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Accumulation of Pb, Cd and Ni in Sediments and Root of Mangrove Plant (*Laguncularia* sp) from the fringes of the Upper Bonny Estuary, Nigeria.

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ABSTRACT: The accumulation of heavy metals in sediments and roots of mangrove plant (*Laguncularia* sp) in relation to the age of the plant root was evaluated. Composite sediment and root samples were collected from three spots per station at three different locations (St.1: Borikiri, St.2: Bundu-Ama, St3: Eagle Island) of mangrove fringes in the upper Bonny estuary. Heavy metal content of sediment and roots were analyzed using spectrophotometric methods while growth rings/bands was used to estimate age of root. There were variations in the metal content of sediments in space and time. Observed heavy metal range (µg/g) in sediments (N: 0.001 - 2.8, Pb: 0.001 - 4.5, Cd: 0.001 - 0.35) and root (N: 0.001 - 3.3, Pb: 0.001 - 7.1. Cd: 0.001 - 0.5) generally indicated higher values in roots compared to sediments. The age of the plant root examined varied between 2.3 - 5.7 years across sites. ANOVA showed significant difference ($p<0.05$) in metal concentration in space and time. The concentration of Pb, Cd and Ni in the root of plants fell within and slightly above standard limits of WHO/FAO Pb: 5.0 µg/g; Cd 0.2 µg/g and Ni: 1.5 µg/g).In conclusion, Pb, Cd and Ni in sediment had strong positive linear relationship with those in the plant root but the age of plant root did not give significant relationship with metal accumulation. *Laguncularia* roots generally accumulated more heavy metals compared to the surrounding sediments which was attributed to discrete exposure of the sites to anthropogenic impacts.

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Long-term pollution due to human activities all over the world had led to elevated concentrations of heavy metals and hydrocarbons in sediments around mangrove forests (Perdomo *et al*., 1998; Harris and Santos, 2000; Daka *et al*., 2007; Moslen and Daka, 2016; Moslen and Miebaka 2017a; Moslen and Ekweozor, 2017). Deterioration of sediment quality by heavy pollution due to increasing anthropogenic activity is of major concern (Moslen and Aigberua 2018a). Due to their physical and chemical properties, mangrove muds have the capacity to accumulate materials discharged to the near shore marine environment (Harbison, 1986).In view of such bioaccumulation and concentration of hydrocarbon and heavy metal pollutants in water, sediment and biota, regular study and monitoring in order to detect variations is necessary (Moslen *et al*., 2017; Moslen and Miebaka 2017b; Moslen and Aigberua 2018b). The Niger Delta coastal fringe is one of such impacted areas due to industrialization. The closeness of mangrove ecosystems to urban areas (Tam and Wong, 2000; MacFarlane, 2002; Preda and Cox, 2002) expose them to impacts of urban and industrial run-off laden with heavy metal contaminants. This study therefore sought to evaluate heavy metals concentration in sediments and bioaccumulation in the root of a mangrove plant with respect to the age of the plant root.

MATERIALS AND METHOD

Site description: The study areas were st.1: (Borikiri), St.2: (Bundu Ama) and St.3 (Eagle island) all in the southern Niger Delta region of Nigeria (Fig. 1). The vegetation in the study area is mangrove with a mix of *Avicennia*, *Laguncularia* and *Rhizophora* with the latter as most dominant. Anthropogenic activities such as dredging, metal fabrication/maintenance works, oil serving company activities, illegal oil bunkering and discharge of waste water into nearby creeks characterized the study area.

Mangrove root samples collection: Three samples (roots) per station were collected and composited on a monthly basis for six months (December 2017 - May 2018). A section of the root samples (not composited) was collected with sharp stainless steel knife and used for estimation of root age. The samples were properly labeled and immediately taken to the laboratory for analysis.

Sediment: Sediment samples were collected from the same stations as the root samples using soil/sediment

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augar. Three spots around the root were sampled and composited. Sediment samples were put in properly labeled polythene bag and taken to the laboratory for analysis. All samples were preserved in mobile coolers while in transit.

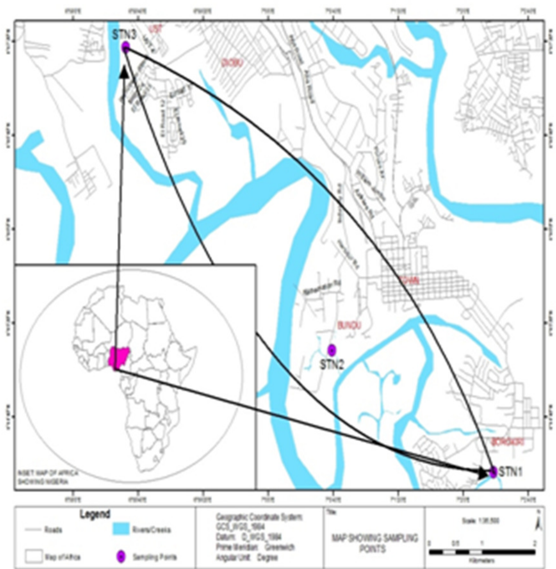

Fig. 1: Map of study area with sampled sites

Sample Analysis: Sediment and plant root samples were dried and digested with HCl/HNO_3 using the method of the American Society for Testing and Materials (ASTM 1986). The concentration of heavy metals in samples were determined with an Atomic Absorption Spectrophotometer (GB Avanta PM AAS, S/N A6600 which had detection limit of 0.001 µg/g). Metal concentration was blank-checked and expressed as µg/g dry weight of sample.

Estimation of Age of Mangrove Root: A section of the mangrove root used for heavy metal analysis was air dried and surface polished to enable visualization of growth zones/ring bands. Three samples were examined to obtain average age. Macroscopic and microscopic observations were made and ring-like formations (concentric circles) counted to estimate age of root. This is similar to methods used by other researchers (Verheyden *et al*., 2004; Menezes *et al*., 2003) to determine age of mangrove plants.

Data Analysis: Analysis of variance (ANOVA - General Linear Model) was used to test significant difference in metal concentrations across stations and also between the months of study. Tukey test was used for post hoc analysis. Pearson correlation coefficient was used to determine relationship between metal concentration in root, sediment and age of plant. The software Minitab 16 was used for the statistical analysis.

RESULTS AND DISCUSSION

The spatio-temporal variation of heavy metal concentration in sediments and roots of *Laguncularia spp*. in relation to the age of the plant root is presented in Fig. 2a- f while the ANOVA summary and correlation output tables are presented in Tables 1, 2 and 3.

There were spatial and temporal variations in the concentration of heavy metals in sediments and roots of *Laguncularia* plant. During the month of December, Ni was the only metal detected and was higher in sediments compared to the plant root except at St.3. The highest value observed in sediment was 2.8 µg/g at St.1 while the highest value of Ni in root was 3.3 µg/g at St.3.

The age of the root of *Laguncularia* also differed (3.3 - 4.3 yrs) across sites but the root with the lowest age (3.3yrs) accumulated more Ni. In January, the concentration of Pb was more than other metals with the highest concentration (7.1µg/g) also observed in roots at St.3 followed by that at St.2 (2.0 µg/g). The concentration of Pb in sediment ranged from 0.5 - 4.5 µg/g. Variations in sediment metal content is attributed to exposure of site to varying degree of anthropogenic activities in addition to effect of physical processes such as waves, salinity differences, and tidal inundations. These processes enable bioturbation, re-suspension and erosion that are known to affect the metal concentrations in surface sediments (Bellucci *et al*., 2002).The age of the root also varied across sites with the maximum Pb concentration also found in root with least age (2.6 yrs). The concentration of Cd in root was higher compared to values in the surrounding sediment. In February Pb and Cd were only observed at St.1 in sediment and roots while Ni was observed in all the stations but only in roots. This also suggests the tendency of accumulation of the metals in roots compared to sediments.

The same trend was also observed in the month of March with higher values of Pb, Ni and Cd observed only in roots compared to sediments. Such values of Cd in both sediment and root in the current study were in consonants with values reported by Nazli and Hashim (2010) who also reported higher values of Pb compared to this study. Age variation also existed but in February the root with the highest age did not accumulate the highest amount of metals but in the month of March, the trend was contrary.

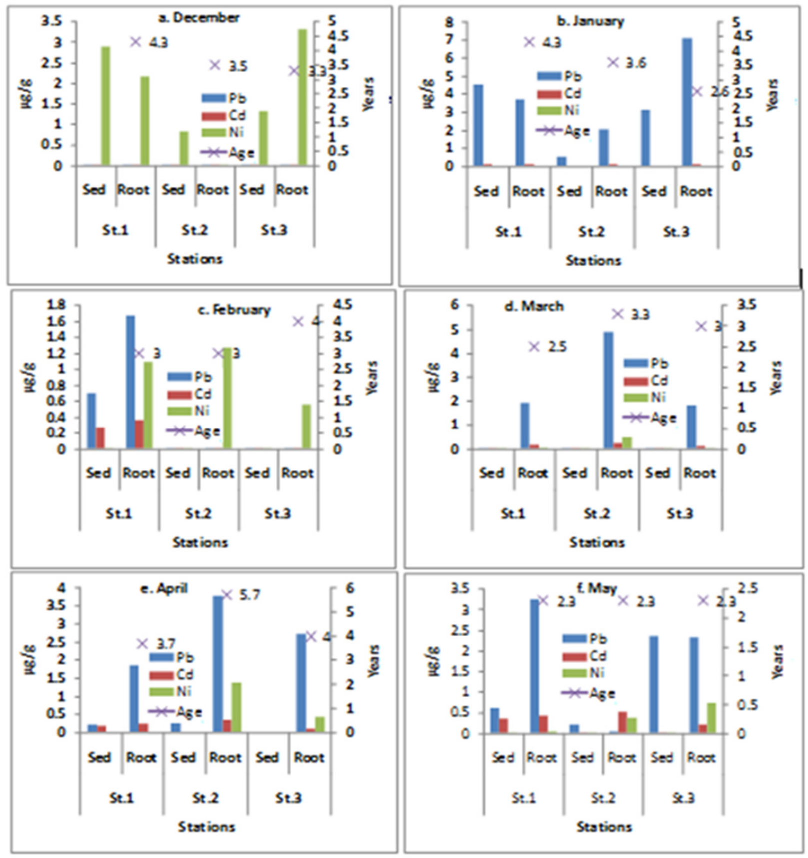

Fig. 2a - f: Variation of heavy metal concentration in sediments and roots across study sites

Table 1: Summary of ANOVA Table - Heavy metals in sediments and root with F and P values

Metals	Pb		Cd		Ni	
Sediments	F-value	P-value	F-value	P-value	F-value	P-value
Location	0.97	0.413	4.45	0.041*	1.00	0.402
Period(Months)	3.51	0.043*	1.7	0.222	7.17	0.004**
Roots						
Location	0.05	0.952	6.17	0.018*	0.24	0.794
Period (Months)	2.41	0.111	6.64	0.006**	1.90	0.181

*significant (p<0.05), ** significant (p<0.01)

Table 2: Correlation output: Metal content in sediment versus metal content in root

	S LcPb	S Lc Cd	S Lc Ni
R LcPb	0.551(0.018)*	0.068(0.789)	
R Lc Cd	-0.040(0.874)	0.550(0.018)*	
R Lc Ni	-0.247(0.324)	-0.101 (0.691)	0.648 (0.004)**

Table 3: Correlation output: Metal content in root versus age of root

	R LcPb	R Lc Cd	R Lc Ni
Lc Age	0.009 (0.972)	-0.376 (0.124)	0.178 (0.481)

***Key**: Pearson correlation; Figure in parenthesis - P-Value; * Significant (p<0.05); ** Significant (p<0.01)*

In April metal concentrations in sediments were Pb (0.2 - 0.3 µg/g), Cd (0.001 - 0.19 µg/g), Ni (<0.001 µg/g) while those in roots were Pb (1.8 -3.7 µg/g), Cd (0.1 -0.3 µg/g), Ni (0.4 - 1.3 µg/g) and the root with the highest age (5.7 yrs) also concentrated the highest amount of all metals at St.2. Sediment content of heavy metals in May were Pb (0.2 - 3.2 µg/g), Cd (0.001 - 0.4 µg/g), Ni (<0.001 µg/g) while those in roots were Pb (0.04 - 3.2 µg/g), Cd (0.2 - 0.5 µg/g) and Ni (0.04 - 0.7 µg/g). The values of Pb, Ni and Cd in sediments of this study also fall within the range reported by Gbosidom *et al*., (2017) but such values of metals observed in roots (current study) were well below those (Cd: 342.08 mgkg-1, Pb: 502.04 mgkg-1 and Pb 609.59 mgkg-1) reported by Erakhrumen (2015) in the root of other Mangrove plants in similar environments of the Niger Delta area. Age variation was not noticed during the month of May but metal accumulations were more in roots compared to sediments. The concentration of metals (Pb, Cd Ni) in this study were lower than values reported by Defew *et al*., (2005) and Perdomo *et al*., (1998) in sediments surrounding the root of *Laguncularia* in similar environments. The concentration Pb, Cd and Ni in the root of plants for this study fell within and slightly above standard limits of WHO/FAO (2007) for such metals (Pb: 5.0 µg/g ; Cd 0.2 µg/g and Ni: 1.5 µg/g). The implication here is that the root of *Laguncularia* found in this study area has potentials for heavy metal pollution. The ability of the root of such plant to accumulate more metals compared to the surrounding soil also indicates the natural phytoremediation potentials of mangrove plants such as *Laguncularia*. The level of Ni in the root for the current study was lower compared to the findings of Abohassan, (2013) but comparable to the concentrations of Pb and Cd in the root of other mangrove plants. ANOVA result showed that only Cd concentration in sediment varied significantly ($p<0.05$) across sites while the concentration of Pb and Ni had significant differences between the months of study. Post hoc analysis show the significant difference in Cd between stations occurred thus St.1<St.2<St.3. It also showed that the concentration of Ni in December was significantly different from those in other months. The concentration of Cd in root had significant difference between sites and also between the months of study and further analysis with Tukey test showed actual difference occurred thus for stations (St.1<St.2<St.3) and months (May<Feb=Apr=Mar<Jan=Dec). Spatial differences may also be due to differences in the behavior of alluvial sediment being deposited at each site (Conrad, and Sanders, (2017) while periodic differences may be influenced by inflow of contaminated runoff into each site. This implies that all the stations were different in terms of Cd concentration in roots of plants while those of the months suggested moderate seasonal difference in the accumulation of Cd. The concentration of Pb in sediment had strong positive linear relationship with that in the plant root. This was also the same for Cd and Ni suggesting that *Laguncularia* root accumulated more metals relative to the surrounding soil/sediment. There was no significant relationship between metal level in the root of *Laguncularia* and the age of the plant root suggesting that age of the root is irrespective of metal accumulation by the roots.

Conclusion: Mangrove fringes in estuarine environment accumulate pollutants such as heavy metals which are absorbed by root of mangrove plants. This study showed variations in heavy metal concentration in sediments and root of plants with significant difference. This is attributable to differential exposure of the different locations to heavy metal contamination. The concentration of Pb, Cd and Ni in the root of plants fell within and slightly above standard limits of WHO/FAO for such metals. Elevated levels of metals were found in roots compared to surrounding sediments irrespective of the age of the root. But sediment metal content showed strong linear relationship with root metal content hence *Laguncularia* plant root showed potentials for phytoremediation.

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