084 ± 0.001	0.058 ± 0.001	0.088 ± 0.001	0.052 ± 0.002	0.022 ± 0.001	0.010 ± 0.000	0.010 ± 0.000

The concentration of zinc in the hyacinth samples ranged from 0.028 ± 0.000ppm to 0.058 ± 0.001ppm (Table 1). The values obtained were below the acceptable level of WHO (2017) and NSDWQ (2007) set at 3.0ppm and 5.0ppm respectively (Table 2). The lowest metal concentration was recorded at sampling point L4, while the highest metal concentration was recorded at sampling point L6. The concentration of zinc in the water ranged between 0.006 ± 0.000ppm to 0.077 ± 0.001ppm (Table 1). These values were below the acceptable limit of WHO (2017) and USEPA (2019) set at 5.000ppm and 5.000ppm respectively (Table 1). In the sediment samples, the concentration of Zinc ranged between 1.775 ± 0.001ppm to 2.500 ± 0.002 ppm. The values were below the permissible values set by WHO (2017). Zinc contamination in river sediments can be caused by a variety of human activities, including Industrial activities such as galvanizing steel, producing brass and bronze, mining activities, and manufacturing of batteries. If these processes are not properly managed, zinc can end up in wastewater and then be discharged into nearby rivers and streams. Like copper, zinc is toxic to many species of fish and other aquatic organisms. Exposure to high concentrations of zinc can destroy their gills, kidneys, and nervous systems, leading to reduced populations of fish and other aquatic animal, Zinc contamination can make water unsuitable for human consumption or recreational use, as well as for agricultural or industrial purposes. Zinc can also interfere with the biological processes that occur in river ecosystems, leading to decreased water quality overall (Sabater *et al..,*). Also, if people consume fish or other organisms that have accumulated high levels of zinc, they can be at risk of health problems such as diarrhea, nausea, and vomiting. Long-term exposure to zinc can also increase the danger of neurological and reproductive problems (Mahurpawar, 2015).

The concentrations of iron in the hyacinth samples ranged between 0.074 ± 0.001ppm to 0.105 ± 0.002ppm (Table 1) which is significantly low compared to the W.H.O (2017) and NSDWQ (2007) standards levels (Table 2). The lowest iron concentration was recorded at sampling point L5, while the highest concentration was recorded at sampling point L4. Iron concentrations in the water samples ranged from 0.070 ± 0.009 ppm to 0.098 ± 0.001ppm (Table 1). The iron availability within the area covered was generally low when compared to the WHO (2017) and USEPA (2019) allowable limit of 0.300ppm (Table 1). The concentration of iron in the sediments ranged between 3.050 ± 0.001 to 4.150 ± 0.002ppm. These values fall below the set values given by WHO (2017). Iron is a naturally occurring element present in various environmental matrices, including water bodies such as rivers (Bacquart *et al.,* 2015). Iron in river water can emanate from both natural and anthropogenic sources. Natural sources of iron include weathering of rocks and soils, while the anthropogenic sources include discharges from industrial activities, agricultural runoff, and domestic sewage (Bacquart *et al.,* 2015). Other sources of iron in river water include erosion and sedimentation. Iron is essential for biological systems. Ingestion of high amount of iron can lead to stomach cramps, vomiting, and diarrhea. Long-term exposure to high amount of iron in drinking water has been linked to an increased health risk of chronic diseases such as diabetes, liver disease, and cancer (Obasi and Akudinobi, 2020). Iron also contributes to the formation of harmful disinfection byproducts during water treatment. Iron in river water can pose negative impacts on aquatic life. High concentrations of iron can cause growth of algae and other aquatic plants, reduced oxygen levels in the water, known as hypoxia, and death of aquatic organisms. Iron- heavy metal in river water is a significant concern for human health and the environment. While iron is an essential nutrient, excessive amount of iron in the water body can have adverse health effects and can contribute to the degradation. It is therefore important to ascertain the sources of iron in river water and take measures to mitigate their impact on human health and the environment. The concentrations of chromium in the hyacinth samples ranged from 0.045 ± 0.002ppm to 0.096 ± 0.001ppm which is far above the WHO (2017) and NSDWQ (2007) standard of 0.05ppm (Table 1). The lowest concentration was recorded at sampling point L3, while the highest concentration was recorded at sampling point L4. The high amount of chromium can be due as a result of human activities such as mining, and the release of industrial effluents into the water body. The effect may lead to the accumulation of this heavy metal causing pollution of the reservoir. The concentration of chromium in the water samples ranged from 0.005 ± 0.000 ppm to 0.025 ± 0.001 ppm. The values obtained in the water samples were close and some were above WHO (2017) and USEPA (2019) standard permissible concentrations. The highest chromium concentration was recorded at location L5 while the lowest value was obtained at location L4. In the sediment samples, Chromium concentration ranged between 0.800 ± 0.001 to 1.375 ± 0.001ppm. The highest and lowest amount was obtained at L5 and L3 respectively. In all the three media, it was observed that the sediment media has the highest concentration of the said metal compared to the water and the hyacinth media. Chromium is a naturally occurring element found in the earth's crust (Shekhawat *et al.,* 2015). However, human activities such as and agriculture, industrial processes, and mining, have increased in the amount of chromium released into the environment, including rivers and other water bodies. A study by Singh and Sharma, (2018), investigated the sources of chromium in river water in India. The study found that the chromium can be introduced into natural water sources through the weathering of chromium-containing rocks, direct release from industrial activities, soil leaching, and other pathways. Similarly, Zhang *et al*. (2020) in China found that industrial activities were the main sources of chromium in river water. The study found that the chromium concentration in river water was positively correlated with the number of industries in the watershed. Chromium is considered a toxic metal and causes serious health implications on humans and aquatic life. Moreover, a review by Das and Samal (2018) reported that exposure to chromium in drinking water increases the risk of respiratory diseases, kidney damage, and reproductive problems. Chromium pollution in river water is a serious environmental issue that can pose significant health implications for both humans and aquatic life. It is important to monitor the levels of chromium in river water and take steps to reduce its release into the environment to protect public health and the environment.

Cadmium is a toxic heavy metal that can accumulate in plant tissues through various routes such as soil, water, and air. Cadmium finds their way into the environment through a variety of anthropogenic sources e.g. Wastewater (Edokpayi *et al*., 2016). The concentrations of cadmium in the hyacinth samples ranged from 0.002 ± 0.000ppm to 0.022 ± 0.001ppm (Table 1). The values were significantly high when compared to the W.H.O (2017) and NSDWQ (2007) standards of 0.003ppm. The lowest concentration was recorded at sampling point L5, while the highest concentration was recorded at sampling point L6. The concentration of cadmium in water samples ranged from 0.003 ± 0.001ppm to 0.020 ± 0.001ppm (Table 1). These values were close and some were above WHO (2017) and USEPA (2019) standards of 0.003ppm and 0.005ppm (Table 1) respectively. The highest value was recorded in the L5. The concentration in the sediment sample varied between 0.675 ± 0.000 to 0.875 ± 0.001ppm. The values are higher than the allowable values established by WHO (2017). Cadmium is a heavy metal that can enter river water through various sources. One of the most significant sources is industrial waste, particularly from industries such as battery manufacturing, smelting, and electroplating (Hegazi, 2015). Agricultural runoff and sewage discharge are also sources of cadmium pollution in river water. The natural weathering of soils and rocks can also contribute to the presence of cadmium in rivers. Cadmium concentrations in river water were highest in areas near agricultural land. Cadmium is a toxic metal that has serious health effects if humans are exposed to it at high concentrations. Long-term exposure to cadmium can lead to kidney damage, bone loss, and an increased risk of cancer (Järup and Åkesson, 2009). Some studies have also linked cadmium exposure to adverse effects on the cardiovascular and reproductive systems. Cadmium pollution in river water was associated with an increased cancer risk among local residents (Järup and Åkesson, 2009). Cadmium pollution in river water is a significant environmental issue with serious health implications. The sources of cadmium in river water include industrial waste, agricultural runoff, sewage discharge, and natural weathering of rocks and soils (Fatoki *et al*., 2002). To minimize the risk of exposure to cadmium, it is important to monitor and regulate industrial and agricultural practices, as well as to implement proper wastewater treatment and disposal methods. The concentrations of arsenic in the hyacinth samples varied from 0.005 ± 0.000ppm to 0.010 ± 0.000ppm (Table 1). It was significantly low when compared to the W.H.O (2017) and NSDWQ (2007) standards of 0.01ppm. The lowest concentration was recorded at sampling point L4, while the highest concentration was recorded at sampling point L6. The concentration of cadmium in the water samples ranged from 0.012 ± 0.000ppm to 0.023 ± 0.000ppm (Table 1). These values were however higher than the permissible value according to WHO (2017) and USEPA (2019) standards of 0.010ppm. The concentration of cadmium in the sediment sample varied between from 0.005 ± 0.000 to 0.600 ± 0.001ppm. The values are higher than the permissible values established by WHO (2017).

Table 2: Permissible Limit of Heavy Metal in Water, Sediment, and Hyacinth Samples

Heavy Metal	WHO, 2017		WHO, 2017	NSDWQ, 2007	USEPA, 2019
	H	S	W	W	W
Cr	0.050	0.1	0.010	0.05	0.05
Fe	0.300	5.00	0.300	0.05 - 0.3	
As	0.010	5.00	0.010	0.01	0.05
Cu	2.000	3.00	1.000	2.00	1.30
Cd	0.010	0.003	0.003	0.003	0.005
Pb	0.010	0.10	0.010	0.01	0.015
Zn	3.000	5.00	5.000	3.00	5.00

*H = hyacinth;*W = water; *S = sediment

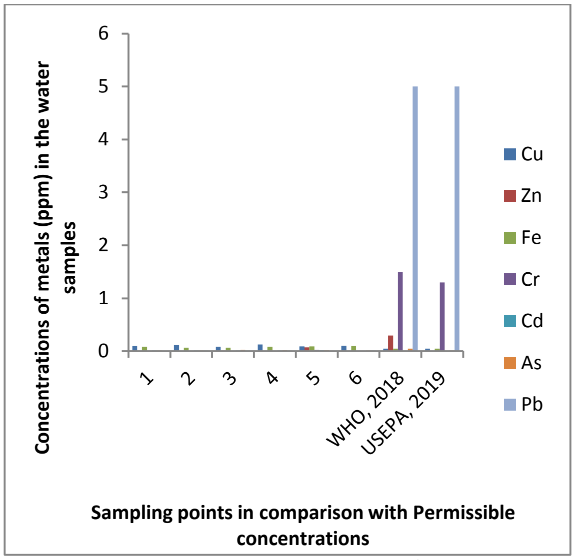

Fig. 1: Chart comparing the concentrations of selected heavy metals in the water samples with permissible values

Arsenic is a toxic heavy metal found naturally in the earth's crust. It enters into the environment by both natural and anthropogenic sources, including mining, smelting, and agricultural activities. Arsenic is present in rocks, soils, and minerals, which can be eroded by water and carried downstream (Duruibe and Egwurugwu. 2007). Additionally, human activities like mining, smelting, and agriculture can enhance arsenic concentration in river water (Duruibe and Egwurugwu. 2007). Mining and smelting activities release arsenic into the air, which can be carried by wind and deposited into river water. In agriculture, the use of arsenic-based pesticides and fertilizers could also contribute to arsenic contamination in river water (Duruibe and Egwurugwu. 2007). Exposure to high concentration of arsenic can cause a variety of health difficulties, including skin lesions, cancer, and neurological disorders. Increased risk of bladder, lung, and skin cancers has been linked to arsenic exposure (Kumar *et al.*, 2005).

Additionally, exposure to arsenic can cause peripheral neuropathy, a condition that affects the peripheral nervous system and can lead to numbness, tingling, and muscle weakness. Long-term exposure to arsenic can also cause skin lesions, including hyperpigmentation and keratosis (Kumar *et al.*, 2005). Arsenic contamination in river water calls for serious concern owing to its probable effect on human wellbeing. Therefore, it is imperative to monitor and regulate arsenic contamination in river water to minimize the danger of health problems associated with exposure.

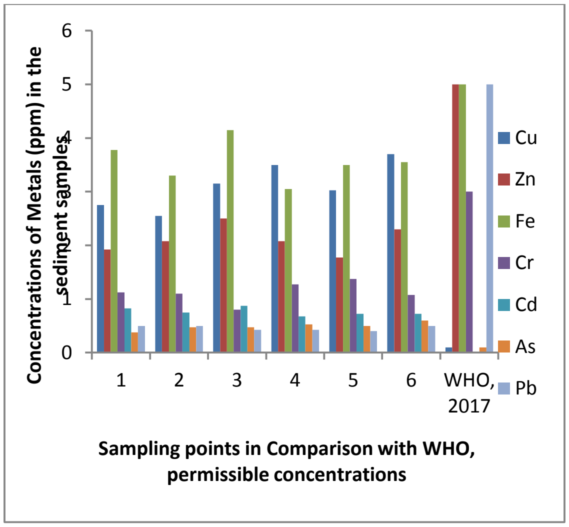

Fig. 2: Chart comparing the concentrations of selected heavy metals in the sediment samples with permissible values

The concentrations of lead in the hyacinth samples were close to the permissible limit. The concentrations of lead ranged from 0.007 ± 0.000ppm to 0.500 ± 0.0000ppm (Table 1). The values were high compared to the WHO (2017) and NSDWQ (2007) allowable limit. The concentrations of lead in the water varied between 0.009 ± 0.000ppm to 0.500 ± 0.000ppm (Table 1). The concentration of lead in the sediment samples were observed between 0.4 ± 0.000ppm and 0.5 ± 0.000ppm. However, these values were high when compared to the WHO (2017) and USEPA (2019) permissible limits of 0.01ppm and 0.015ppm respectively. The key sources of lead are household plumbing, lead paints used domestically, and lead ammunition utilized during communal clashes. Lead is a toxic heavy metal commonly found in river water. Other sources of lead in river water are natural weathering of rocks, erosion of soils, atmospheric deposition via anthropogenic activities, industrial effluents, and wastewater discharge (Fayiga *et al*, 2018).

Several studies have investigated the sources of lead in river water, and they have identified various anthropogenic activities as the primary sources of lead contamination. Exposure to high concentration of lead in river water can result to severe health implications, particularly for children and pregnant women. Lead is a neurotoxin that can affect the developing brain and nervous system of pre-born and young children, resulting to behavioral problems, learning disabilities, and lower IQ scores.

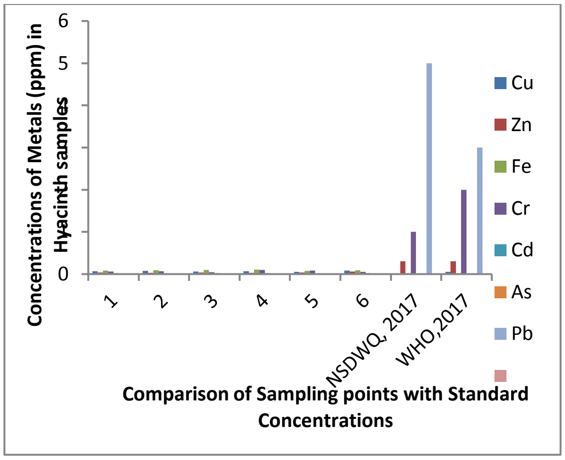

Fig. 3: Chart comparing the concentrations of selected heavy metals in the hyacinth samples with permissible values

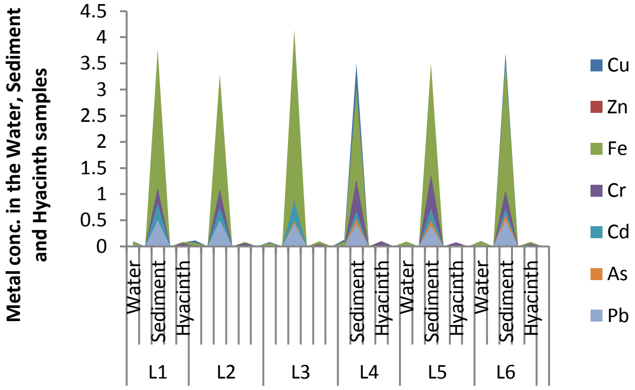

Fig. 4: Levels of specific heavy metals in the water, sediment, and hyacinth samples

Exposure to high concentration of lead has also been associated to increased chances of cardiovascular disease, kidney damage, and cancer (Jarup, 2003). Several studies have investigated the health implications of lead in river water, and they have reported various serious health problems linked with lead exposure. Lead contamination in river water is a significant environmental problem with severe health implications. Anthropogenic activities such as industrial effluents, sewage and urban runoff are also sources of lead contamination in river water. Adverse health effects of lead exposure highlight the need for effective management and regulation of lead emissions to prevent further contamination of river water.

Assessment According to Contamination Factor (C_f): The contamination status of sediments in Opa River, OAU, Ile-Ife was determined and the results are presented in Table 3. In all the six sampling locations, the metals showed low contamination factor except for Fe which indicated moderate contamination factor in all the locations and chromium which also showed a moderate contamination factor in locations 4 and 5. This shows that this study area is rich in Fe and that the fourth and fifth locations are also moderately rich in chromium.

Assessment according to Pollution Load Index (PLI): The pollution load Index of the sediments samples was determined (Table 3). The results revealed the metals were all within the range of unpolluted in all the sampling locations except for cadmium.

Pollution Assessment According to Geo-Accumulation Index (Igeo): The results obtained for the determination of the geo-accumulation index are presented in Table 4. The values obtained for the metals in all the six locations of the study area indicated an unpolluted geo-accumulation index.

Pollution Assessment According to Enrichment Factor (EF): The enrichment factor for the sediment sample was also determined to check for the degree of contamination. The concentrations of Fe, Cr, Zn and Pb and Cu indicates depletion to minimal enrichment in all the six sampling locations while that of As shows significant enrichment, cadmium indicates extremely high enrichment in all the sampling locations (Table 5). This may be as a result of industrial discharges such as mining, smelting, or cadmium-containing fertilizers and pesticides used on farm lands.

Table 3: Contamination factor (C_f) and Pollution load index (PLI) of Heavy metals of Opa River

C_f	Cu	Fe ($\times10^{-5}$)	Zn	Cr	Cd	Pb ($\times10^{-3}$)	As
L1	0.011	5.808	0.012	0.013	1.964	6.250	0.029
L2	0.010	5.077	0.013	0.012	1.786	6.250	0.037
L3	0.013	6.385	0.015	0.008	2.083	5.313	0.037
L4	0.014	4.692	0.013	0.014	1.607	5.313	0.040
L5	0.012	5.385	0.011	0.015	1.726	5.000	0.039
L6	0.015	5.462	0.014	0.012	1.726	6.250	0.046
PLI	**0.012**	**5.442**	**0.013**	**0.012**	**1.808**	**5.704**	**0.038**

Table 4: Geo-accumulation Index (I-geo) of Heavy Metals of Opa River

Heavy Metals	Fe ($\times10^{-5}$)	Cu ($\times10^{-3}$)	Zn ($\times10^{-3}$)	Cr ($\times10^{-3}$)	Cd	As ($\times10^{-3}$)	Pb ($\times10^{-3}$)
L1	1.166	2.208	2.341	2.509	0.394	5.789	1.254
L2	1.019	2.047	2.524	2.453	0.358	7.332	1.254
L3	1.281	2.529	3.041	1.784	0.418	7.332	1.066
L4	1.117	2.810	2.524	2.843	0.323	8.105	1.066
L5	1.081	2.428	2.159	3.066	0.346	7.719	1.003
L6	1.096	2.970	2.797	2.397	0.346	9.262	1.254

Table 5: Enrichment factor of Heavy Metals of Opa River, Ile-Ife

Heavy Metals	Fe ($\times10^{-3}$)	Cu	Zn	Cr	Cd	Pb	As
L1	5.280	1.000	1.061	1.136	37.50	0.455	1.705
L2	4.977	1.000	1.233	1.198	36.765	0.490	2.328
L3	5.067	1.000	1.203	0.705	34.722	0.337	1.885
L4	3.352	1.000	0.898	1.012	24.107	0.304	1.875
L5	4.450	1.000	0.889	1.263	29.959	0.331	2.066
L6	3.690	1.000	0.942	0.807	24.493	0.338	2.027

Conclusion: The concentrations of heavy metals (Cu, Zn, Fe, Cr, Cd, As, and Pb) were determined in the hyacinth, water, and sediment samples collected from Opa Reservoir, located within Obafemi Awolowo University, Ile-Ife, Nigeria. Results revealed that Cu and Zn concentrations in both hyacinth and water samples were below the limits set by regulatory bodies. However, in sediment samples, Cu concentrations exceeded the said limits, while Zn concentrations were lower. Fe concentrations in all samples were generally lower than the regulatory limits, while Cr and Cd concentrations exceeded these limits. As and Pb concentrations were low compared to regulatory limits but in water and sediment samples, the values were higher. Although the pollution load index and geo accumulation index revealed that all metals were within the range of unpolluted geo-accumulation index, enrichment factor indicated varying degrees of contamination. While some metals exhibited depletion to minimal enrichment, others revealed significant or even extremely high enrichment pollution indices. Considering the pollution status of the Opa reservoir, it is therefore recommended that regular monitoring of the reservoir be put in place to ensure the safety of human and aquatic ecosystems in general.

Declaration of Conflict of Interest: The authors declare that they have no conflict of interest regarding this study.

Data Availability Statement: Data are available upon request from the corresponding author.

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