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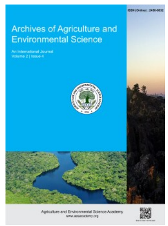

ORIGINAL RESEARCH ARTICLE

Assessment of heavy metals pollution in surface sediments of a tidal creek in the Niger Delta, Nigeria

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ABSTRACT

The present investigation was carried out to assess the heavy metals pollution in surface sediments of a tidal creek in the Niger Delta, Nigeria. Sediments obtained from Azuabie creek were examined for heavy metals *viz.*, Cd, Cr, Pb and Zn pollution using the Okujagu creek as a control point. Three stations were established on the Azuabie creek while the control creek had one station. Sediments samples were collected in duplicates on a monthly basis for three months (October - December, 2015) and analyzed using atomic absorption spectrophotometry. Results show that Azuabie creek had higher metal concentrations compared to the control creek with mean metal values as follows Zn: 27.5 - 293.3 mg/kg; Cd: 0.0 - 0.6 mg/kg; Cr: 2.8 - 35.7 mg/kg and Pb:5.7 - 22.5 mg/kg. Zn levels in sediment had significant difference ($p<0.05$) between stations which occurred thus: St1 < St2 = St3 < St Control. The values of Contamination factor (CF) ranged from 0.00 - 3.1 indicating low to moderate level of sediment contamination. The values of the degree of contamination computed ranged from 1.28 at the control station to 5.98 at St.1 while the PLI values generally indicated "no pollution" except at St.3 where the values was slightly >1. Generally, EF and I_{geo} values were lowest at the control station compared to other stations. The study concluded there was low to moderate level of contamination indicating heavy metal input from anthropogenic origin was found in the study area.

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INTRODUCTION

In the Niger Delta, the problem of water and sediment pollution has been of concern to all stakeholders, following the rate and extent of degeneration of the environment and water bodies by human activities, particularly from industrial and domestic sources (Daka and Moslen, 2013; Moslen and Miebaka, 2017). Coastal waters and sediment systems are vulnerable to pollution by organic, industrial and chemical pollutants/wastes from several industries and human habitats located by the banks and water fronts (Ekweozor and Moslen, 2016). Bryan and Langston, (1992) also stated that contaminated sediments are major sources of pollution in estuaries and are repositories for many different organic and inorganic contaminants which are capable of accumulating such contaminants to concentrations of concern in aquatic ecosystems. Heavy metals are often major constituents of wastes discharged into the aquatic system which ultimately deposit into the underlying sediment. Heavy metal pollution is one of the challenges of coastal water pollution due to human activities such as oil exploration and exploitation, construction and fabrication of marine boats, disposal of industrial and domestic wastes and sailing (Moslen and Miebaka, 2016, 2017). Studies had also observed that heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al*., 2014; Nagajyoti *et al*., 2010). A metropolitan creek (Azuabie creek) in Port Harcourt city is one of such creeks that is prone to both industrial and domestic wastes discharges. Daka and Moslen (2013) had identified major waste inputs into the creek to include run-off from surrounding lands, animal wastes from a major abattoir, human/domestic waste from a high density settlements along the creek and industrial effluents from Trans-Amadi industrial area, hosting a number of manufacturing and oil servicing companies. Daka *et al.* (2007) had a comparative study of the sediment quality and characteristics of Azuabie and Obufe creeks and established that anthropogenic and industrial activities led to lower relative quality of the Azuabie creek. Moslen and Daka (2014) also reported that the distribution/pattern of macro invertebrate assemblage was strongly related to salinity gradient, sediment composition/characteristics and anthropogenic influence within the Azuabie creek. This work further examined sediment pollution using indices such as contamination factor (CF), enrichment factor (EF), Degree of contamination (Cd) and pollution load index (PLI) and geo-accumulation Index (I_{geo}).

MATERIALS AND METHODS

Study area

The study was done on Azuabie and the Okujagu creeks. The creeks are tidal in nature and located in the Trans-Amadi industrial area of Port Harcourt Metropolis, Nigeria (Figure 1). The creeks have input of domestic, commercial and industrial wastes products with more into the Azuabie creek compared to the Okujagu creek. Hence, three locations were established on the Azuabie creek and a control point sited at the Okujagu axis. Sediment samples were collected in duplicates on a monthly basis for three months (October - December 2015) using an Ekman grab.

Analysis of sediment for heavy metals

Small quantities of the sediment samples were air-dried under room temperature. Then 1g of each was digested with Equia-Regia (mixture of HCI and HNO_3 in the ratio of 3:1). The digested sediment samples were filtered with 20 ml of de-ionized water and the filtrates were stored in clean acid- washed and appropriately labeled 30 ml sample containers. Analysis was done using Atomic Absorption Spectrophotometer, AAS (Model 210VGP BUCK Scientific, USA).

Evaluation of risk associated with heavy metals in sediments

To evaluate the degree of contamination in the sediment three ecological pollution indices were used: Enrichment Factor (EF), contamination factor (CF) and pollution load index (PLI). The enrichment factor (EF) of metals is a useful indicator reflecting the status and degree of environmental contamination (Feng *et al.*, 2004). The EF calculations compare each value with a given background level, either from the local site, using older deposits formed under similar conditions, but without anthropogenic impact, or from a regional or global average composition (Choi *et al.*, 2012). The EF was calculated using the method proposed by (Sinex and Helz, 1981) given as

$$EF = \frac{\left(\frac{Me}{Fe}\right)_{Sample}}{\left(\frac{Me}{Fe}\right)_{Background}}$$

Where (Me/Fe) sample in the metal to Fe ratio in the sample of interest; (Me/Fe) background is the natural (Me/Fe). Iron was chosen as the element of normalization because natural sources (1.5%) vastly dominate its input. Background level of heavy metal in crust: Fe (47200), Cr (90), Zn (95), Pb (20) and Cd (0.3)

Contamination factor (C_F)

The level of contamination of sediment by metal is expressed in terms of a contamination factor (C_F) calculated thus: C_F = C_m sample/C_m background where, C_m Sample is the concentration of a given metal in sediment. C_m background is value of the metal equals to the Average Shale Value (ASV) given by (Turekian and Wedepohl, 1961).

Degree of contamination

The degree of contamination is calculated as proposed by Håkanson (1980).

$$Cd = \sum_{i=1}^{N} CF_i$$

Where Cd = Degree of Contamination, CF = Contamination Factor

Pollution load index (PLI)

Pollution load index (PLI), as a means of assessing the quality of the study area with respect to heavy metals concentration was evaluated following the method proposed by Tomlinson *et al.*, (1980). PLI = $(CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots CF_n)^{1/n}$ (Raju *et al.*, 2012). Where, n is the number of metals, CF is the contamination factor of individual metals

Geo-accumulation index (I_{geo})

Geo-accumulation Index (I_{geo}) compares current concentration of heavy metals with pre-industrial level. The geo-accumulation index (I_{geo}) values were calculated for the different metals using

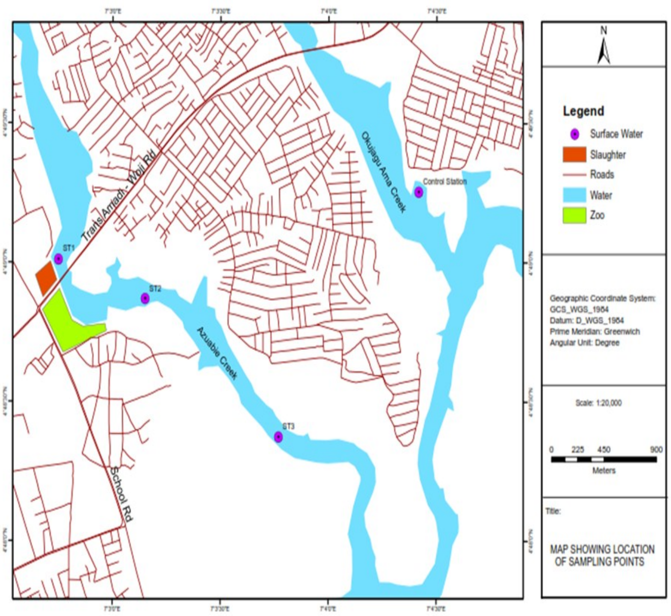

Figure 1. *Map of study area showing sampled points.*

the equation of Muller (1969).

$$I_{geo} = \log_2 [\frac{C_{mSample}}{(1.5 \times C_m Background)}]$$

Where: C_m = measured concentration of element m in the sediments sample, C_mBackground = geochemical background for the element m.

The factor 1.5 is used to compensate for possible variations with respect to background lithological variations. Muller (1981) proposed seven classes of Igeo-accumulation index. Class 6 is an open class and comprises all values of the index higher than Class 5. I_{geo} of 6 indicates almost 100 fold enrichment above background value. In these computations, Average shale value (ASV) by Turekian and Wedepohl, (1961) in mg/kg {Cr (90), Zn (95), Cu (45), Pb (20), Mn (850) and Ni (68), As (13), Cd (0.3), Fe (47,200), Co (19)} was considered as the background values to estimate $I_{geo.}$

RESULTS AND DISCUSSION

The mean concentration of heavy metals in sediments of the study area showed variations across the sites studied with least values observed at the control station (Figure 2). The ranges were as follows Zn: 27.5 - 293.3 mg/kg, Cd: 0.0 - 0.6 mg/kg, Cr: 2.8 - 35.7 mg/kgand Pb: 5.7 - 22.5 mg/kg. The concentration of Zn was higher than other metals examined, this was followed by those of Cr and Pb while Cd had the least value. The levels of Zn and Cd obtained in this study was comparable to those (135.6 & 0.423 mg/kg) while Cr and Pb levels obtained in this study were less than those (76.4 & 37.0 mg/kg) respectively reported by Yi *et al*. (2011). Daka *et al*. (2007) recorded highest mean values of metals as Zn (214.4 mg/kg), Pb (30.0 mg/kg), Cu (17.26 mg/kg) and Cd (0.62 mg/kg) during the wet season in the study area. The variation in the level of Zn in sediment was significantly different (p<0.05) while the concentrations of Cd, Cr and Pb in sediment did not differ significantly (p>0.05) between the stations examined (Table 1). Tukey test showed that the significant difference occurred thus: St1 < St2 = St3 < St Control. In another study of a dredging site in the Niger Delta, Moslen and Daka (2014) reported that the concentration of heavy metals (Arsenic, Cadmium, Chromium, Copper, Iron, Mercury, Lead, Zinc, Vanadium and Nickel) were higher downstream of the dredging position due to the remobilization of sediment-bound metals as a result of dredging activities. Also, the value of Cd concentration obtained in this study accords with the 0.1332 - 0.6229 mg/kg range recorded at Abonema shoreline (Ideriah *et al*., 2012) in the Niger Delta.

Risk assessment of heavy metals in sediment

Measurement of contamination indication were done with indices such as Contamination factor (CF), Degree of Contamination (Cd), Pollution load Index (PLI), Enrichment Factor (EF) and Geo-accumulation Index (I_{geo}), for the assessment of the risk of heavy metals in sediments collected from the study area.. Calculated values of the pollution indices are presented in Tables 2- 4. The values of Contamination factor (CF) ranged from 0.00 - 3.1. Cd had the least at St. 2 while Zn had the highest at St.1. Cr generally had the least CF values among the metals while the control station generally had the lowest CF values across the stations examined. The CF values obtained indicated low to moderate level of contamination. The values of the degree of contamination computed ranged from 1.28 at the control station to 5.98 at St.1 while the PLI for the heavy metals was lowest (0.00) at St.2 and highest (1.14) at St.3. Saha and Hossain (2011) reported contamination factor (CF) of Pb, Cd, Cu and Zn that were responsible for considerable contaminations of sediments in their study. However, Goher *et al.* (2014) in a metal pollution assessment study reported CF thus: Zn (0.732), Cr (0.324), Pb (0.545) and Cd (0.585). Elias *et al.* (2014) reported values of degree of contamination between <8 - 43.2 for low and very high degree of contamination respectively. The PLI values generally indicated "no pollution" except at St.3 where the values was slightly >1. Salah *et al*., (2012) recorded PLI values between 0.45 - 1.15 at all sampling sites which they suggested no overall pollution of site quality.

In order to know the possible natural or anthropogenic input and impact in sediments, enrichment factor (EF) was computed. Generally, EF values were lowest at the control station compared to other stations (Table 3). The EF of Cr ranged from 0.03 at St. control to 0.4 at St. 3 while those of Zn differed between 0.29 at St. control to 3.09 at St.1. Similarly Cd and Pb had the lowest EF value (0.67 & 0.29) at the control station and the highest at St.1 (1.33 & 1.34) respectively. The result of enrichment factor revealed depletion to moderate enrichment. A considerable show of depletion to moderate level of enrichment from anthropogenic input was recorded for Zn (0. 29 – 3.09), Cd (0.67 -1.33) and Pb (0.29-1.34) which is comparable to the findings of Mamat *et al.* (2016) but Elias *et al.* (2014) reported EF values between 1.1 - 7.2 for surface sediments with Cd showing enrichment at some stations while Cr, Pb and Zn were within background levels. Daka *et al.* (2007) had earlier reported the following range of EF values in the study area Zn (0.3 - 5.1), Pb (0.6 - 3.9), Cu (0.9 - 4.4) and Cd (0.1 - 2.3) which could also compare with results obtained in the current study. The contamination levels of sediment heavy metal were evaluated by comparing present contaminations with background levels using the Muller scale for I_{geo}. The I_{geo} of metals in sediments is given in Table 4. Values for each metal were as follows Cr: 0.006 - 0.08; Zn: 0.06 - 0.62; Cd: 0.00 - 0.40; Pb: 0.06 - 0.27. Observation shows that values of I_{geo} *were* generally lowest at the control station. The results revealed that all metals showed an I_{geo} less than 1, indicating that the sediment was uncontaminated to moderately contaminated. The Igeo values in this study for Cd and Pb accords with those of Mamat *et al.* (2016) who also reported low to moderate pollutions for the said metals but found Zn and Cr under 'no pollution status' in their study of surface sediments. Li (2014) reported geoaccumulation indices (I_{geo}) that suggested the magnitude of heavy metal pollution of the sediment of Yanghe River decreased in the order of Cd > Zn >Pb> Cr > Ni. According to Saha and Hossain (2011) I_{geo} index was used to ascertain moderately polluted condition for Pb, Cd, Cu, Zn in the sediments quality.

Table 1. ANOVA with F-values for sediment concentrations of heavy metals.

Heavy metals	Location (F-values)
Sediment	
Zn	7.03*
Cd	1.00^{ns}
Cr	4.32^{ns}
Pb	4.32^{ns}
Key	* = P ≤ 0.05, ns = (not significant)

Table 2. Contamination Factor (CF), Degree of contamination (C_d) and Pollution load index of metals across study sites.

Station	CF (Cr)	CF (Zn)	CF (Cd)	CF (Pb)	Degree of Contamination (C_d)	PLI
St1	0.02	3.1	1.33	1.35	5.98	0.58
St2	0.02	2.11	0.00	1.00	3.13	0.00
St3	0.40	2.00	2.00	1.05	5.45	1.14
St control	0.03	0.29	0.67	0.29	1.28	0.20

[PL1 = Pollution load index, C_d = Degree of contamination, CF = Contamination factor, CF < 1 (Low contamination), 1 ≤ CF < 3 (Moderate contamination), 3 ≤ CF < 6 (Considerable contamination), CF > 6 (Very high contamination), PLI < 1 (No pollution), PLI >1 (Pollution/site deterioration) PL1 = 1 (Baseline levels).].

Table 3. Enrichment factor (EF) of heavy metals in sediments.

Station	Cr	Zn	Cd	Pb
St1	0.02	3.09	1.33	1.34
St2	0.18	2.12	0.03	1
St3	0.4	2	2	1.13
St control	0.03	0.29	0.67	0.29

[EF < 2 (Depletion to moderate enrichment), 2 ≤ EF < 5 (Moderate enrichment), 5 ≤ EF < 20 (Significant enrichment), 20 ≤ EF < 40 (Very high enrichment), EF < 40 (Extremely high enrichment)].

Table 4. Geo-accumulation Index (I_{geo}) of heavy metals in sediment.

Station	Cr	Zn	Cd	Pb
St1	0.004	0.62	0.27	0.27
St2	0.04	0.42	0.00	0.2
St3	0.08	0.40	0.40	0.23
St control	0.006	0.06	0.13	0.06

[I_{geo}< 0 (Practically uncontaminated), I_{geo}< 1 (Uncontaminated to moderately contaminate), I_{geo}< 2 (Moderately contaminated), 2<I_{geo}< 3 (Moderately to heavily contaminated), 3<I_{geo}< 4 (Heavily contaminated), 4 <I_{geo}< 5 (Heavily to extremely contaminated), 5 <I_{geo}< 6 (Extremely contaminated)].

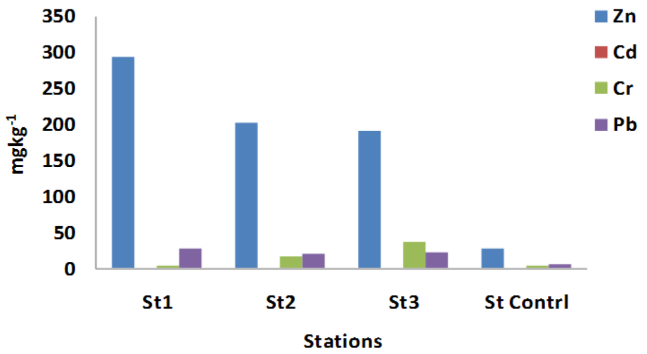

Figure 2. *Variations of heavy metal concentration in sediments across stations.*

Conclusion

In this study sediment samples from two adjacent creeks in the upper Bonny estuary were examined. The results indicated higher concentration of heavy metals (Zn>Cr>Pb>Cd) at stations within the Azuabie creek compared to the control creek (Okujagu). ANOVA showed significant difference in the concentration of heavy metals between the sites examined. Stations within the Azuabie creek had significantly different metal concentration compared to the control site which is traceable to higher anthropogenic activities within the Azuabie creek. Values of contamination factor, degree of contamination and pollution load index were higher at stations within the Azuabie creek compared to the control creek. Values of other ecological risk assessment indicators (enrichment factor and geo-accumulation index) also peaked at stations within the Azuabie creek particularly, at station 1 and 3 suggesting such sites as hotspots. EF values also suggested traces of heavy metals input due to human activities hence regular monitoring is required The study therefore concluded that the sediment status of the study area is of low to moderate level of contamination. This study therefore, serves as basis for future reference and studies.

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