

17(4): 1-11, 2018; Article no.JGEESI.44485 ISSN: 2454-7352

Heavy Metal Concentrations in Mangrove Sediments and *R. racemosa* **in Niger Delta, Nigeria**

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Authors' contributions

This work was carried out in collaboration between both authors. Author NN designed the study, performed the sampling and statistical analyses, managed the literature searches, wrote the protocol, and wrote the draft of the manuscript. Author HI designed and wrote the manuscript with author NN managed the laboratory and XRF analyses of the study. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JGEESI/2018/44485 *Editor(s):* (1) Dr. Wen-Cheng Liu, Department of Civil and Disaster Prevention Engineering, National United University, Taiwan and Taiwan Typhoon and Flood Research Institute, National United University, Taipei, Taiwan. (2) Dr. Ioannis K. Oikonomopoulos, Core Laboratories LP., Petroleum Services Division, Houston Texas, USA. *Reviewers:* (1) Ita, Richard Ekeng, University of Uyo, Nigeria. (2) Aminanyanaba Onari Asimiea, University of Port Harcourt, Nigeria. Complete Peer review History: http://www.sciencedomain.org/review-history/26949

Original Research Article

Received 12 August 2018 Accepted 26 October 2018 Published 31 October 2018

ABSTRACT

This study assessed the concentration of As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, Zr, Cl, TS, TiO₂, MnO, CaO and P₂O₅ in the mangrove sediment and *R. racemosa* samples from Choba, Ogbogoro and Isaka in Niger Delta, Nigeria. A total of 6 sediment and 9 *R. racemosa* samples were collected using the simple random sampling. Two core sediment samples of 10 cm depth and three *R. racemosa* leave, stem and root samples were collected from each of the sampled locations. Both the sediment and *R. racemosa* samples were oven dried, powdered, made into briquettes and analyzed using XRF. The results showed contrasting heavy metal concentrations in the sediments and *R. racemosa*. As, Pb, Cu, Ni, Y, Nb and Zr had higher concentrations in the sediments while the concentrations of Zn, Sr, Cl, TS, MnO, CaO and P2O5 were more in *R. racemosa* tissue. However, Cr, V and TiO₂ which had relatively high concentrations in the sediments were not detected in *R*. *racemosa*. Graphical analyses revealed a correlation between concentrations in sediment and *R. racemosa* as well as a similar pattern of heavy metal concentrations in the *R. racemosa* leaves, stems and roots in Choba, Ogbogoro and Isaka. But variations were found in the leaf/stem and leaf/root upward transport relationship. Most heavy metals were found to concentrate in *R. racemosa* roots while the least concentrations were found in the leaves.

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Keywords: Mangroves; sediments; R. racemosa; heavy metals; Niger Delta. heavy

1. INTRODUCTION

Mangroves are unique floral assemblage found in the inter-tidal zones of tropical and sub-tropical regions of the world. They are mostly shrubs that grow in the marine or estuarine environments and thus are halophytic. As an adaptive strategy, the mangroves have a complex root system that enables them to cope with saline water and wave action. Mangroves function as a significant sink for classics, $CO₂$, detritus as well as anthropogenic pollutants. It stabilises shorelines by trapping sediments, contributes to climate protection by sequestrating carbon and also provides valuable breeding ground for fish and other organisms that inhabit the ecoregion. s are halophytic. As an adaptive strategy,
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Niger Delta mangrove forest is the largest concentration of mangroves in Africa. It has an protection by sequestrating carbon and also
provides valuable breeding ground for fish and
other organisms that inhabit the ecoregion.
Niger Delta mangrove forest is the largest
concentration of mangroves in Africa. It has wetland area was formed due to sediment deposition by the River Niger and located between longitudes 5°E to 8°E and latitudes 4°N to 6ºN [2,3]. According to [1], the Niger Delta was formed due to sedime
the River Niger and locate
des 5°E to 8°E and latitudes 4°

60% of the fishes caught between the Gulf of Guinea and Angola.

ITRODUCTION mangroves are unique floral assemblage found Cuinea and Angola.

in ther-tidal zones of topical and sub-tropical conto Guinea and Angola.

in the marine or estuarine environments due to natural and anthropogeni Despite its importance, mangroves are degraded due to natural and anthropogenic pollution from urban and industrial waste, leaching from bedrocks and soils [4], atmospheric deposition [5] and tidal inflow [6]. Although mangroves are referred to as sink for pollutants, changing physio-chemical conditions within the ecosystem could turn them into pollution sources [7]. Hence the need to investigate the heavy metal concentration in mangrove sediments and R. *racemosa* in Niger Delta mangroves. Specifically, this study seeks to: (a) determine the concentration of trace and major elements in Niger Delta mangrove sediments, (b) determine the concentration of trace and major elements in *R. racemosa* roots, stems and leaves and (c) racemosa in Niger Delta mangroves. Specifically,
this study seeks to: (a) determine the
concentration of trace and major elements in
Niger Delta mangrove sediments, (b) determine
the concentration of trace and major elemen locations within Niger Delta mangroves have the same heavy metal uptake pattern. and industrial waste, leaching from

tidal inflow [6]. Although mangroves are

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chemical conditions within the ecosystem

urn them into pollution sources [7]. Hence

eed to investigate

Fig. 1. Map of the study location showing sampling locations [8]

2. MATERIALS AND METHODS S

2.1 Study Site

The mangrove forests used for this study are located in Choba and Ogbogoro along the banks of the New Kalabar River as well as Isaka along The mangrove forests used for this study are located in Choba and Ogbogoro along the banks of the New Kalabar River as well as Isaka along the banks of the Bonny River (4°26 to 4°53N and 6º45 to 7º15) on the Eastern Niger Delta (Fig.1). These rivers drain through the areas of hydrocarbon exploration and exploitation [9], emptied into the Atlantic Ocean and equall serve as tidal inlets. The tidal amplitude ranges between $1 - 3$ m $[10, 11]$. The area has an equatorial climate with high relative humidity and mean annual rainfall of about 4,500 mm [12]. Temperatures are high all year round and range between 18ºC to 33ºC [11]. The geology consists of mainly alluvial sedimentary basin and basement complex [13]. Settlements, oil and gas industries, fishing and crop farming, are the major land use within the study area. 15) on the Eastern Niger Delta (Fig.1).
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en 18°C to 33°C [11]. The geology consists
ainly alluvial se

2.2 Study Species

R. racemosa also known as red mangroves is the mangrove species used for this study. It belongs to the family of Rhizophoraceae. This species is limited to the Atlantic East Pacific (AEP) with the largest concentration on the Atlantic coast of West Africa [14]. In Niger Delta, the *R. racemosa* is locally called Angala or Ngala.
It is the most predominant species and consists
of about 90% of the mangrove forest [15,16]. *R*. It is the most predominant species and consists of about 90% of the mangrove forest [15,16]. R. *racemosa* is a pioneer species with numerous aerial stilt roots and can grow to a height of 45 m [17]. The locals mostly exploit it for firewood and timber. *emosa* is a pioneer species with num
ial stilt roots and can grow to a height of
]. The locals mostly exploit it for firewood

2.3 Sediment Collection and Preparation Sediment

Sediment core samples of 10 cm depth were collected from Choba, Ogbogoro and Isaka. Two core samples were collected from each location $(n = 2)$. Thus, a total of 6 core sediment samples were collected. The cores were taken using a transparent 2-inch diameter PVC pipe. Prior to coring, the PVC pipes were decontaminated using ethanol. The cores were manually driven into the muddy mangrove sediments and carefully retrieved. Homogenization of the retrieved core sediment samples was done after which they were placed in ziplock bags, labelled and transported out and stored at 4°C. The samples were air dried for 48 hours to reduce weight before repackaging and putting them in a Sediment core samples of 10 cm depth were collected from Choba, Ogbogoro and Isaka. Two core samples were collected from each location (n = 2). Thus, a total of 6 core sediment samples were collected. The cores were taken plastic box for export to the Geoscience Laboratory, Shimane University, Japan.

About 30 g each of the sediment samples were put in decontaminated beakers and covered with aluminium foil and using the ISUZU Muffle Furnace, and they were oven dried at 160°C for 48 hours. Sediment grinding was done using the Automatic Agate Mortar and Pestle for 20 minutes. The powdered sediments were made into briquettes by compressing about 5 g each using 200 kN for 60 seconds. ent samples were
and covered with
a ISUZU Muffle
Iried at 160°C for hours. Sediment grinding was done using the
omatic Agate Mortar and Pestle for 20
uttes. The powdered sediments were made
briquettes by compressing about 5 g each
ng 200 kN for 60 seconds.
R. racemosa Sample Collection an

2.4 *R. racemosa* **Sample Collection and Preparation**

The *R. racemosa* samples were equally collected from Choba, Ogbogoro and Isaka. The stilt aerial roots, stems and leaves of three *R. racemosa* plants were sampled in each location $(n = 3)$. plants were sampled in each location (n = 3).
Thus, a total of 9 *R. racemosa* samples were collected. The samples were cut into smaller sizes and placed in plastic ziplock bags and labelled. The samples were immediately taken to the Nigerian Stored Products Research Institute (NSPRI) Port-Harcourt where they were dried at 80° C for 24 hours. Then, they were repackaged and carefully arranged in plastic boxes, sealed and exported to the Geoscience Laboratory, Shimane University, Japan. is samples were cut into smaller
aced in plastic ziplock bags and
samples were immediately taken to
Stored Products Research Institute
Harcourt where they were dried at
ours. Then, they were repackaged
arranged in plastic

About 20 g of the root, stem and leaf samples each was put in decontaminated beakers, covered with aluminium foil and using the ISUZU Muffle Furnace, they were oven dried at 110^oC for 24 hours and later at 160° C for 48 hours. They were ground using the Automatic Agate Mortar and Pestle for 20 minutes. Also, the powdered *R. racemosa* samples were made int briquettes by compressing about 5 g each using 200 kN for 60 seconds. at 160°C for 48 hours.
hy the Automatic Agate
20 minutes. Also, the
samples were made into

2.5 XRF Analysis

Thirteen trace elements; As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, Zr, Cl and TS as well as four major briquettes by compressing about 5 g each using
200 kN for 60 seconds.
2.5 XRF Analysis
Thirteen trace elements; As, Pb, Zn, Cu, Ni, Cr,
V, Sr, Y, Nb, Zr, Cl and TS as well as four major
elements; TiO₂, MnO, CaO and P₂ analysed for both sediment and *R. racemosa* samples using X-ray fluorescence (XRF) RIX-200 spectrometer. In accordance with [18], all the XRF analysis were made from pressed powder briquettes with average errors being less than \pm 10%. In accordance with [18], all the

e made from pressed powder

rage errors being less than \pm
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ent and *R. racemosa* samples

2.6 Statistical Analysis

The mean concentrations of the trace and major elements in sediment and *R. racemosa* were done using Microsoft Excel 2013. The KaleidaGraph 4.0 was used to plot the concentration graphs for trace and major elements in the sediments and *R. racemosa* roots, stems and leaves.

3. RESULTS

3.1 Concentration of Heavy Metals in Sediments

The mean concentration and standard deviations of elements and oxides in the mangrove core sediments in Choba, Ogbogoro and Isaka are presented in Table 1. For the sediment characteristics, see [8,9]. Choba sediments have higher concentrations of elements compared to Ogbogoro and Isaka sediments. The highest concentrations of Zr, V, Cr, Zn, Ni, Pb, Cu, Nb and Y were all recorded in Choba sediments. Though Cl and TS were most concentrated in Isaka, however, Isaka sediments are the least contaminated of the three locations sampled. $TiO₂$ concentrated more in Choba sediments, CaO and P_2O_5 were more concentrated in Ogbogoro sediments while MnO is equally concentrated in Choba and Ogbogoro sediments. Interestingly, similar heavy metal concentration pattern was observed in the sampled sediments. The sequence of elemental concentration in Choba is Zr>V>Cr>Sr>Zn>Ni>Pb>Cu>Nb>Y>As; Zr>V>Cr>Sr>Zn>Ni>Pb>Nb>Y>Cu>As in Ogbogoro and Zr>Cr>V>Sr>Zn>Ni>Pb> Cu>Nb>Y>As in Isaka. The major elements have the same concentration sequence in all the locations; $TiO₂ > CaO > P₂O₅ > MnO$. Fig. 2 shows

the graphical representation of the heavy metal concentration sequence in the study area.

3.2 Heavy Metals Distribution in *R. racemosa*

Table 2 shows the heavy metal concentrations in the leaves, stems and roots of *R. racemosa* samples from Choba, Ogbogoro and Isaka mangroves. Among the thirteen trace elements and four major elements tested for, Cr, V and TiO₂ were not detected.

3.2.1 Choba

The *R. racemosa* leaves, stems and roots sampled at Choba mangroves along the banks of the New Kalabar River showed varied concentrations of both trace and major elements. As (2.2, 1.0) and Pb (8.6, 5.0) had the highest concentrations in the roots and least concentrations in the leaves. Zn (170.2, 47.1) and Ni (24.7, 15.0) concentrated most in the stems but least in the leaves. The highest and least concentrations of Cu (7.0, 3.1) and P_2O_5 (0.7, 0.4) were found in the leaves and roots respectively while Cl (63973.3, 11590.0) an TS (14779.7, 3501.0) were most concentrated in the leaves and least in the stems. Sr (102.0, 53.2), Zr (27.7, 22.2), MnO (0.2, 0.1) and CaO (2.7, 1.8) were found to concentrate mostly in the stems and minimally in the roots while Y (3.5, 2.5) and Nb (2.5, 1.9) concentrated more in the roots and least in the stems.

 ± ---- Standard deviation

Fig. 2. Pattern of heavy metal concentrations in Choba, Ogbogoro and Isaka mangrove 2. Pattern mangrove of [19].Pattern Ogbogoro sediments normalized to the UCC values of [19].

3.2.2 Ogbogoro

The trace and major element concentrations in The *R. racemosa* leaves, stems and roots sampled in Ogbogoro mangroves also along the banks of the New Kalabar River showed different concentrations. As (2.0, 1.0), Pb (7.7, 5.4), Zn (151.8, 41.8) and Nb (2.2, 1.9) concentrated mostly in the roots and least in the leaves. The concentrations of Cu (3.2, 1.0) and Ni (23.0, 12.9) were highest in the stems and lowest in the leaves. Sr (171.5, 69.2), Zr (39.6, 23.5), CaO (4.5, 2.1) and P_2O_5 (0.6, 0.4) had most concentrations in the leaves and least concentrations in the roots while Cl (56087.0, 10943.0) an TS (16430.3, 3233.3) were most concentrated in the leaves and least in the stems. Y (3.0, 2.4) was found to be most concentrated in the roots and least concentrated in the stems while MnO (0.1, 0.0) had the highest and lowest concentrations in the stems and roots respectively. /er showed different
1.0), Pb (7.7, 5.4), Zn
lb (2.2, 1.9) were concentrated mostly in the roots and least in the leaves. The concentrations of Cu $(3.2, 1.0)$ and Ni $(23.0, 12.9)$ were highest in the stems and lowest in the leaves. Sr $(171.5, 69.2)$, Zr $(39.6, 23.5)$, CaO $(4.5, 2$

3.2.3 Isaka

The trace and major element concentrations in R. *racemosa* leaves, stems and roots sampled in Isaka mangroves along the banks of the Bonny River indicated variations in concentration. As (1.5, 1.0), Zn (187.5, 30.8), Ni (18.0, 4.0) and Nb (2.0, 1.7) had the highest concentrations in the roots and lowest in the leaves. The concentrations of Pb $(6.8, 4.2)$ and Cu $(3.8, 2.5)$ were most in the stems and least in the leaves. Isaka mangroves along the banks of the Bonny
River indicated variations in concentration. As
 $(1.5, 1.0)$, Zn $(187.5, 30.8)$, Ni $(18.0, 4.0)$ and Nb
 $(2.0, 1.7)$ had the highest concentrations in the
roots and lowest in Sr (283.1, 149.4), Zr (53.0, 36.0), CaO (6.9, 3.6) were found to have the most concentrations in both stems and least concentrations in the roots. The concentration of Y (2.6, 2.4) and Cl (77597.5, 17386.3) were highest in the leaves and lowest in the stems while TS (13239.3, 3382.3), MnO $(0.2, 0.1)$ and $P_2O_5(0.6, 0.3)$ were highest in the leaves and lowest in the roots. Sr (283.1, 149.4), Zr (53.0, 36.0), CaO (6.9, 3.6)
were found to have the most concentrations in
both stems and least concentrations in the roots.
The concentration of Y (2.6, 2.4) and Cl (77597.5,
17386.3) were highest i

Generally, it is interesting to note that R . racemosa sampled in Choba, Ogbogoro and Isaka mangroves were found to have similar heavy metal uptake and concentration pattern in their leaves, stems and roots. However, the leaf/stem and leaf/root upward transport relationship showed some variations. This is shown in Figs. 3 and 4. mangroves were found to have similar
metal uptake and concentration pattern in
leaves, stems and roots. However, the

3.3 Comparison between Heavy Metal arison Concentrations in Sediments and *R. racemosa*

The comparison of the sediment heavy metal concentration mean values in Table 1 and *R. racemosa* heavy metal concentration mean values in Table 2 showed variations in concentrations. It was found that As, Pb, Cu, Ni, Y, Nb and Zr concentrations were higher in the sediments while Zn, Sr, Cl, TS, MnO, CaO and P_2O_5 had higher concentrations in R. racemosa relative to the sediments. However, Cr, V and relative to the sediments. However, Cr, V and
TiO₂ were not detected in *R. racemosa* despite having sediment concentration values of 136.67, having sediment concentration values of 136.67,
201 and 1.29 ppm respectively. The graphical Table 2 showed variations in
is. It was found that As, Pb, Cu, Ni,
in concentrations were higher in the
nile Zn, Sr, Cl, TS, MnO, CaO and
her concentrations in *R. racemosa*

comparison of heavy metal concentrations in sediments to concentrations in *R. racemosa* leaves, stems and roots for the sampled

locations are shown in Fig. 5 for Choba, Ogbogoro and Isaka respectively.

 Fig. 3. Concentration pattern of Heavy metals in Fig. R. racemosa leaves, stems and roots in Choba, Ogbogoro and Isaka and Isaka. (Ch --- Choba, Og --- Ogbogoro, Is --- Isaka)

Fig. 4. Leaf/Stem and Leaf/Root trace metals and major elements concentration in Choba, Ogbogoro and Isaka.

Table 2. Concentration of trace and major elements in Niger Delta mangrove R. racemosa in Choba, Ogbogoro and Isaka

nd --- not detected, ± --- Standard deviation

Fig. 5. Concentration trends of heavy metals in sediments and *R. racemosa* leaves, stems and **roots in Choba, Ogbogoro and Isaka. Isaka.** *(Ch --- Choba, Og --- Ogbogoro, Is --- Isaka)*

4. DISCUSSION

Heavy metal accumulation in plants is a multistep process that includes mobilisation from soil into the soil solution, uptake by roots, xylem loading and transport to the shoots [20]. This multi-step process is largely determined by pH. Thus, acidity is the most important soil characteristic that determines the bioavailability of heavy metals as it affects both the chemical speciation of metals in soil and its binding capacity to the active sites on biota [21]. This is because a decrease in the rhizosphere's pH increases metal solubility which might enhance uptake by plants [22]. In an earlier study, Nwawuike and Ishiga [8] reported that Choba, Ogbogoro and Isaka sediments have pH ranges of 5.75 - 6.36, 5.84 - 6.31 and 6.19 - 7.03 respectively. These pH ranges indicate that the study area sediments are slightly acidic. Hence, the moderate impact on the solubility and bioavailability of the metals analysed. into the soil solution, uptake by roots, xylem
loading and transport to the shoots [20]. This
multi-step process is largely determined by pH.
Thus, acidity is the most important soil
characteristic that determines the bioa

concentrated most on the *R. racemosa* roots in Choba, Ogbogoro and Isaka. However, Ni, CaO Choba, Ogbogoro and Isaka. However, Ni, CaO
and MnO as well as Cu, Sr, Zr and P₂O₅ had the highest concentrations in stems and leaves respectively. highest concentrations in stems and leaves
respectively.
Higher As concentration in the *R. racemosa* roots Comparatively, As, Pb, Zn, Nb and Y

N Comparatively, As, Pb, Zn, Nb and Y
cumulation in plants is a multi- Choba, Ogbogoro and Isaka. However, Ni, CaO
tincludes mobilisation from soil and MnO as well as Cu, Sr, Zr and P₂O_s had the
uttion, uptake by ro observed in this study is consistent with the findings of [23] that As is not readily transported observed in this study is consistent with the
findings of [23] that As is not readily transported
to the aerial plant parts. Though Pb is a nonessential metal, its concentration and translocation in plants are determined by salinity. Thus, Pb accumulates mostly in the roots at low salinity while at higher salinity, more proportion of Pb is translocated to the shoots [24]. Zn had a higher concentration in shoots compared to Cu. However, the observed high translocation of Zn and Cu particularly from the roots to the stems might be because they are essential for plant However, the observed high translocation of Zn and Cu particularly from the roots to the stems might be because they are essential for plant growth. The concentration of Zn in the *R*. *racemosa* leaves corresponds to concentration in al metal, its concentration and
cation in plants are determined by salinity.
Pb accumulates mostly in the roots at low
while at higher salinity, more proportion of
anslocated to the shoots [24]. Zn had a
concentration in s

sediments. This implies high translocation. Ni concentration was higher in Choba and Ogbogoro relative to Isaka. According to Yusuf et al. [25], Ni uptake in plants usually declines at high soil solution pH values due to the formation of less soluble complexes. Cr, V and $TiO₂$ had comparatively high concentrations in the mangrove sediments but were not detected in the *R. racemosa* roots, stems and leaves. Though the metals were available in the sediments, they were unavailable for uptake. This might be due to phytoexclusion. However, it has been argued by [26,27] that unavailability of metals for plant uptake might be due to adsorption onto the surface of minerals like clay, iron or manganese oxy-hydroxides. The observed Sr concentration in the *R. racemosa* tissue far exceeded their concentration in the sediments. This indicates active translocation and is suggestive that *R. racemosa* might be a good phytoextractor or accumulator of Sr, Y, Nb and Zr. Concentrations in the sediments were much higher compared to concentrations in the *R. racemosa* tissue.

The electrical conductivity (EC) values of the mangrove sediments in Choba, Ogbogoro and Isaka range from -285 to -199 mV, -289 to 93 mV and -229 to -15 mV respectively [8]. By this, the sediments are in anoxic condition. According to [28], Mn tends to undergo a reduction in an anoxic environment and as such, it is more available for uptake. This is in line with the findings of this study that Mn in oxidised form was found more in *R. racemosa* tissue than in the sediments. Similarly, the uptake of Cl, TS, CaO and P_2O_5 were high. According to Medina et al. [29], *Rhizophora* species have high phosphorous requirement than any other mangrove species. Thus, *R. racemosa* is a good phytoextractor of Cl, TS, MnO, CaO and P_2O_5 .

Salts are incorporated into the mangroves from the substrates and eventually transported to the leaves [30]. Rhizophora species have highly efficient initial salt exclusion and minor salt secretion capacity [31]. However, when the saline conditions are high, the survival rate of the plant is dependent on its ability to effectively regulate internal salt concentrations and as such prevent the ions from becoming toxic [32]. Therefore, salt secretion in mangroves is a regulatory mechanism used to control high internal salt concentrations. The secretion of salt is done by the salt glands in the leaves which screen the salinity of the nutrient solution [33]. Though NaCl is mostly secreted, the secretion

solution also contains calcium, sulphur and zinc [34]. High CaO in the leaves helps to increase the rate of salt secretion by the salt glands [35] and thus facilitates salt balance. Also, a high concentration of P_2O_5 in the leaves play an important role in the enhancement of the food chain quality given that it is critical to ATP (adenosine triphosphate) [36,37] and phosphorus cycling in the ecosystem. This is consistent with the findings of this study which indicate high concentrations of Cl, TS, MnO, CaO and P_2O_5 in the *R. racemosa* leaves relative to the stems and roots.

On the average, it was found that heavy metals were concentrated most on the *R. racemosa* roots and least on the leaves. Given that about 90% of the Niger Delta mangrove forest is dominated by *R. racemosa*; low concentration of metals in its leaves suggests low metal contamination of the detrital food chain. This is because the major components of the detrital food chain are the leaf litter [38].

5. CONCLUSION

Variations were observed on the analysed heavy metal concentrations in both sediment and *R. racemosa* samples. TS and Cl had the highest concentration in sediments while Cl and TS were most concentrated in the *R. racemosa*. However, despite the high concentrations of Cr and V in the sediments, they were not detected in the *R. racemosa* tissue. This might be due to phytoexclusion or adsorption onto the surface of minerals like clay, iron or manganese oxyhydroxides. *R. racemosa* in Choba, Ogbogoro and Isaka mangroves were found to have similar heavy metal uptake pattern in their leaves, stems and roots. However, the leaf/stem and leaf/root upward transport relationship showed some variations. Heavy metals concentrated most on the roots and least on the leaves. The low concentration of metals on the leaves indicates that the detrital food chain might be uncontaminated. However, there is a need for constant monitoring.

ACKNOWLEDGEMENTS

We are grateful to the Ministry of Agriculture, Forestry and Fisheries, Kobe, Japan for import permission; Nigeria Agricultural Quarantine Service, Port-Harcourt, Nigeria for export permission; Dr. Emmanuel Attah Ubuoh and Donald Osujieke for their help with sampling.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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