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METAL CONTENTS IN *CYPERUS ARTICULATUS* AND SEDIMENTS OF ZOBE RESERVOIR, NIGERIA

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ABSTRACT

This study evaluated the iron, copper, zinc and lead contents, and the relationship among these metals in *Cyperus articulatus* and sediments of Zobe reservoir, Dutsinma, Nigeria. Samples of *Cyperus articulatus* and sediments were obtained, fortnightly for three months, from three sampling locations sited in up-, mid-, and downstream sections of the water body. Standard methods were used in sample collection and preparation while the metal contents were determined spectrophotometrically. In both sample types, copper and zinc were detected at concentrations below 0.5 mg/kg; the sediment samples contained higher iron contents (5.368±1.174 mg/kg) than the plant samples (2.897±2.031 mg/kg) while lead was not detected. The higher metal contents observed in the sediment samples corroborated the importance of aquatic sediment as a sink for metals in aquatic ecosystems. *Cyperus articulatus* from Zobe reservoir can be deemed safe for use due to its relatively low metal contents (iron 2.897±2.031 mg/kg; copper 0.291±0.119 mg/kg; zinc 0.067±0.111 mg/kg) which were within the allowable limits of local and international standards. The correlative relationship between iron contents in both sample types (R = 0.509) was significant at a 5% confidence level while a significantly stronger association (R = 0.659; 0.681) was observed between iron content in *Cyperus articulatus* and the copper and zinc concentrations in the sediment samples, respectively. Hence, Zobe reservoir can be referred to as safe from iron, copper, zinc and lead pollution. Periodic assessment of metals in Zobe reservoir is recommended for adequate monitoring of metal levels in the reservoir.

Keywords: *metal accumulation, aquatic macrophytes, water pollution, Zobe reservoir*

INTRODUCTION

The importance of water and aquatic resources to man has been so enormous that their exploration has not become exhausted. Besides water provision for several purposes, aquatic resources support human existence with food, medicinal products, industrial raw materials and source of livelihood. Contrastingly, human activities have been implicated in distorting the quality of water bodies through activities of domestic, industrial and agricultural nature. The deposition of wastes along the channel of water bodies and/or deliberate dumping of wastes in water bodies have manifested adverse impacts on the quality parameters of receiving water bodies (Omitoyin, 2018; Oladele *et al*., 2019; Abdelaal *et al*., 2021). Among the effects of pollution on water bodies is the accumulation of hazardous chemicals in water, sediment, and flora and fauna components of aquatic ecosystems (Gborade *et al*., 2015; Jenyo-Oni and Oladele, 2016; Ajani, 2019; Eid *et al*., 2020). Bioaccumulation and magnification of metals in aquatic biota have made studies on metal contents of aquatic organisms pertinent.

Although metal content in water samples reveals the current condition of an aquatic environment, the concentration of metals in aquatic sediments provides information on the pollution state of water bodies over an extended period (Duncan *et al*., 2018). Besides that the inhabitants of aquatic ecosystems magnify metal contents in their environment, they serve as a link for metal transfer from water bodies to man (Oladele and Jenyo-Oni, 2015; Omitoyin, 2018; Eid *et al*., 2020). Inhibition of proper functioning of human body parts and systems, manifestation of diseased conditions, and death, in severe cases, have been reported as some of the consequences of metal poisoning (Dutta *et al*., 2013; Sengupta *et al*., 2014; Anzene, 2019). Although some metals have nutritional qualities as micronutrients, others have hazardous impacts on man. Despite the nutritional importance of such metals as iron, copper and zinc among others, concentrations beyond the nutritional levels pose a grave danger of toxicity (Jaishankar *et al*., 2014). Hence, the need for studies centred on the determination of metal contents in water, sediment, flora and fauna of aquatic ecosystems.

Aquatic plants have been used as bioindicators of metal pollution in aquatic environments. Their widespread abundance, diversity, tolerance to changes in environmental conditions, and capacity to accumulate metals have been explored in environmental pollution studies (Fawzy *et al*., 2012; Kassaye *et al*., 2016; Abdelaal *et al*., 2021). Aquatic macrophytes have displayed greater capacities in these features than lower plants, hence, they have been used for monitoring metals in aquatic ecosystems (Omitoyin *et al*., 2017; Haroon, 2022). Besides their usage as pollution biomarkers, aquatic macrophytes with food and medicinal values have greater tendencies to transfer metals to man. Therefore, the determination of metal contents of such macrophytes is necessary to ascertain their safety for human consumption.

Cyperus articulatus is one of the freshwater plants which belong to the group of aquatic macrophytes utilized by man for its medicinal properties (Shamkuwar *et al*., 2012; Herrera-Calderon *et al*., 2018; Machado *et al*., 2020). Besides its medicinal values in the treatment of headaches and migraine, stomach disorders as well as its usage as a sedative, antimalaria, anticonvulsant and antioxidant, among others, the plant, locally referred to as “Kajiji” in Northern Nigeria (Abubakar *et al*., 2000) is used as an insect repellent, and for pest control (Abubakar *et al*., 2000; Machado *et al*., 2020; Haroon, 2022), while its remediating capacity has also been demonstrated (Mganga *et al.*, 2011; Galal *et al*., 2017). This plant is found growing abundantly in Zobe Reservoir, one of the freshwater reservoirs in Katsina State, North-western Nigeria. In addition to the potable water supply to Dutsin-Ma and surrounding communities, the reservoir supports irrigated farming and fish hunting. These socio-economic features could have prompted the establishment of several human settlements around the water body. The practice of crop and livestock farming as well as domestic activities around Zobe reservoir may predispose the reservoir to domestic and agricultural wastes, hence, the need for evaluation of the metal content of the reservoir. The choice of sediments and *Cyperus articulatus* was based on their capacities to reveal the metal content of Zobe reservoir over an extended time, while iron, copper, zinc and lead were selected for evaluation due to their presence in wastes from domestic and agricultural sources (Ukpong *et al*., 2013; Gong *et al*., 2019). Therefore, this study investigated the iron, copper, zinc and lead contents as well as the relationship among these metals in *Cyperus articulatus* and sediment of Zobe reservoir.

MATERIALS AND METHODS

Zobe reservoir is located in Dutsin-Ma local government area of Katsina State, Nigeria. The freshwater reservoir, located between latitude 12°22'16"N to 12°37'19"N and between longitude 7°28'59"E and 7°48'31"E, covers a rocky land area of 4,500 hectares and stores up to 177 million cubic metre of water (Atalabi *et al*., 2018). Besides its primary function of supplying potable water to Dutsin-Ma town and its surrounding communities, the reservoir serves the purpose of water provision for livestock farming and crop irrigation. Several fish species which inhabit the water body have made fishing an additional occupation among members of communities surrounding the reservoir.

For this study, samples of *C. articulatus* and sediments were collected fortnightly from three sampling locations for three months (April to July 2021). Sampling was done in locations which represent the up-, mid-, and downstream sections of the water body, with respect to the point of damming the water flow. These locations were named after the community/landmark which is closer to the points of sampling. Hence, the up-, mid-, and downstream sampling locations were named Garhi, Makera and Damgate, respectively. Three sampling points were situated in each of the sampling locations to ensure that the samples taken were representative of each location. Using standard methods, samples of the *C. articulatus* and sediment were collected in the early hours (6.30 and 9.30 hours) of the sample collection dates. Samples of the aquatic macrophyte were obtained as a whole plant and carefully uprooted to minimize damage, while a Van Veen grab was used to collect sediment samples from each of the sampling locations. A mixture of samples from the three sampling points, within each of the locations, was used to make up a composite sample for each location. Collected plant samples were thoroughly rinsed with distilled water to remove adhering soil and other particulate materials before being transported in labelled polyethylene bags to the laboratory for drying and metal content determination. Similarly, labelled polyethylene bags, which were pre-treated with 5% nitric acid and rinsed with distilled water, were used to transport the sediment samples to the laboratory (Oladele *et al*., 2018).

Under room temperature, the plant and sediment samples were air-dried, grounded and filtered with a 2.0 mm sieve. The resulting particulate samples were digested using the methods of Abou El-Anwar (2019) while the concentrations of iron, copper, zinc and lead in the digested samples were determined using atomic absorption spectrophotometer. Data analysis was carried out using the Statistical Package for Social Sciences (IBM SPSS) version 20. Mean and standard deviation were used to present the concentration of the metals in each of the sample types, analysis of variance was employed to test the significance of the mean concentration of each metal among the locations, while correlation was used to test the relationship between the metals in the plant and sediment samples.

RESULTS

The concentrations of metals in samples of *C. articulatus* and sediments from Zobe reservoir are revealed in Tables 1 and 2, respectively. These tables show that iron, copper and zinc were present in both sample types, whereas lead was not detected in all the sampling locations. Also, the tables revealed that iron and zinc had the highest and lowest concentrations, respectively, in both *C. articulatus* and sediment samples.

Table 1: Metal concentration (mg/kg) in *C. articulatus* samples

Location	Iron	Copper	Zinc	Lead
Garhi	1.180±0.731[b]	0.267±0.140[a]	0.053±0.130[a]	ND
Makera	2.142±0.747[b]	0.313±0.128[a]	0.085±0.101[a]	ND
Damgate	5.368±1.174[a]	0.292±0.099[a]	0.063±0.117[a]	ND

ND: Not Detected

Different letters as superscripts within the column for each parameter indicate significant differences (P<0.05)

Table 2: Metal concentration (mg/kg) in sediment samples

Location	Iron	Copper	Zinc	Lead
Garhi	5.408±0.798[b]	0.223±0.023[b]	0.117±0.012[c]	ND
Makera	4.478±1.422[b]	0.328±0.072[a]	0.237±0.126[b]	ND
Damgate	7.311±1.315[a]	0.372±0.031[a]	0.362±0.063[a]	ND

ND: Not Detected

Different letters as superscripts within the column for each parameter indicate significant differences (P<0.05)

As evident in Table 1, the *C. articulatus* samples obtained from the Damgate location had iron contents (5.368±1.174 mg/kg) which were significantly ($P < 0.05$) higher than those of the other two locations while Makera had the highest copper and zinc contents (0.313±0.128 mg/kg and 0.085±0.101 mg/kg) which were not significantly different from those of Garhi and Damgate.

Likewise, Table 2 shows that the Damgate had significantly ($P < 0.05$) higher iron contents (7.311±1.315 mg/kg). Similarly, copper and zinc contents (0.372±0.031 mg/kg and 0.362±0.063 mg/kg, respectively) were significantly ($P < 0.05$) higher at the Damgate, than what was observed at Garhi. Comparing the metal contents in the two (2) sample types, Tables 1 and 2 reveal that the sediment samples had higher concentrations of each of the metals evaluated.

The correlation coefficients of iron, copper and zinc in the *C. articulatus* and sediment samples are revealed in Table 3. The metal contents in the *C. articulatus* and sediment samples were represented by the chemical symbol of the metals (Fe, Cu and Zn) suffixed, respectively, with -CA and -SD, which are used as abbreviations for *C. articulatus* and sediments. It is important to note that the relationship between lead and other metals cannot be evaluated due to non-detection of the metal in each of the sample types. As evident in the table, the iron and copper contents in *C. articulatus* samples were positively correlated (0.103), while zinc in the plant samples had negative correlative relationships with the iron and copper contents (-0.222 and -0.285, respectively). The relationship between iron concentrations in *C. articulatus* and sediment (0.509) was significant at a 5% confidence level while the iron contents in the plant samples were significantly correlated, at a 1% confidence level, with the copper and zinc concentrations in the sediment samples (0.659 and 0.681, respectively). Although the copper contents in *C. articulatus* samples had positive correlations with the metals in the sediment samples, zinc concentrations in the plant samples were negatively correlated with all the metals in the sediment samples. Furthermore, zinc and other metals in the sediment samples had significantly positive correlative relationships among each other at a 5% confidence level.

Furthermore, Table 4 shows the metal contents of *C. articulatus* from Zobe reservoir in comparison with allowable metal limits of the National Agency for Food and Drug Administration and Control (NAFDAC), World Health Organization (WHO), and Food and Agricultural Organization (FAO). The table revealed that all the metals were present in concentrations lower than the allowable limits of these local and international organizations.

Table 3: The relationship among the metal contents in *C. articulatus* and sediment samples of Zobe Reservoir

Metal contents	Fe-CA	Cu-CA	Zn-CA	Fe-SD	Cu-SD	Zn-SD
Fe-CA	1					
Cu-CA	0.103	1				
Zn-CA	-0.222	-0.285	1			
Fe-SD	0.509*	0.093	-0.271	1		
Cu-SD	0.659**	0.384	-0.130	0.352	1	
Zn-SD	0.681**	0.103	-0.084	0.520*	0.558*	1

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

Table 4: Comparison of metal contents (mg/kg) in *C. articulatus* samples with local and international standards

	Iron	Copper	Zinc	Lead
This study	2.897±2.031	0.291±0.119	0.067±0.111	-
*NAFDAC	3.000	40.000	50.000	2.000
*WHO/FAO	3.000	73.000	100.000	0.300

*NAFDAC and WHO/FAO maximum allowable limits

DISCUSSION

The detection of the majority of the metals evaluated in the *C. articulatus* and sediments samples corroborated the capacity of each of the sample types to accumulate metals. The variation observed in metal content within each sample type reflects the differences in the concentrations of these metals among the sampling locations. Besides natural occurrences, these differences may be attributed majorly to human activities within and/or around the vicinity of each of the sampling locations. According to the findings of Oyebode (2015), Jenyo-Oni and Oladele (2016), Omitoyin (2018), and Ajani (2019) among others, anthropogenic activities and deposition of wastes in water bodies are the major sources of pollutants in aquatic environments. However, non-detection of lead, coupled with a relatively low concentration of other metals, may have indicated that discharge of wastes, which contained these metals, in the reservoir has been quite low. Relatively higher metal content observed in the sediment samples aligns with the submission of Singovszka *et al*. (2017) that aquatic sediments are reservoirs for metals in aquatic ecosystems.

Relatively higher concentrations of iron, when compared with other metals, in *C. articulatus* can be attributed to the essentiality of iron as a macronutrient (Uchida, 2000). The ferruginous nature of tropical soils (Olowu *et al*., 2010) may have also made iron readily available for the plant's uptake. Among the sampling locations, the significantly higher iron content observed in *C. articulatus* from the Damgate location can be attributed to the above factors, in addition to the likely accumulation of materials transported from the Garhi and Makera locations. Similarly, the significantly higher metal content observed in the sediment samples from the Damgate location corroborated that there may be transportation, deposition and settling down of materials from the Garhi and Makera locations in the Damgate section of the reservoir.

As an aquatic plant with medicinal values, a comparison of the metal content in *C. articulatus* with local and international standards reveals that the iron, copper and zinc contents observed in the *C. articulatus* samples were within the allowable limits, as reported by Adefarati *et al*. (2017) and presented in Table 4. This implies that the plant is safe for human consumption, and its usage for medicinal purposes will not pose threats to human health.

The positively correlative relationship observed between iron and copper contents in the *C. articulatus* samples could be attributed to the importance of iron and copper as nutrient elements required by the plant for growth and other metabolic activities. However, the negative correlative association between zinc and other metals in the plant samples may have resulted from differences in the uptake pattern and use of these metals by the plant. This is corroborated by the findings of Uchida (2000) which affirmed that plants have preferences and specific needs for metals, especially as macro- or micronutrients, and this may have accounted for the negative association observed.

Furthermore, the significantly positive correlation observed between iron concentrations in the *C. articulatus* and sediments samples may have resulted from the affinity of the plant for iron as a macronutrient (Uchida, 2000) as well as iron abundance in tropical soils (Olowu *et al*., 2010). The dependence of *C. articulatus* on the aquatic sediments as its major source of plant nutrients (Galal *et al*., 2017) as well as the essentiality of iron, copper and zinc as nutrient elements may have led to the strong significant association recorded between iron contents in the plant samples and the sediment's copper and zinc concentrations. The essentiality of copper as a micronutrient in *C. articulatus* may have also accounted for the positive correlative relationship between the copper contents in the plant and the concentration of metals in the sediment samples. The negative relationship between zinc contents in the *C. articulatus* and sediments samples may be attributed to the absorption and utilization of the metal by *C. articulatus* contrary to its build-up and storage in the aquatic sediment. However, a significantly positive correlative relationship between zinc and other metals in the sediment samples of Zobe reservoir may have resulted from the storage capacity that the aquatic sediment has for metals. This is supported by the findings of Singovszka *et al*. (2017) and Abou El-Anwar (2019) which affirmed that aquatic sediment serves as a sink for metals in the aquatic ecosystem.

CONCLUSION

Relatively low metal contents observed in *Cyperus articulatus* and sediments of Zobe reservoir indicated that the water body is not polluted with these metals. Receipt of relatively low volumes of domestic and agricultural wastes as well as the self-purifying properties of a flowing water body, among other factors, may have contributed to the low metal levels recorded. Also, the *C. articulatus* in Zobe reservoir can be deemed safe for human use, since the metal contents observed in the plant were relatively low, and were within the allowable limits of local and international standards. The detection of the metals in both sample types corroborated their values as indicators of metal presence in aquatic ecosystems. Therefore, the detection of the metals calls for timely monitoring of human activities in communities that surround the water body. Waste disposal along the water channels should be discouraged to preserve the quality of the water body. Periodic studies on the pollution status of the reservoir are recommended for adequate monitoring of the state of the water body.

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