Ecological Risk Factor (EF), Potential Ecological Risk Index (RI) and Enrichment factor assessment of Selected Heavy Metals in Sediments of Kaani River, Ogoni axis, Rivers State, Nigeria.

Anate, S. Ganiyu¹ ; Momta, P. NukebaBari² ; Ndifreke, B. Nde³ ; Amacha, Mathew⁴

Department of Chemistry, Ignatius Ajuru University of Education,

Rumuolumeni, Port Harcourt, Rivers State, Nigeria Corresponding Author: anatesumga24@gmail.com

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Abstract

The community's residents have traditionally exploited the fresh water of the Kaani River for home and agricultural uses. Surface sediment samples were taken from four stations: Maa di Binnise Igbara water side (station 1), Mann stream (station 2), Woman stream (station 3), and Nwii ke ma kor stream (station 4). The samples were then digested and subjected to an atomic absorption spectrophotometric method to determine the concentrations of certain heavy metals. The order of metal concentrations were iron (Fe) > zinc (Zn) > lead (Pb) > chromium (Cr) > nickel (Ni) > copper (Cu) > manganese (Mn) > arsenic (As) > cadmium (Cd), according to the obtained data. Fe was [124.981±2.673]mg/kg, Zn was [36.356±1.593]mg/kg, Pb was [7.647±0.081]mg/kg, Cr was [6.361±0.074]mg/kg, Ni was [5.734±0.024]mg/kg, Cu was [5.541±0.071]mg/kg, Mn was [4.000±0.021]mg/kg, As was [0.182±0.002]mg/kg, and Cd was [0.049±0.002] mg/Kg, according to their respective mean values. A few model indices (contamination factor, ecological risk factor, possible ecological risk index, and enrichment factor) were used to further assess the results. The sediments were found to be somewhat contaminated, according to an examination of sediment contamination factors. According to an ecological risk assessment, the metals are safe for the ecosystem at the current quantities. All of the metals, with the exception of Cd in Nwii ke Ma Kor Stream (station 4) and Fe at Mann Stream (station 2), had considerable anthropogenic enrichment at the various stations, according to enrichment factor analysis. Thus, it is important to implement sufficient and ongoing monitoring to stop the introduction of an increased amount of anthropogenic heavy metals into the river.

Keywords: contaminant, Possible Ecological Risk Index, Ecological Risk Factor, and Contamination Factor

Introduction

Scholars and legislators burdened with legislation have paid more attention to the environmental build-up of heavy metals in recent years. The main reason for this focus is that they are persistent and toxic in the surrounding environment, which causes them to accumulate in aquatic plants and animals (Varol, 2011). A key element in determining the types of pollution or the characteristics

IIARD – International Institute of Academic Research and Development Page **21**

of river or marine systems is the quality of the sediments. This is due to their dual roles as environmental contaminants' transporters and sinks, as well as the historical data they provide regarding pollution and the sources of pollutants that enter aquatic systems (Tao et al., 2010). In aquatic environments, quantities of heavy metals over permissible limits exhibit toxicological characteristics.

The accumulation of trace metals in sediments and water environments is dependent on various factors, including the nature of the sediment contents and the physicochemical conditions of the surrounding environment (Shomar et al., 2005). According to Saeed et al. (2004), there is a general increase in the flow of heavy metals and other environmental pollutants to shoreline zones, primarily as a result of rising global economic activity.

Sediments serve as the last sink for pollutants and toxins, which at certain concentrations cause them to be re-suspended into the water and accumulate, particularly on bottom-dwelling biota, which are in close proximity to the sediment. According to recent studies, pollutants such as carbon-based chemicals, heavy metals, nutrients, and disease-causing organisms in sediments are ubiquitous and pose serious risks to both aquatic animals and humans (Robin et al., 2012; Pinedo et al., 2014; Olayinka et al., 2017). Although background standards and sediment quality processes have limitations, they are widely utilized to determine or assess various risks associated with heavy metal contamination in any type of aquatic environment (Ogoyi et al., 2011). In a similar vein, several experimental and numerical techniques have been created in response to ecological concerns and have proven to be invaluable instruments for monitoring pollution in water systems. Consequently, the purpose of this investigation was to investigate the levels, ecological danger, and enrichment factor of several heavy metals in the sediment of Kaani River.

1.2 Materials and Methods.

1.2.1 Description of the Study Area: The investigation was carried out in a freshwater local river in Kaani, in the Ogoni axis of Rivers state. Kaani is a 1,050 square km plot of land in Khana Local Government Area, South South Nigeria, which is part of the Rivers state's south-east senatorial region. The region is situated in Rivers State, east of Port Harcourt, on the Gulf of Guinea coast. It covers much of Nigeria's Niger Delta as well as the Khana Local Government Areas.

Kaani village is bordered by host communities that are close by, including kor, kpong, and yege communities. These communities' residents mostly work as sand drillers, fishers, and engage in illicit petroleum exploration and exploitation (sometimes referred to as "kpoo fire") for financial gain.

The Kaani village is situated at latitude 1.5074^oS of the equator and longitude 37.3707^{o}E of the Prime Meridian, with a relatively humid environment. According to the river's GPS, it is located at latitude 4.6920^ON and longitude 7.3527 ^OE. The majority of the area is forested, with patches of mosaic grassland and shrubland. The climate is tropical, with short dry seasons during the monsoon.

1.2.2 Sample Collection and Preparation: Using a plastic trowel, sediment samples were gathered during low tide. To prevent contamination, the samples were sealed in polythene bags and sent to the laboratory. The samples were air dried in the lab until their weight didn't change. The samples were then sieved using a 0.02 mm mesh screen after being macerated in a ceramic

mortar with a pestle. Glass vials with tight closures were used to store the resulting powdered sediments. Nwajei et al. (2014)'s technique was used to digest two grams (2g) of the dried silt, and the digest was then obtained by filtering.

1.2.3 Sample Analysis: The amounts of the heavy metals were subsequently determined by analyzing the digests using an atomic absorption spectrophotometer (AAS).

Model Assessments: In order to determine the effects on the environment, the heavy metal results were then evaluated using pollution and contamination model equations. Contamination factor, ecological risk factor, possible ecological risk index, and enrichment factor are some of these models.

Contamination Factor: The heavy metals' Contamination Factor (CF) was computed using Lacatusu's (2000) methodology: CF is equal to Cm/Cb, where Cb is the background concentration of the same metal in average shale or any other standard (in this case, the DPR standard), and Cm is the measured concentration of metal in the sample. The following intervals are the foundation for interpreting the contamination factor/pollution index, per Lacatusu's (2000) proposal.

CF/PI	Significance				
< 0.1	slight Very				
	contamination				
$0.10 - 0.25$	Slight contamination				
$0.26 - 0.5$	Moderate				
	contamination				
$0.51 - 0.75$	Severe contamination				
$0.76 - 1.00$	Very severe				
	contamination				
$1.1 - 2.0$	Slight pollution				
$2.1 - 4.0$	Moderate pollution				
$4.1 - 8.0$	Severe pollution				

Table 1: The importance and intervals of the pollution/contamination index

Adapted from Lacatusu (2000)

Ecological Assessment: According to Hakanson (1980), the ecological risk factor (E_F) provides the potential ecological risk of specific heavy metal pollutant, while the potential ecological risk index (RI) evaluates the multiple effect of heavy metal pollutions in the sediments of the marine environment.

They are mathematically expressed as:

 E_F = Tr x C_F $RI = \sum E_F$

Where CF is the contamination factor of specific metals and Tr is the toxic response factor (numerical values are assigned to each elements). Based on Hakanson's (1980) suggestion, the

following phrases are used to interpret ecological risk: >320 , severe ecological danger; $160 < Er$ \leq 320, pronounced ecological risk; Er < Er \leq 80, reasonable ecological risk; and 80 < Er \leq 160, considerable ecological risk.

Enrichment Factor: According to Buat-Menard & Chesselet (1979), the measured heavy metals' Enrichment Factor (EF) analysis was computed as follows:

$$
EF = \frac{\left(\frac{Cn}{Cref}\right) sample}{Bn/Bref}
$$

where Bn is the background concentration of the metal under investigation, Bref is the concentration of the reference element (Fe), Cn is the metal concentration detected in the sample, and Cref is the concentration of the reference material (Fe in this case). $EF < 2$ absence to insignificant enrichment, $EF = 2-5$ fair enrichment, $EF = 5-20$ severe enrichment, $EF = 20-40$ extreme enrichment, and EF>40 very high enrichment were the categories used to forecast the enrichment factor classes (Edori et al., 2020).

Results and Discussion:

Table 2 presents the findings of the concentrations of heavy metals in the sediment at various places. Station 1 (Maa di binnise Igbara water side) had the highest concentration of iron (Fe) at $[137.348\pm3.226]$ mg/kg. Zinc (Zn) was next at station 3 (woman stream) at $[98.481\pm5.619]$ mg/kg, lead (Pb) at station 3 (woman stream) at [9.474±0.198] mg/kg, chromium (Cr) at station 3 (woman stream) at 8.166±0.018 mg/kg, and nickel (Ni) at station 1 (Maa di binnise Igbara water side) at [7.212±0.038] mg/kg. The majority of the dissolved metals that should have settled in the river bed are moved by river current, which is responsible for the low values found in the sediments at the different locations (Ama et al. 2017). Cadmium (Cd) mean values in the tested sites ranged from NA to [0.126±0.000] mg/kg. The results were below the average concentration in shale, which is 0.8 mg/kg. The results of Edward & Muhib's (2020) study on the concentration of heavy metals in the water, sediment, and fish near the Escravos River in Delta State, Nigeria, were, nevertheless, supported by these data. Even though cadmium is dangerous in high concentrations, the findings of this study give no cause for alarm. Lead (Pb) values varied between [6.327±0.046] and [9.474±0.198] mg/kg. These results indicated that lead was present in addition to silt. Compared to the levels reported by Saha and Hossain (2011) in the Buriganga River, Bangladesh, which ranged from 60.3 to 105.6 mg/Kg, these values are incredibly low. Lead (Pb) is a toxic metal that has been linked to cancer. Additionally, it reduces the efficiency of a number of the body's natural systems. Elevated lead concentrations have the potential to be toxic and cause severe illnesses. The sediment's iron (Fe) concentration ranged from $[111.614 \pm 2.278]$ to $[137.348 \pm 3.226]$ mg/Kg. Even though iron (Fe) is good for humans and animals alike, excessive consumption can be harmful. The Fe concentrations found in the sediment at each of the locations are less than both the DPR requirement for Nigerian soil and sediment and the global average value. Blood circulation is significantly impacted by iron (Edori & Kpee, 2018).

Heavy		$Mean \pm SD$	DPR	WASV			
metals		2	3	4		Limit	
(mg/Kg)							
Mn	5.362 ± 0.054	3.675 ± 0.007	4.316 ± 0.011	2.648 ± 0.011	4.000 ± 0.021	850	850
C _d	NA	0.126 ± 0.000	0.000 ± 0.001	0.069 ± 0.005	0.049 ± 0.002	0.8	0.3
Cu	6.154 ± 0.014	6.164 ± 0.049	4.666 ± 0.010	5.179 ± 0.212	5.541 ± 0.071	36	45
Cr	5.372 ± 0.217	5.377 ± 0.012	8.166 ± 0.018	6.361 ± 0.074	6.361 ± 0.074	100	90
Pb	7.403 ± 0.053	7.383 ± 0.028	9.474 ± 0.198	6.327 ± 0.046	7.647 ± 0.081	85	20
Fe	137.348±3.226	132.348±2.505	118.613 ± 2.683	111.614 ± 2.278	124.981 ± 2.673	38T	47T
Zn	16.118 ± 0.356	16.118 ± 0.291	98.481 ± 5.619	14.707 ± 0.106	36.356 ± 1.593	140	120
As	0.363 ± 0.001	0.196 ± 0.001	0.073 ± 0.004	0.094 ± 0.003	0.182 ± 0.002	13	10
Ni	7.212 ± 0.038	4.423 ± 0.003	6.243 ± 0.019	5.056 ± 0.034	5.734 ± 0.024	35	68

Table 2: The average concentration of heavy metals of sediment samples collected from the Kaani River at various stations.

WASV (World Average Shale value) of sediment, 2002. NA (Not Available)

Copper (Cu) values in the sampled sites ranged from $[4.666\pm0.010]$ to $[6.164\pm0.049]$ mg/Kg. In shale, every result was below concentration. The amounts of copper found in the sediment from this study were significantly lower than those found in the Warri River, Niger Delta, Nigeria, sediment reported by Aghoghovwia et al. (2015). The absence of industries in these locations that could release copper into the environment could be the reason for the low amount of copper. The investigation found that the levels of zinc (Zn) in the stations ranged from $[14.707\pm0.106]$ to [98.481 \pm 5.619] mg/Kg. When compared to the DPR standard of 140 mg/kg, this number is extremely low. Additionally, the values in this study were lower than those found in the sediments of the Island of Lesvos, Aegean Sea, by Ahmad et al., (2021) and Aloupi & Angelidis, (2001). Since there aren't many activities that could affect the amount of zinc released into the environment, the low quantity of zinc metal was not surprising. Secondly, the sampled site is far from the residential zones. Arsenic (As) levels were measured at [0.073±0.004] to [0.363±0.001] mg/kg in all of the locations. The work's observed arsenic (As) value is less than the global average for shale (13mg/kg) and the DPR standard (10mg/kg). According to Edori and Kpee (2016), arsenic is hazardous and extremely damaging even at very low concentrations. It is therefore discouraged to disseminate it to any environmental media. In the studied stations, chromium (Cr) was found to be present in the range of $[5.372 \pm 0.217] - [8.166 \pm 0.018]$ mg/Kg. These findings fell short of the DPR requirement in soil and sediment and value in shale. This was significantly less than studies conducted in benthic sediments from tropical ecosystems using multivariate statistical methodologies by Ama et al., (2017) and Benson et al., (2016). The high chromium concentration may be caused by ongoing human activity along these stations' coasts. The concentration of nickel (Ni) measured at each location varied between $[4.423 \pm 0.003]$ mg/kg and $[7.212 \pm 0.038]$ mg/Kg. When compared to the global average of 68 mg/kg and the DPR value of 35 mg/kg, this figure is

extremely low. Additionally, the values in this study were lower than those found in the sediments of the Island of Lesvos, Aegean Sea, by Ahmad et al., (2021) and Aloupi & Angelidis (2001). Elevated concentrations of nickel in sediment can be hazardous to aquatic life and have a number of negative environmental effects, especially on aquatic ecosystems. The levels of manganese (Mn) found in all the locations varied between $[2.648\pm0.011]$ mg/kg and $[5.362\pm0.054]$ mg/Kg. The Mn value found in this paper is less than the DPR- standard (850 mg/kg) and the global average value found in shale. Additionally, the values in this investigation were less than what Bibi et al. (2007) found. The complex and variable nature of manganese concentration in sediment is influenced by various factors, including the sensitivity of aquatic species, ambient circumstances, and sediment properties. Many creatures require manganese as a micronutrient, but excessive amounts can be harmful to aquatic life.

Table 3 provides the values of the contamination factor. With the exception of Ni at station 1 (Nwi ke maa kor stream), which was moderately contaminated, and Zn at station 3 (woman stream), which was severely contaminated, all of the sediment-bound metals in the various stations fall within the 0-1 range (which is no contamination to negligible contamination), according to the contamination factor values calculated from the heavy metals results (Lacatusu, 2000). This suggests that, with the exception of station 3, there was little human input at any of the stations. According to Edori and Kpee (2017), the contamination factor is used to understand the degree to which heavy metals have an impact on the pollution of any ecosystem, including soil, water, and sediment. Within the stations used in the investigation, the contamination factors of the heavy metals that were studied in the sediments of the Kaani River were as follows: Mn ranged from 0.0031-0.0063, Cd; NA-0.1575, Cu; 0.1296-0.1712; Cr, 0.0537-0.0817, Cd, 16.1667-103.4333; Ni; 17.8860-397860, Cr; 0.1280-0.9280, Co; 2.1500-27.7500, Pb; 0.0871-0.1115, Fe; 0.0029- 0.0036, Zn; 0.1051-0.7034, As; 0.0056-0.0279, and Ni; 0.1264-0.2061.

According to the Table's results, the stations' contamination factors were ranked as follows: Station $3 >$ Station 2 > Station 1 > Station 4. In Station 1, the heavy metal contamination factors were as follows: $Ni > Cu > Zn > Pb > Cr > As > Mn > Fe > Cd$; in Station 2; $Cu > Cd > Ni > Zn > Pb >$ $Cr > As > Mn > Fe$; in Station 3; $Zn > Ni > Cu > Pb > Cr > As > Mn > Fe > Cd$; and in Station 4; $Ni > Cu > Zn > Cd > Pb > Cr > As > Mn$.

Table 3: Heavy Metal Contamination Factor (CF) in Kaani River Sediment Samples at Various Stations

Tr is the toxic response factors of the investigated heavy metals (Orisakwe et al. 2015). NA (Not Available)

Table 4 displays the results of the examination of the sediment at several Kaani River stations for the ecological risk factor (Ef) and probable ecological risk index (RI). In terms of Mn, the risk factor ranged from 0.0031 to 0.0061, whereas for Cd, NA, 4.7250, Cu, 0.1074–0.1634, Pb, 0.3720– 0.55575, Fe, Zn, 0.0560–0.2790, As, and Ni, the range was 0.6480–1.0080. The Kaani River sediments yielded findings for the possible ecological risk index (RI) ranging from 2.8238 to 7.4430.

For every metal tested in this investigation, the ecological risk values found were less than the base value of 40 (Hakanson, 2000). This suggests that there is no environmental or ecological risk associated with the metals under investigation. This observation is consistent with research conducted in the surface sediments of the New Valley, Western Desert, Egypt, by Mahmoud et al. (2017). When the Kaani River stations were compared to the intervals of Hakanson (2000), the risk factor analysis revealed no risk of heavy metals in any of them.

The levels of the ecological risk factor and possible ecological risk index of heavy metals found in earlier research conducted in Niger Delta environments (Edori & Kpee 2016) are lower than the observations or conclusions mentioned above. According to Davies and Abolude (2016), there was no ecological risk of heavy metals in the sediments of River Nun in Bayelsa State, Nigeria, although there were indications of potential risk in the near future, particularly for Cd. According to Bibi et al., (2007), there was a modest increase in the risk of heavy metals in the sediments of the New Calabar River in Port Harcourt, Nigeria. Metals including nickel and copper exhibited potential environmental hazards in the future.

Heavy				
metals.	$\mathbf{1}$	$\overline{2}$	3	$\overline{4}$
Mn	0.0063	0.0043	0.0051	0.0031
C _d	NΑ	4.7250	NA.	2.5890
Cu	0.8545	0.8560	0.6480	0.7195
Cr	0.1074	0.1076	0.1634	0.1306
Pb	0.4355	0.4345	0.5575	0.3720
Fe	0.0180	0.0175	0.0155	0.0145
Zn	0.1151	0.1151	0.7034	0.1051
As	0.2790	0.1510	0.0560	0.0720
Ni	1.0080	0.6320	0.8920	0.7225
\mathbf{R}	2.8238	7.4430	3.0409	5.5283

Table 4: Ecological risk factor (EF) and potential ecological risk index (RI) of Sediment samples from various stations in the Kaani River.

NA (Not Available)

Table 5 displays the values of the enrichment factors from the current investigation. Mn 1.7453, 1.2409, 1.6268, 1.0607; Cd NA, 45.3333, NA, 29.3683; Cu 47.3135, 49.1808, 41.5396, 48.9979; Cr 14.8627, 15.4385, 26.1614, 22.2252; Pb 24.0963, 24.9391, 35.7081, 25.3422; Fe NA, NA, NA, NA; Zn 31.8526, 33.0559, 225.3595, 35.7652; As 7.7256, 4.3289, 1.7990, 2.4618; Ni 57.0525, 36.2861, 27.1480, 49.1846 are the heavy metal enrichment status in sediment at different stations. Cu was extremely enriched in all sampled stations, Ni was exceptionally enriched at stations 1 and 4, Cd was exceptionally enriched at station 2, and Pb, Mn, As, Zn, and Cr showed insignificant to moderate enrichment, according to the data found in this study. Fe indicated that there was no enrichment in any of the examined locations. According to Han et al. (2006), the enrichment factor result shows that humans have an impact on the presence of several metals in the environment.

NA (Not Available)

Conclusion: The investigation's findings provided crucial information about the degree of metal contamination in the Kaani River's surface sediments in River State's Ogoni axis. The metals were distributed as follows: $Fe > Zn > Pb > Cr > Ni > Cu > Mn > As > Cd$. Ecological risk assessment and contamination factor showed that there was no environmental risk for heavy metals. On the other hand, enrichment factor analysis indicated that the entry of heavy metals into the environment was influenced by humans. Hence offering a foundation for further evaluation to reduce potential health risks caused by elevated levels of certain heavy metals

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