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LETTER

Spatial and temporal distribution and contamination assessment of heavy metal in Woji Creek

Amalo Ndu Dibofori-Orji, Owhonda Chikeru Ihunwo, Kufre Solomon Udo, Amir Reza Shahabinia, Mark Obinna Onyema and Prince Chinedu Mmom

1 Department of Chemistry, Faculty of Natural and Applied Sciences, Ignatius Ajuru University of Education, Port Harcourt, Nigeria
2 Niger Delta Aqua Research Group, Department of Biochemistry and Chemistry Technology, School of Science Laboratory Technology (SSUT) University of Port Harcourt, Choba, Rivers State, Nigeria
3 Groupe de Recherche Interuniversitaire en Limnologie (GRIL), Département des Sciences Biologiques, Université du Québec à Montréal (UQAM), Succ. Centre-Ville, Case Postale 8888 Montréal, Québec H3C 3P8, Canada
4 Department of Pure and Industrial Chemistry, University of Port Harcourt, Rivers State, Nigeria

E-mail: owhonda.ihunwo@hotmail.co.uk

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Abstract

Land use is one major factor that affects river water quality which is related to anthropogenic activities. Studies have shown that abandoned boats on watershed, petroleum and untreated wastewater from abattoirs can lead to anthropogenic pollution in surface waters. This study, therefore, was designed to assess spatial and temporal variation of selected heavy metals and level of pollution in Woji Creek. The study was carried out in the months of August, September and October 2018. Water samples were collected from five stations along the creek over a 3.2 km stretch. Water was collected to be analysed for heavy metals (Nickel, Cadmium, Copper, Lead and Iron). Results were subjected to ANOVA and heavy metal pollution index (HPI) was calculated using aquatic toxicity reference values (TRV) as threshold values. Heavy metal dominance in Woji was in the order of Pb > Ni > Fe > Cd > Cu. In the river, Ni had mean values ranging from 0.379 ± 0.259 mg l⁻¹ in August to 0.545 ± 0.369 in October, while Pb with the highest concentration had mean values ranging from 0.229 ± 0.333 mg l⁻¹ in October to 1.534 ± 0.103 mg l⁻¹ in September. Concentrations of metals analysed were high than the TRV. Temporal analysis of HPI calculated for the study was above the critical heavy metal pollution index (100) (August = 329.358, September = 361.796, October = 112.715). A correlation was observed between heavy metals analysed during the study. Spatial analysis of HPI showed higher pollution level at Station 3 with the highest anthropogenic activity along the creek. Cu showed a negative correlation to other metals analysed. Sources of pollution on this creek was identified to be both natural and majorly anthropogenic sources. This study, therefore, points out the need for proper environmental management as regards commercial activities around the waterways.

1. Introduction

Land use is one major factor that affects river water chemistry which is related to anthropogenic activities. Forestation and farming on watershed play a major role in the river water chemistry and river water quality [1]. Air quality has also been seen to affect river water chemistry and water quality [2]; as well as urban planning on the watershed, improper urban planning on the watershed carries untreated sewage from the watershed into the fluvial system [3–5].

The surface waters in the Niger Delta region of Nigeria are faced with several environmental problems. These problems are anthropogenic in nature and are related to three major sources; municipal discharge, transportation and petroleum exploration [6]. In addition, to the vast petroleum deposit in the Niger Delta, this region is coastal and therefore, has a higher population compared to other parts of the country. The increasing population in the
area and the demand exerted by the population in coastal regions give rise to additional environmental issues when the environment is not properly managed [6].

Freshwater runoff, the atmosphere, and point source of human activities are the main sources of metal input to estuaries and coastal waters [7]. Although some metals commonly called Heavy Metals (with atomic weight ranging from 63.546 to 200.590 and having similar electrons in its outermost shell) have been seen to have high toxic potential to aquatic organisms when they are above the natural environmental threshold [8], many of them are essential to proper biota metabolism when they exist within the threshold concentrations. Some examples of these essential metals are: cobalt, copper, iron, magnesium, molybdenum, vanadium, strontium, and zinc etc.

Heavy metal contamination of the coastal environment continues to attract the attention of environmental researchers because of its increasing input to coastal water, especially in the developing countries. In recent decades, industrial and urban activities have contributed to the increase of heavy metal contamination in the marine environment and have directly influenced the coastal ecosystem [9]. Heavy metals are one of the most persistent pollutants; they don’t degrade but can accumulate throughout the food chain leading to potential human health risk and ecological imbalance [10]. Heavy metal distribution in an aquatic organism is posing great dangers in many communities in the south-south region of Nigeria because of the nature of the terrain. The aquatic environment is one of the receiving ends for pollutants, particularly heavy metals which are ploughed back into the food chains through bioaccumulation in plankton and invertebrate to fishes and finally biomagnified in man [10].

Based on the abundance of metals in geochemistry and biology, the term ‘trace metals’ have been used to define certain metals in the periodic table. These metals are usually found in the Earth’s crust and in cells and tissues of organisms in trace amounts (< 100 parts per million atoms (ppma) or < 100 μg g⁻¹ or <0.1%) [11]. There are non-essential metals (Cd, Hg, Pb) and essential metals (Co, Cu, Fe, Mn, Mo and Zn). The essential metals play a key role in the physiological and biochemical processes in plants and animals. Metals such are Na, K, Mg, Ca, Fe, Mn, Co, Cu, Zn and Mo have been identified as essential elements for life and body of human beings [12]. However, at certain concentrations, both essential and non-essential metals can be toxic to living organisms [13–15]. In the Niger Delta, V, Cr, Co, Ni, Mn, Fe and Cu are trace elements that have been identified in the geology of the Niger Delta [16].

Environmental problems have been identified as a major challenge to the people of Niger Delta. There has been a global call for urgent remediation of environmental pollution in the region. Based on this call, government agencies, the private sector and environmental scientist are making relentless efforts to find solutions to the problems. The study area, which is Woji creek in Niger Delta region of Nigeria, is not excluded in this problem. This creek is affected by accidental oil spill, effluent from abattoir and boat manufacturing companies sited along the creek. These activities lead to the discharge of untreated waste which contains oil and other chemicals into the aquatic ecosystem. One aspect of environmental problems that are being overlooked in the Niger Delta region of Nigeria is the issue of abandoned boats in the estuaries. Abandonment boats have been identified as a health risk due to the toxic substances that leach into the environment from the boats [17]. This can be a major source of Pb contamination in the water [18]. Process of rusting of steel, which is a major component of boat fabrication due to its tensile strength and low cost, can also lead to the release of Fe (II) into the aquatic system. The processes carried out in abattoirs in Nigeria have also led to the input of metals, through wastewater discharge, into the environment [19–22].

To study the impact of rapid industrialization and urbanization in Guangxi Province on the coastal environment in recent years, seven metals (Hg, Cu, Pb, Cd, Cr, Zn and As) were investigated in the surface seawater and sediments of the northern Beibu Gulf. The study observed higher concentrations of metals nearshore area, particularly in the northwest, which may be related to the rapid industrial development in coastal areas [23]. Another study monitored the seasonal variation of heavy metals in surface water of a tropical mountainous river in Kerala, India [24]. Mean concentration of heavy metals such as Cu, Cr, Zn and Pb during post-monsoon are comparatively higher than that in the other seasons. As and Cd concentrations are below the detectable limit in all seasons. Research has also shown that metals such as Cd, Cu, Ni, Pb and Fe have been associated with crude oil pollution in the environment [25–28].

A study was performed between October, 2012 and September, 2014 on Woji Creek to assess the physicochemical characteristics of the surface water and heavy metals levels in sediment. The study concluded that that sediment of the study area has a low level of contamination from heavy metals [29]. This research, therefore, was designed to assess the concentration of some heavy metals (Ni, Cd, Cu, Pb and Fe) in the water column of Woji Creek. The aim of this study is to (1) determine the concentrations of Ni, Cd, Cu, Pb and Fe in water (2) ascertain the level of heavy metal pollution in the water by the use of Heavy Metal Pollution index, (3) assess the relationship between the metals by correlation analysis. This is the first study on Woji creek that links metals pollution to sources of pollution due to anthropogenic activities taking place on the creek.
2. Methods

2.1. Study area
Woji Creek is in Obio/Akpor Local Government Area of Rivers State, Nigeria. The river is important to the City of Port Harcourt because it is used as a route of transportation to and from other parts of the state where goods and services are required. This creek is also important to the local community because they fish from the river and sells the produce in the local market. This creek is also affected by petroleum spill through legal and illegal oil bunker activities due to its importance as a transport route.

This study area has several point source pollutions that impact on the general environmental conditions of the river. The most physically impacted area on our study river is in Station 3 (figures 1 and 2). In this location, there is an abattoir whose effluent empties into the river. Station 3 also has a sight for boat maintenance and manufacturing. Downstream, in Station 1 there is another boat packing site along the creek of which they clean and empty their condemned Deisel from their tanks into the river. In addition to the point sources of pollution, there is urban runoff from precipitation on the watershed which is densely populated and would therefore, affect
the physicochemistry of the river from its municipal wastes. All of these can cause pollution in the aquatic ecosystem.

### 2.2. Sample collection and analysis

An investigation of the study area was embarked on, this led to the identification of five sample stations based on accessibility and the nature of the activities along the river stretch. Samples were collected in both reverse and free flow (that is from upstream to downstream and downstream to upstream). At each station, five samples were collected transversely and mixed together to form a composite sample representing each station. Sterilized containers were used to collect samples of water to be analysed for metals. Few drops of nitric-acid (HNO₃) was added for the preservation of the sample.

Surface water sample (100 ml) was measured and transferred into a beaker followed by the addition of 5 ml of concentrated nitric acid (HNO₃). The beaker with its content was placed on a hot plate and reduced by evaporation to about 20 ml. The beaker was kept to cool and another 5 ml of concentrated nitric (HNO₃) was added. After which it was returned to heating. As heating continued, a small portion of HNO₃ was added till the solution became light coloured and clear. After cooling, the beaker and watch glass were washed with distilled water into a filter paper and filtered to remove insoluble materials that could clog the equipment. The filtrate was poured into a 100 ml flask and the volume adjusted to 100 cm³ with distilled water.

A GBC SensAA Atomic Absorption Spectrophotometer System was the instrument used in this determination with a detectable limit of 0.001.

### 2.3. Statistical analysis

Heavy Metal Pollution Index (HPI) was used to assess the level of pollution on the creek for every month of study. HPI was calculated with the following equation:

$$\sum_{i=1}^{n} (Q_i \times W_i) \over \sum_{i=1}^{n} W_i$$

where $W_i$ is the unit weight of ith parameters, $Q_i$ is the sub-index of the ith parameter, n is the number of parameters considered. Weighted arithmetic index method has been used for calculation of HPI.

The unit weight ($W_i$) has been found out using the formula:

$$W_i = K / S_i$$

where $K$ is the proportionality constant (1) and $S_i$ is the standard permissible value of the ith parameter.

The sub-index of ($Q_i$) of the parameter is calculated by:

$$\sum_{i=1}^{n} M_i \over S_i \times 100$$

where $M_i$ is the monitored value of the heavy metal of the ith parameter, $S_i$ is the standard value of the ith parameter, in ppb (μg l⁻¹) (table 1).

After completion of the result, the concentration of each pollutant was converted into HPI. The higher HPI value causes greater damage to aquatic health. Generally, the critical heavy metal pollution index HPI value is taken to be 100.

Pearson’s correlation was used to assess the relationship between metals with mean concentrations at different stations. This was done to analyse the relationship between metals and their sources.
Table 2. Status categories of HPI.

| HPI  | Quality of Water |
|------|------------------|
| 0–25 | Very good        |
| 26–50| Good             |
| 51–75| Poor             |
| Above 75 | Very poor |

Table 3. Spatial and temporal analysis of Cadmium concentrations of surface water from Woji Creek.

| Station ID | August | September | October | Mean ± SD | P-Value |
|------------|--------|-----------|---------|-----------|---------|
| 1          | 0.001  | <0.001    | 0.010   | 0.004 ± 0.006 | >0.05 |
| 2          | 0.020  | <0.001    | 0.087   | 0.036 ± 0.046 | >0.05 |
| 3          | 0.490  | 0.002     | 0.099   | 0.197 ± 0.258 | >0.05 |
| 4          | <0.001 | <0.001    | 0.067   | 0.022 ± 0.039 | >0.05 |
| 5          | <0.001 | <0.001    | 0.047   | 0.016 ± 0.027 | >0.05 |
| Mean ± SD  | 0.102 ± 0.217 | 0.0004 ± 0.0009 | 0.062 ± 0.035 |          |
| P-Value    | >0.05  | >0.05     | <0.05   |           |         |

Table 4. Spatial and temporal analysis of Nickel concentrations of surface water from Woji Creek.

| Station ID | August | September | October | Mean ± SD | P-Value |
|------------|--------|-----------|---------|-----------|---------|
| 1          | 0.264  | 0.032     | 0.533   | 0.276 ± 0.251 | >0.05 |
| 2          | 0.137  | 0.005     | 0.922   | 0.355 ± 0.496 | >0.05 |
| 3          | 0.369  | 0.035     | 0.848   | 0.417 ± 0.409 | >0.05 |
| 4          | 0.309  | 0.145     | <0.001  | 0.151 ± 0.155 | >0.05 |
| 5          | 0.816  | 0.018     | 0.424   | 0.419 ± 0.399 | >0.05 |
| Mean ± SD  | 0.379 ± 0.259 | 0.047 ± 0.056 | 0.545 ± 0.369 |          |
| P-Value    | >0.05  | <0.05     | >0.05   |           |         |

3. Results and discussion

3.1. Spatial and temporal concentration of heavy metals

Cadmium concentration in surface water was highest in station 3 with a mean concentration of 0.197 ± 0.258 mg l\(^{-1}\), while station 1 had the lowest concentration of Cadmium (0.004 ± 0.006 mg l\(^{-1}\)) along the study area. In the spatial variation of Cadmium, the month of August had the highest concentration (0.102 ± 0.217 mg l\(^{-1}\)). Results from the one-sample t-Test revealed no statistically significant difference in Cadmium spatially for the month of October (p > 0.05), however, showed no statistically significant difference for other months and for the temporal concentration (p > 0.05) (table 3).

Temporal variation of Nickel concentration in surface water ranged from 0.173 ± 0.282 mg l\(^{-1}\) in station 1. In the months of August and September, the water samples did not record the presence of Nickel in station 4. Spatial variation of Nickel in surface water had concentrations of 0.468 ± 0.428 mg l\(^{-1}\) in August, 0.256 ± 0.262 mg l\(^{-1}\) in September and 0.652 ± 0.403 mg l\(^{-1}\) in October. Temporally, results from one sample t-Test revealed no statistically significant difference in each station (p > 0.05). Similarly, spatial variation showed a statistically significant difference in a one-sample t-Test for the months of August and September (p > 0.05) (table 4).

Results of Iron concentration showed no statistically significant difference (p > 0.05) temporally in the surface water when one sample t-Test was performed. Spatially, there was no statistically significant difference (p > 0.05) in Iron concentration in the months of August and October. However, there was a statistically significant difference (p < 0.05) in the temporal data in the month of September. Temporal data had the highest mean concentration in station 5 (0.419 ± 0.399 mg l\(^{-1}\)) while spatial data had the highest concentration of Iron in surface water in the month of October (table 5).
September

Lead was not detected in stations 1, 2 and 5. Spatially, the highest mean concentration of lead was in the month of October. Mean concentration values of temporal data were lowest in station 3 adding Pb in petrol has been phased out. Petroleum in the creek suggests that some of the heavy metals in the samples analysed come from petroleum. Seawater nickel is present at concentrations of 0.1–0.5 μg l⁻¹[39]. Studies have shown that trace metals exist in substantial amount in crude; Ni, in particular, can be present in crude oil at a concentration of up to 350 ppm [40, 41]. In this study, concentrations of Ni measured from water samples exceed the natural concentration.

The degradation of the abandoned boats can also account for the high concentration

Copper was not detected in stations 2, 3, 4 and 5 in the month of August, and in station 1 in the month of October. Heavy metal dominance in Woji was in the order of Pb > Ni > Fe > Cd > Cu. The visible presence of petroleum in the creek suggests that some of the heavy metals in the samples analysed come from petroleum sources. Worldwide, Lead was added to the production process of petrol [35], however, since 2012 the process of adding Pb in petrol has been phased out [36]. The illegal processing of crude in Nigeria, however, could see to the spatial distribution in every month of study. In station 3, one sample t-Test also showed a statistically significant difference (p = <0.05) in the temporal data. In the month of October, Lead was not detected in stations 1, 2 and 5. Spatially, the highest mean concentration of lead was in the month of September (1.534 ± 0.103 mg l⁻¹) (Table 6). Copper was not detected in stations 2, 3, 4 and 5 in the month of August, and in station 1 in the month of October. Mean concentration values of temporal data were lowest in station 3 (0.014 ± 0.014 mg l⁻¹) and highest in station 5 (0.036 ± 0.056 mg l⁻¹). Spatially, the highest concentration was recorded in the month of October (0.041 ± 0.044 mg l⁻¹) and the lowest concentration in the month of August (0.0102 ± 0.0023 mg l⁻¹) (Table 7).

Heavy metal dominance in Woji was in the order of Pb > Ni > Fe > Cd > Cu. The visible presence of petroleum in the creek suggests that some of the heavy metals in the samples analysed come from petroleum sources. Worldwide, Lead was added to the production process of petrol [35], however, since 2012 the process of adding Pb in petrol has been phased out [36]. The illegal processing of crude in Nigeria, however, could see to the introduction of lead and can account for the high concentration of Pb in the creek. Petroleum could also account for the other trace metals identified [25, 37, 38]. Nickel is the 24th most abundant metal in the Earth’s crust. In seawater nickel is present at concentrations of 0.1–0.5 μg l⁻¹ [39]. Studies have shown that trace metals exist in substantial amount in crude; Ni, in particular, can be present in crude oil at a concentration of up to 350 ppm [40, 41]. In this study, concentrations of Ni measured from water samples exceed the natural concentration.

The degradation of the abandoned boats can also account for the high concentration

| Table 5. Spatial and temporal analysis of Iron concentrations of surface water from Woji Creek. |
|------------------------------------------------|
| Station ID | August | September | October | Mean ± SD | P-Value |
|-------------|--------|-----------|---------|-----------|---------|
| Station 1   | 0.264  | 0.032     | 0.533   | 0.276 ± 0.251 | >0.05   |
| Station 2   | 0.137  | 0.005     | 0.922   | 0.355 ± 0.496 | >0.05   |
| Station 3   | 0.369  | 0.035     | 0.848   | 0.417 ± 0.409 | >0.05   |
| Station 4   | 0.309  | 0.145     | <0.001  | 0.151 ± 0.155 | >0.05   |
| Station 5   | 0.816  | 0.018     | 0.424   | 0.419 ± 0.399 | >0.05   |
| Mean ± SD   | 0.379 ± 0.259 | 0.047 ± 0.036 | 0.545 ± 0.369 |         |
| P-Value     | >0.05  | <0.05     | >0.05   |           |         |

| Table 6. Spatial and temporal analysis of Lead concentrations of surface water from Woji Creek. |
|------------------------------------------------|
| Station ID | August | September | October | Mean ± SD | P-Value |
|-------------|--------|-----------|---------|-----------|---------|
| Station 1   | 1.183  | 1.485     | <0.001  | 0.889 ± 0.785 | >0.05   |
| Station 2   | 1.844  | 1.388     | <0.001  | 1.077 ± 0.960 | >0.05   |
| Station 3   | 1.728  | 1.534     | 0.733   | 1.332 ± 0.527 | <0.05   |
| Station 4   | 0.194  | 1.638     | 0.412   | 0.748 ± 0.778 | >0.05   |
| Station 5   | <0.001 | 1.625     | <0.001  | 0.542 ± 0.938 | >0.05   |
| Mean ± SD   | 0.990 ± 0.855 | 1.534 ± 0.103 | 0.229 ± 0.333 |         |
| P-Value     | <0.05  | >0.05     | >0.05   |           |         |

| Table 7. Spatial and temporal analysis of Copper concentrations of surface water from Woji Creek. |
|------------------------------------------------|
| Station ID | August | September | October | Mean ± SD | P-Value |
|-------------|--------|-----------|---------|-----------|---------|
| Station 1   | 0.051  | 0.027     | <0.001  | 0.026 ± 0.026 | >0.05   |
| Station 2   | <0.001 | 0.003     | 0.076   | 0.026 ± 0.043 | >0.05   |
| Station 3   | <0.001 | 0.028     | 0.014   | 0.014 ± 0.014 | >0.05   |
| Station 4   | <0.001 | 0.089     | 0.015   | 0.034 ± 0.048 | >0.05   |
| Station 5   | <0.001 | 0.008     | 0.1     | 0.036 ± 0.056 | >0.05   |
| Mean ± SD   | 0.0102 ± 0.0023 | 0.031 ± 0.034 | 0.041 ± 0.044 |         |
| P-Value     | <0.05  | >0.05     | >0.05   |           |         |
of other heavy metals, such as Iron, in the sample station [43, 44]. Steel, which is an alloy of Fe and C, has high tensile strength and is inexpensive. It is a major component in the fabrication process of boats in this creek. In the process of water and oxygen, the Fe in the metal is oxidized into Fe\(^{II}\) compounds [45].

Heavy metals have also been associated with abattoir discharge. Concentration of copper as high as 0.85 ± 0.16 mg l\(^{-1}\) has been measured when metals were assessed on surface water under the influence of effluent from abattoir in River Katsina–ala of Benue State, Nigeria [19], these values were higher than those measured in Station 3 which receives the direct input from the abattoir in Woji creek.

3.2. Spatial and temporal assessment of heavy metal pollution index (HPI)

Temporal assessment of Heavy Metal Pollution Index (HPI) in surface water for the months of August was 329.358 (table 8), September was 361.796 (table 9) and October was 112.715 (table 10). These high values were similar to the results obtained from some sites in the evaluation of surface water quality indices and ecological risk assessment for heavy metals in scrapyard neighbourhood [46] and the assessment of heavy metal pollution through index analysis for Yamuna Water in Agra Region in India [47]. The break from the raining reason in August and part of September led to recorded high HPI. But as the begins to fall in October, there is an observed dilution of the metals leading to a lower HPI. This result is in agreement with the assessment of heavy metal pollution through index analysis for Yamuna Water in Agra Region in India [47] which recorded lower HPI in the Post-rainy season. Similarly, research has shown that heavy metal concentration in a tropical mountainous river in Kerala, India reduces in the rainy season compared to other reasons [24].

Spatial assessment HPI (figure 3) in every station greater than 1000, with Station 3 having the highest value of 7615.022. Station 3 has been identified on this creek to be the centre with the highest activities, this is reflected in the high value of HPI. These site-specific high values are similar to those measured in River PovPov in Itakpe Iron-Ore mining area, Kogi State in Nigeria [48] and River Yamuna, Delhi stretch in India [49].
3.3. Correlation and pollution source analysis

The summary of the Pearson’s correlation is presented in table 11. A high correlation of metals indicates a similar source of pollution. A correlation was observed between heavy metals analysed during the study. Cu showed a negative correlation every other metal indicating that copper in the water can be attributed to natural sources. On the other hand, Cd, Pb, Ni and Fe showed a positive correlation, indicating that they come from similar sources, specifically anthropogenic in nature. Ni-Fe showed a significant correlation, this can be attributed to a similar petroleum source. Cd-Pb also showed a significant positive correlation, these can be attributed to deposition from abattoir manure. Therefore, the presence of heavy metal in Woji Creek is influenced by natural as well as anthropogenic sources.

4. Conclusion

This study was designed to access the concentration of some heavy metals in the water column of a 3.2 km stretch of Woji Creek. In addition to this, this study used Heavy Metal Pollution index to ascertain the levels of heavy metal pollution by comparing the concentrations of the metals to Aquatic Toxicity Reference Values (TRV).

Results from the research have shown high values of metal concentration in surface water from Woji Creek, these values are much higher than the Aquatic Toxicity Reference Values (TRV). Cadmium and lead were the major contributors to contamination in this creek. Employing HPI in analysing the level of pollution compared to TRVs, the results indicates a heavily polluted water body with values over 100. These high values were majorly
due to the contribution of Pb, Cd and Ni in the water. The concentrations in water, therefore, could pose a threat for aquatic biota in this Woji Creek.

There is a need for proper management and clean-up of the aquatic system, especially in Woji Creek. This study successfully relates the metal concentration in the creek to the possible sources of pollution. This study also identified the station of the creek with the highest level of pollution having the most impact from anthropogenic activities. This can be a road map to the proper clean-up and management of this creek. This should first include the removal of scrap metals and abandoned boats from the creek, followed by metal removal through phyto remediation or other processes. Pre-treatment of wastewater coming from the abattoir before final disposal into the river should be carried out. This will help in removing pollutant from that source. The creation of a constructed wetland is also another management strategy that can be applied to this creek.

This research will add to the knowledge gathered by other scientific researchers in the field of environmental research. The study also opens a case for further study on this river to assess metal bioaccumulation and possible health risk assessment from the high levels of metal concentration in this river.

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Conflict of interest

There are no conflicts of interest to declare on this study.

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ORCID iDs

Amalo Ndu Dibofori-Orji https://orcid.org/0000-0002-7589-0015
Owhonda Chikeru Ihunwo https://orcid.org/0000-0003-0676-6886
Amir Reza Shahabinia https://orcid.org/0000-0001-8593-5478

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