Ecological and Human Health Risk Assessment of Heavy Metals in Sediment of Selected Creeks in Rivers State, Nigeria

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Abstract
There has been much concern about the rate at which industrial and household wastes are released into Creeks in Rivers State. The study examined the status of heavy metal pollutants (Cd, Cu, Zn, Cr, Pb, and Ni) in sediment and to determine the extent of damage caused by these human factors using the most recent pollution index and Sediment quality guidelines (SQGs). The research was carried out in four important creeks along the Delta River network in Rivers State, Nigeria (Okrika, Borokiri, Eagle Island, and Kaa). Triplicate sediment samples were collected at a depth of 0-20 cm and extracted with 20cm^3 of aqua ragia (a 3:1 mixture of HCl and HNO_3) and 10cm^3 of 30% H_2O_2. The metal concentrations were measured using an Atomic Absorption Spectrophotometer (AAS). The concentrations of the heavy metals ranged from 11.147–18.919mg/kg, 11.918–14.379mg/kg, 8.321–11.691 mg/kg, 6.405–11.72mg/kg, and 5.718–12.125mg/kg, and 2.429-7.725mg/kg respectively and followed the sequence Zn > Pb > Cr > Ni >Cu > Cd. Geo-accumulation Index (Igeo) calculated was less than 0 i.e. uncontaminated for all metals except Pb in Borokiri Creek and Cd in all sampled creeks, showing moderate contamination. Eco-toxicological risk assessment (RI) indicated that the creeks were uncontaminated. Despite the low level of contamination, it is recommended that relevant authorities to regulate the indiscriminate dumping of domestic waste and untreated industrial effluents into the river to prevent the deterioration of the creeks.

Keywords: *Heavy metals, Geo-accumulation index, Ecotoxicological risk assessment index.*

Introduction

1.1 Background to the study

Pollution is a significant global issue that has culminated in several approaches to finding effective solutions to mitigating its impacts. Industrial, demographic, and economic expansion have resulted in vast production and a plethora of diverse compounds and chemicals. The majority of these compounds contain undesirable molecules that are either contaminants, pollutants, or toxicants. Some of the chemicals put into the environment have negative consequences and pose threats to plants, animals, and man, the ultimate consumer of the environment (Espinoza-Quinones et al., 2005). Most industrial complexes in Rivers state are constructed along river channels for simple trash disposal. Furthermore, the use of pesticides and chemical fertilizers in agricultural areas, the operations of illicit crude refiners, urban run-off, and air depositions all contribute to water body contamination. Among the most persistent and common pollutants are the heavy metals.

Heavy metals are metallic elements that exist naturally and have a high atomic weight and a density at least five times that of water (Tchounwou et al., 2012). When present in low quantities, they operate as important nutrients for flora and fauna and are thus classified as micronutrients. They also play important roles in metabolism and growth control. Iron, for example, is a component of haemoglobin, which assists in the delivery of oxygen A few of them, however, are harmful, while others are poisonous when their concentration surpasses the tolerable permitted level. The kinds of metal contaminants that are present in discharged water govern their release into the aquatic ecosystem (Kpee et al., 2022). Heavy metals are tenacious and poisonous to ecosystems and can bio-accumulate in sediment.

Sediment, being a key component of riverine ecosystems, acts as both a sink and a source of heavy metals (Pejman et al., 2015; Haung et al., 2019). When the physicochemical or hydrological conditions change, heavy metals in the sediment may desorb or re-suspend, resulting in secondary contamination in the water body (Liang et al., 2015; Kouidri et al., 2016). Heavy metal deposition in sediment directly impacts benthic animals and indirectly effects many other creatures through the food chain (Sakan et al., 2009; Khan et al., 2020), threatening the aquatic ecosystem's health.

Heavy metal risk assessment approaches based on total concentration computation have been extensively advocated (Islam et al., 2015; Xia et al., 2020), with two primary categories: background values and sediment quality criteria. The actual permitted amounts of a certain chemical compound in sediments that does not impair benthic aquatic life or other related water functions are known as sediment quality guidelines (SQGs) (Madzin et al., 2015). It was against this backdrop the study was done to quantify the levels of heavy metals in sediment samples of creeks in Rivers State and to carry out a risk assessment to ascertain the degree or extent of damage done by continuous pollution of the Waterbodies.

3.0 Materials and Methods

3.1 Study Area

The operation was conducted in Rivers State, Nigeria, at the Okrika, Borokiri, Eagle Island, and Kaa Creeks. These study areas are situated in 4°43′53.58″N 7°4′36.52″E, 4°45′24.39″N 7°1′31.98″E, 4°47′10.62″N 6°58′36.68″E, and 4°34′10.86″N 7°22′9.97″E, respectively. The Creeks are subjected to waste discharges from companies located along their banks. Many anthropogenic activities take place in the study region, which include dredging, building, water transportation, illegal oil bunkering, commerce, agricultural, and fishing.

3.2 Sample Collection

At each sampling location, triplicate sediment samples were collected at a depth of 0-20 cm. Using a stainless scoop and hand-moved augers, the grab samples were collected and put into clean polyethylene containers. A small fishing motorboat was used to help with sampling in places where the water was deep. The samples were labeled and stored in an ice-cold container without any chemical processing after collection. After the collection session, samples were transferred to the laboratory for chilling at 1°C to 4°C before analysis.

3.3 Sample Digestion and Analysis

0.5g of sediment was weighed into an acid-washed glass beaker, and the sample was digested by adding 20cm^3 of aqua ragia (a 3:1 mixture of HCl and HNO_3) and 10cm^3 of 30% H_2O_2. Hydrogen Peroxide (H_2O_2) was introduced in tiny amounts to minimize overflow, which might result in material loss from the beaker. The beaker was then covered with a watch glass and heated at 90°C for 2 hours before being washed with reagent water and filtered into a 100 ml volumetric flask. The volume was made up to 100ml mark with reagent water. Blanks solution was handled the same way as the samples, and thereafter, each metal (Cd, Cu, Zn, Cr, Pb and Ni) concentration was determined using the Perkin Elmer Analyst Atomic Absorption Spectrometer (AAS) with appropriate lamps and standard. Experiments were carried out thrice.

3.4 Statistical tool for Analysis of Results

The raw data was subjected to descriptive statistical analysis like One-way Analysis of Variance (ANOVA).

3.5 Assessment Methods

The following assessment techniques were employed and determined based on total concentrations of heavy metals, background values, and SQGs:

Geoaccumulation Index (Igeo): The geoaccumulation index (Igeo), which was initially established by Muller, (1969) has been widely utilized in the evaluation of heavy metal contamination. It exposes the link between heavy metals in sediments and geochemical background values.

The Igeo value is defined as

$$I_{geo} = \log_2 \frac{(C_n)}{1.5B_n} \qquad \text{eqn 1}$$

where Cn represents the measured concentration of metal(n) in mg/kg,

Bn represents the geochemical background value of metal (n) (mg/kg), and

1.5 is a factor used to minimize the impact of background value caused by lithological variation (Khan et al., 2020).

Potential Ecological Risk Index (RI): To estimate the ecological effect and potential danger of heavy metals exposure, the potential ecological risk of individual factor Er and the potential ecological risk index (RI) developed by Hakanson et al., (1980) were employed. It depicts ecological sensitivity and vulnerability to harmful heavy metals and assesses the overall ecological risk. The following elements are taken into account: the kind of target heavy metals, the observed concentration, the toxicity coefficient, and the susceptibility of the water body to heavy metals.

$$Er^{Me} = Tr^{Me} \times CF^{Me}$$

where CF^{Me} represents the contamination factor, $\mathbf{C_{FMe} = C_n/B_n}$

and Tr^{Me} represents the toxicity coefficient of a single heavy metal

$$RI = \sum Er^{Me}$$

The classifications of ecological risk levels are shown in Table 7.

4.0 Results and Discussion

Results of the heavy metals present in sediment sample is presented in Table 1.

Table 1: Concentrations (Mean ± S.D) of Heavy metals (mg/kg) in Sediment Samples

Heavy metals/ Location	Okrika Creek	Borokiri Creek	Eagle Island Creek	Kaa Creek
Cd	7.725±1.256	6.169±0.968	4.786±0.051	2.429±0.019
Cu	11.989±0.425	9.427±0.967	12.125±0.114	5.718±0.086
Zn	18.919±1.119	15.894±0.239	13.72±0.525	11.147±0.567
Cr	9.895±0.172	11.691±0.526	8.321±0.687	10.607±0.075
Pb	13.691±0.648	14.379±0.214	12.895±1.330	11.918±0.354
Ni	8.894±0.158	11.72±0.759	9.907±0.098	6.405±0.093

Table 2: Geochemical Index of Sediment

Heavy Metals/ Locations	Okrika Creek	Borokiri Creek	Eagle Island Creek	Kaa Creek
Cd	1.44	0.95	0.55	0.26
Cu	0.85	0.11	2.79	1.47
Zn	1.63	2.28	3.27	3.11
Cr	3.42	3.53	4.02	3.67
Pb	0.46	0.36	1.22	1.33
Ni	1.36	0.47	2.64	1.79

Table 3: Degree of Contamination

Index Class	Igeo values	Degree of Contamination
0	Igeo < 0	Uncontaminated
1	0 <Igeo <1	Uncontaminated to moderately contaminated
2	1 <Igeo <2	Moderately contaminated
3	2 <Igeo <3	Moderately to heavily contaminated
4	3 <Igeo <4	Heavily contaminated
5	4 <Igeo <5	Heavily to extremely contaminated
6	Igeo > 5	Severely contaminated

Table 4: Ecological Risk Index of Sediment Samples

Heavy Metals/ Location	Okrika Creek	Borokiri Creek	Eagle Island Creek	Kaa Creek
Cd	122.00	87.00	66.00	54.00
Cu	4.14	6.94	1.08	2.700
Zn	0.48	0.31	0.15	0.17
Cr	0.28	0.26	0.18	0.24
Pb	5.45	9.63	3.22	2.98
Ni	2.97	5.40	1.21	2.17

Table 5: Human Health Risk Index of Sediment Quality

Location	Risk Index value	Degree of Risk
Okrika Creek	135.31	Low
Borokiri Creek	109.55	Low
Eagle Island Creek	71.85	Low
Kaa Creek	62.26	Low

Table 6: The classifications of ecological risk levels

Er^{Me} value	RI value	Ecological Risk
$Er^{Me} \leq 40$	RI < 150	Low
$40 < Er^{Me} \leq 80$	$150 \leq RI < 300$	Moderate
$80 < Er^{Me} \leq 160$	$300 \leq RI < 600$	Considerable
$160 < Er^{Me} \leq 320$	-	High
$Er^{Me} > 320$	$RI \geq 600$	Very High

The results of cadmium in sediment varied from 2.429±0.019 to 7.725±1.256mg/kg, compared to 0.3mg/kg for shale. The values found in the current study's sediment samples were similar with the value range of 4.36-6.21 mg/kg reported by Chen et al., (2022). Akan et al. (2010), on the other hand, found higher cadmium levels of 7.34-64.0 mg/kg in sediment samples from the Ngada River in Borno State. Cd is very vital in the monitoring of aquatic environment; this is due to its toxicity to aquatic flora and fauna. Cadmium levels in water can induce renal illness, lung damage, and bone fragility (Bernard, 2008).

The copper concentration in all creeks varied from 5.718±0.086 to 12.125±0.114mg/kg (Table 1), which is comparable to value reported by Kieri et al., (2021), but higher than 0.09±0.03 reported by Okey-Wokey & Wokeh (2022). All the values reported in all samples differs significantly from each other ($P<0.05$). Consumption of crabs and shellfish containing Cu levels over the allowable limits has a deleterious influence on both the neurological and circulatory systems (Hussain et al., 2021).

The concentrations of zinc in the sediment samples of the creeks ranged from 11.147±0.567to 18.919±1.119 mg/kg mg/kg (Table 1). The range of zinc level in the sediment samples of the creeks were below the average Shale value of 95mg/kg. The result from the study was within value range reported by Kieri et al., (2021). However, it contradicted other reports. It was lower than the values reported by Decena et al., (2018) in the Philippines' Mangonbangon River (76.83-263.63 mg/kg) and Sivakumar et al., (2016) in Tamilnadu, India's South East Coast (26.8-48.8 mg/kg), but higher than the value of 5.49±0.005 mg/kg in sediment samples from the same New Calabar River reported by Nwineewii & Unochukwu (2018).

The Cr levels found in the sediment varied from 8.321±0.687 to 11.691±0.526mg/Kg(Table 1), which was lower when compared to 90mg/Kg for the global average shale value. Cr values obtained in Silver River sediments were lower than values of 70.00-130.02mg/kg observed in the Tembi River, Iran by Shanbehzadeh et al., (2014) and 44.18-201.70mg/kg as observed by Chen et al., (2022). It was, however, higher than the 0.05±0.01mg/kg reported by Okey-Wokeh & Wokeh, (2022) in sediment samples of Mini-Ezi Stream, Elele-Alimini, Rivers State and the 6.228±1.752mg/kg obtained by Kieri et al., (2021) for sediment samples of Silver River, Southern Ijaw, Bayelsa State. The low Cr levels found in sediment tests indicate that the creeks are not contaminated by Cr ion, which can be linked to less human activities along the course.

The concentration of lead (Pb) in Table 1 varied from 11.918±0.354 to 14.379±0.214mg/kg, which is slightly low when compared to the global surface rock average (16 mg/kg) and mean shale concentration (20 mg/kg). The results of this investigation are comparable with the values of 7.33-16.89mg/kg reported by Onoyima et al., (2021) in their study of Kaduna River sediment quality. it differed from other researchers reported values. Aigberua et al. (2020) found a lower mean value of 7.50mg/kg, while Daka et al. (2007) and Moslen et al. (2018) found values of 30.0mg/kg and 5.7-22.5mg/kg, respectively. Sources of lead include gas stations and smokes from automobiles and boats. This might be linked to the location of Borokiri and Okrika creeks, which had the greatest amount of lead contamination. Plants exposed to high levels of lead increase the generation of reactive oxygen (ROS), causing damage to the lipid membrane and, eventually, damage to the chlorophyll and photosynthesis processes, inhibiting the development of all plants (Najeeb et al., 2014).

Ni values in sediment samples varied from 6.405±0.093 to 11.72±0.759mg/kg, which was lower than the shale average of 68mg/kg. The sediment result was in resonance with the value of 5.413-8.449mg/kg published by Kpee et al., (2022) and less than the value of 20.901±0.47 mg/kg reported by Kpee & Ekpete (2014) in the examination of heavy metal levels of Kalabari Creek sediment sample. However, the finding was greater than the values of 3.521-5.605mg/kg and 6.570±1.102mg/kg reported in different investigations (Edori et al., 2020; Kieri et al., 2021). Nickel enters the water body through trash discharged by industries producing batteries, dyes, and catalysts, as well as ceramic enterprises. Because nickel has been found to generate free radicals, it is also involved in carcinogenesis (Valko et al., 2005).

Assessment Methods

Based on Table 2, the geoaccumulation index (I_{geo}) values indicated that all the sampling sites were uncontaminated to moderately contaminated by metals such as Cd, Cu, Zn, Cr and Pb. The I_{geo} value for Cd showed that Borokiri creek, Eagle Island creek and Kaa creek has an index class of 1 showing uncontaminated to moderately contaminated while Okrika creek had an Igeo value of 2 indicating moderate contamination. The other metals fall within the I_{geo} value of 0 except Lead (Pb) that had an I_{geo} value of 1 for Borokiri creek showing uncontaminated to moderate Contamination (Table 3). Sediments always reflect the contamination history of water bodies. It can be inferred that the heavy metals in sediments of the various creeks show fairly recent pollution. This is also confirmed by previous studies carried out around those creeks (Bubu et al., 2017; Moslen et al. 2020). The Igeo values in this study for Cd and Pb was also in accord with those of Mamat et al. (2016) who reported low to moderate pollutions for the said metals but found Zn and Cr under 'no pollution status' in their study of surface sediments.

The monomial potential ecological risk index (or potential ecological risk factor) (Er), introduces a toxic response factor for a given pollutant (Kormoker et al., 2019). From Table 4, it was was observed that the average monomial risk factors (Er) were ranked in the following order: Cd > Pb > Cu > Ni > Zn. All the metals constituted low ecological risk at the studied sites within the study period as the risk factors were all below the lower threshold (Er < 40) except cadmium. Cadmium has an Er value of 122.0 for Okrika creek, 87.0 for Borokiri creek, 66.0 for Eagle Island creek and 54.0 for Kaa creek respectively. The Er value of cadmium in Eagle Island and Kaa creek show moderate ecological risk while that of Okrika and Borokiri creek showed considerable ecological risk (Table 6). The study result was in sharp contrast to the reported value of Er <40 by Onoyima et al., (2021). This is a pointer to more pollution in the Niger-delta which could be attributed to anthropogenic activities such as illegal refining of crude and wastes from industries.

Ecological risk index (RI) was used to evaluate the total risk caused by all the studied metals. RI represents the sensitivity of the biological community to the toxic metal and illustrates the potential ecological risk caused by the overall metals (Islam et al., 2017). The result displayed on Table 5 shows there was a low risk to the local ecosystem at all the sites from the studied metals (RI < 136). A high ecological risk index means that marine or benthic organisms are exposed to environmental risk. The order of ecological risk (RI) of the creeks was Okrika > Borokiri > Eagle Island > Kaa. This also align with previous studies (Onoyima at al., 2021; Chen et al., 2022).

Conclusion

The findings of the study clearly indicate levels of the heavy metals in the sequence Zn>Pb>Cr>Ni>Cu>Cd in the sediment. The Geo-accumulation index(Igeo) calculated was less than 0, that is, uncontaminated for all metals except for Pb in Borokiri creek and Cd in all sampled Creeks that showed moderate contamination. The result of the ecological risk index

indicates a low risk to the ecosystem at all the creeks of the studied metals (RI<136). The sequence of the RI of the Creeks was Okrika>Borokiri>Eagle Island>Kaa.
Despite the low level of contamination of sediment in the sampled areas, it is recommended that relevant authorities should regulate the indiscriminate dumping of domestic waste and untreated industrial effluents into the rivers to prevent the deterioration of the Creeks.

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