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Distribution and Potential Environmental Risks of Heavy Metals in Riverine Sediments of Maa-Dee-Tai River in Sogho Community, Ogoniland, Rivers State, Nigeria

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Abstract: Ecological Risk Assessments are executed to appraise the probability of adverse ecological effects occurring as a consequence of exposure to biological, physical, or chemical factors that causes hostile responses in the environment. Several studies have shown extensive heavy metals and crude oil contamination of soils, sediments, rivers, creeks, and ground waters in Ogoniland, Nigeria. However, the Sogho Community in Ogoniland has not been studied. Hence, this paper evaluates the distribution and ecological risk assessment of heavy metals in riverine sediments of Maa-Dee-Tai River in Sogho Community, Ogoniland, Rivers State, Nigeria using Solaar Thermo Elemental Atomic Absorption Spectrophotometer, Model SN-SG 710960 after total dissolution of riverine sediments by hydrofluoric acid (HF) and aqua regia (HNO_3: HCl; 1:3, v/v) at a temperature of 100°C. Distribution of heavy metals in the sampling stations reveal that Werri had the maximum magnitude of nickel (Ni) among the three stations assessed and the mean value for the three stations is 4.21±0.92mg/Kg. The average values recorded for Ni in the three stations were; 3.52±0.58, 4.04±1.04 and 5.07±1.14mg/Kg for Dee-Tai, Barawansah and Werri respectively. The average mean concentration of the sampling stations for each metal (mg/kg) are Ni (4.21), Zn (3.56) Cr (3.35), Pb (3.25), Cu (1.59), Co (0.8), As (0.12) and Cd (0.12). The order of abundance of the metals in the riverine sediments is Ni>Zn>Cr>Pb>Cu>Co>As>Cd. In all the stations examined, Nickel (Ni) was the most abundant metal. The pollution indices revealed that the river was unpolluted with the different heavy metals studied. The potential environmental risks assessment of heavy metals in riverine sediments of the Maa-Dee-Tai River in Sogho Community, Ogoniland reveals that the river poses low risks in terms of pollutants with reference to heavy metals in the sediment. Hence, it is necessary to preserve the natural state of the river.

Keywords: Heavy Metals, Ecotoxicology, Risk Assessment, Riverine Sediment

1. Introduction

Riverine sediments investigation is a widely used technique for environmental quality assessment, since the riverine sediments accumulate organic and inorganic pollutants [1-4] over time causing direct or indirect effects on the overlying water system as well as on human beings, hence, valuation of heavy metals in the riverine sediments is indispensable [5]. Riverine sediment at the bottom of a river plays a significant role in the pollution scheme of such river system as they could act as a 'sink' or 'source' of heavy metals [6-8]. Marine sediments constitute part of the contaminants in aquatic environments. The bottom sediment serves as a reservoir for heavy metals, and therefore, deserves special consideration in the planning and design of aquatic pollution research studies. Heavy metals such as cadmium, mercury, lead, copper, and zinc, are regarded as serious marine pollutants because of their toxicity, tendency to be incorporated into food chains, and ability to remain in an environment for a long time [9, 10].

Sediments are known to act as the main sink for heavy metals in coastal ecosystems that are impacted by anthropogenic activities. The concentration of heavy metals in sediments can be influenced by variation in their texture, composition, reduction/oxidation reactions, adsorption/desorption, and physical transport or sorting in addition to anthropogenic input. Potentially, toxic compounds, especially heavy metals, are adsorbed on mineral or organic particles either in their organic or inorganic forms. Studies on the distribution of trace metals in sediments and other media are of great importance in the context of environmental pollution [11, 12].

Sediments of rivers, lakes and estuaries in a large number of locations have been contaminated by inorganic and organic materials. Among the inorganic materials metals are frequent and important contaminants in aquatic sediments. They are involved in a number of reactions in the system including sorption and precipitation, and they are greatly influenced by redox conditions in the sediments. Heavy metals are transported as either dissolved species in water or an integral part of suspended solids. They may be volatilized to the atmosphere or stored in riverbed sediments. They can remain in solution or suspension and precipitate on the bottom or can be taken up by organisms. Several studies on potential toxic metals in sediments are available in some of the areas in the Niger Delta region. They include [13-15].

Therefore, adequate data on riverine sediment is necessary for assessing the total environmental status of aquatic ecosystems [16]. Hence, the riverine sediments can reveal better information concerning the pollution status of estuaries, inter-tidal flats, riverbank and riparian ecological zones of a river system. Since sediment environment directly influences the physicochemical and ecological dynamics of aquatic resources, a deteriorated sediment quality may severely impact the supports that sustain aquatic life and the surrounding ecosystem, which also includes human beings, dependent on it [17]. To date, traditionally, the Ogoni people are agricultural, also known for livestock herding, fishing, salt and palm oil cultivation and trade. Several studies have shown extensive oil contamination of rivers, creeks, and ground waters in Ogoniland, Nigeria [18]. Because of the unique environmental conditions of Ogoniland and its important oil and gas industries and the attendant oil pollution and heavy metal contamination, the United Nations Environmental Programme [19], published an environmental assessment report of Ogoniland and subsequently, several research has been the focus of previous investigations [20-26] Also, Environmental pollution arising from crude oil exploratory activities has adversely impacted both the living and non-living components of the ecosystem. An insight into the impact of such activities with focus on Goi Creek in Ogoniland was assessed [22]. All so, several indices have been widely applied to evaluate the toxicity, ecological risk, and contaminated levels of heavy metals in soil and sediment. For example, the potential ecological risk index (PERI) [27] and the hazard index (HI) [28] have been applied to evaluate the risk and toxicity in soil, respectively [29], while the pollution condition evaluations of soil and sediments were supported with the geo-accumulation index (Igeo), enrichment factor (EF) pollution index (PI), and Nemerow integrated pollution index (PN) [30-33]. The use of pollution indicators is crucial for assessing the degree/level of heavy metals in soil contamination and the potential environmental risks [34]. Also, pollution indices may help to identify the source of Trace elements in soil [35].

However, the surface water, soil and riverine sediment pollution assessment of Sogho Community, Ogoniland have scarce information in terms of heavy metals distribution and their potential environmental risks Hence, the objective of this work is to assess the distribution and potential environmental risks assessment of heavy metals in riverine sediments of Maa-Dee-Tai River in Sogho Community in Ogoniland, Rivers State, Nigeria.

2. Materials and Methods

Study area: The Maa-Dee-Tai River is situated in Sogho community, Ogoniland, Niger Delta Region, Nigeria. The river has tributaries with Imo and Bori rivers and served as a source of water for cassava fermentation, drinking and washing of fabric materials. Also, fishing activities are commonly carried out by the people residing within the community. The town is reportedly known for farming activities that uses fertilizers and pesticides on their farmland. Although there are no industrial activities within the town but it is close to Afam power and Korokoro Flow Stations in Oyigbo and Tai Local Government Areas respectively (Figure 1).

2.1. Sample Collection

Riverine sediment samples were collected at four depth that is four samples per site and 8m away from the flowing water using a sediment grab and were kept in clean glass containers. Atmospheric temperature was used to dehydrate the sediment samples, dry samples were ground into a homogenous mixture using a porcelain mortar and pestle and sieved through a 2 mm mesh screen to remove coarse materials because particles >2 mm may consist of shells, rocks, wood, and other detrital materials, and are usually not a source of bioavailable contaminants [36]. Even though, large debris, shells and visible organisms were removed prior to grinding.

2.2. Sample Digestion

For metal analysis, 2 g of dried and grounded riverine sediment were weighed and mineralized using a reference method for marine pollution studies [37]. The sample were mineralized in 3 ml HCl (90%) for 24 h and 9 ml HNO_3 (90%) for 30 minutes using Teflon container. The principle of this method is based on the total dissolution of the riverine sediments by hydrofluoric acid (HF) and aqua regia (HNO_3: HCl; 1:3, v/v) at high temperature. The use of HF is essential because it is the only acid that completely dissolves silicates and all metals [37]. 0.2 g of dry, homogeneous sediment or soil sample placed in a Teflon tube previously washed with acid underwent hot mineralisation using 1 mL of aqua regia (HNO_3: HCl; 1:3, v/v) and 6 mL of concentrated HF (48%).

Heating was carried out in a water bath at 120°C for 2 hours 30 minutes. After cooling in ambient air, the residue was taken up in a boric acid solution (2.70 g in 20 mL of distilled water). The final volume was reduced to 50 mL and left to stand for 6 hours. After the samples were concentrated and digested, the heavy metal concentrations were determined by Solaar Thermo Elemental Atomic Absorption Spectrophotometer, Model SN-SG 710960.

A one (1) gram of the sample was digested with a mixture of 4.0 mL of 65% v/v HNO_3 and 2.0 mL of 35% v/v H_2O_2. After evaporation, 4.0 mL of concentrated HNO_3 and 2.0 mL of concentrated H_2O_2 were added to the residue and heated until a clear digest appeared. The digestion time of 3 h at 130°C was employed. The digest was made up to the 5.0 mL with 1.0 M HNO_3. The concentrations for lead (Pb), Zinc (Zn) and Copper (Cu) were then estimated Each digested sediment sample was analyzed for heavy metals using Solaar Thermo Elemental Atomic Absorption Spectrophotometer, Model SN-SG 710960. Concentrations of heavy metals are expressed in mg/kg as calculated by:

Calculate the concentration using the equation below:

$$Sample\ Conc.(mg/kg)dry - weight\ basis = \frac{C\ xVxD}{W} \quad (1)$$

Where C = Concentration from AAS measurement (mg/L); V = Volume of final digest (L, 5.0 mL = 0.005 L); D = Dilution factor [(volume (50µL = 0.00005 L) of digest taken for AAS measurement [L] divide by final volume (0.005 L) = 0.01]; W = Weight of sample digested (g x 0.001 = 0.001 kg)

= Sampling Stations

Figure 1. *Map showing Maa-Dee-Tai River in Sogho Community, Ogboniland.*

3. Potential Environmental Risk Assessment (PERA) Techniques

In this study, the potential environmental risk assessment techniques employed for the heavy metals in the riverine sediments are Contamination Factor (CF), Enrichment Factor (EF), Geoaccumulation Index (Igeo), Pollution Loading Index (PLI), Degree of Contamination (Cd), Modified degree of contamination (mCd), Monomial potential ecological factor (Er) and Comprehensive potential ecological risk index (RI). In this study, the metal concentration values of the upper continental crust (UCC) were used as reference values (Table 1). The upper crust is the most accessible portion of the continental crust, and hence, its composition is the best constrained. Estimates of the composition of the upper continental crust are based on wide scale surface sampling. The UCC (Table 1) was used as reference [38], because they were shown to be the most appropriate for the riverine sediments of the Coastal Niger Delta area where the Maa-Dee-Tai River belongs.

Table 1. *Metal content of the upper continental crust (UCC), mg/kg.*

Metal	Ni	Zn	Cr	Pb	Cu	Co	Cd	As	Mn	Fe
Content (mg/kg)	47	67	92	17	28	12	0.09	4.8	775	39,000

Source: Rudnick and Gao [38]. (2003)

3.1. Contamination Factor (CF)

Contamination factor. The contamination factor is obtained from a ratio between the measured concentration of the heavy metals in riverine sediment of the river under investigation and the pre-industrial reference value for the same metal [27]. The degree of contamination is defined as the sum of all contamination factors. The contamination factor (CF) is evaluated from the relationship in equation 2:

$$CF=\frac{[M]_s}{[M]_b} \quad (2)$$

Where: $[M]_s$ is the concentration of the metal in the riverine sediment in mg/kg; $[M]_b$ is the concentration of the metal in UCC in mg/kg.

The different levels of contamination according to the CF values are grouped in the table 3.

Table 2. *Contamination levels according to CF values.*

CF value	Levels of contamination
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF ≥ 6	Very strong contamination

The degree of contamination is defined as the sum of all contamination factors, which is called the contamination index (C_d) and it is used to measure the quality of overlying water and wastewater [39]. The contamination index is calculated from the equation 3.

$$C_d = \sum_{i=1}^{n} C_F^i \quad (3)$$

Where C_F^i are the individual contamination factors for the metals and n is the number of the C_fs examined for specific element. The (C_d) is computed separately for each sampling site as a sum of contamination factors (C_f) of individual elements exceeding the permissible limits. Backman and co-workers [39] described the degree of contamination (C_d value) as: $C_d < 1$ = low ($1 < C_d < 3$ = medium, and ($C_d > 3$ = high).

3.2. Enrichment Factor (EF)

In order to assess the enrichment degree of heavy metals in the riverine sediments, the Enrichment Factor (EF) was used. The enrichment factor (EF) compares the concentration of an element in samples with the concentration of the same element in the non-contaminated area (i.e. geological background, which is the concentration of an element in a mineral or rock relative to its crustal abundance of the Earth's crust, most often Continental or Upper Continental Crust (UCC). Background metal concentrations for EF calculation were used as the UCC as present in Table 1. The enrichment factor (EF) is used to assess the level of contamination and the possible anthropogenic impact on the sediments of the study area. Al, Fe, or Si could be used as the geochemical normalization. However, researchers have successfully used Fe for the geochemical normalization of metal contaminants [40-46]. Therefore, Fe was used as a conservative tracer to differentiate natural from anthropogenic components in this study.

The EF is defined in equation 4, [47]:

$$EF = \frac{(C_i/C_{ref})_{sediment}}{(C_i/C_{ref})_{backround}} \quad (4)$$

The corresponding categorizations of the EF are shown in Table 3.

Table 3. *Enrichment factor (EF) categorization.*

EF	Enrichment Level
<1	No enrichment
1-3	Minor enrichment
3-5	Moderate enrichment
5-10	Moderately severe enrichment
10-25	Severe enrichment
25-50	Very severe enrichment

The Data are from Wei and Co-workers [48]

3.3. Geo-Accumulation Index

The geo-accumulation index establishes a relationship between the measured concentration of a metal in the fine fraction of sediments and the geochemical background concentration chosen as a reference for the metal under study, including a corrective factor (1.5) for lithological variations of the metal elements. The geo-accumulation index ($I_{géo}$) is calculated from the following formula:

$$I_{géo}=\log_2\left(\frac{[M]_s}{1.5\times[M]_b}\right) \quad (5)$$

Where: $[M]_s$ is the concentration of the metal in the riverine sediment in mg/kg; $[M]_b$ is the concentration of the metal in UCC in mg/kg.

In application, I_{geo} values greater than 1 indicate moderate contamination of a sediment sample by the metal under study, while those greater than 3 indicate high contamination [37]. The I_{geo} values are used to define seven levels of contamination (Table 4).

Table 4. *The different classes of sediment contamination.*

Class	Value	Levels of contamination
0	$I_{géo}<0$	Uncontaminated
1	$0< I_{géo}<1$	Uncontaminated to moderately contaminated
2	$1< I_{géo}<2$	Moderately contaminated
3	$2< I_{géo}<3$	Moderately to severely contaminated

Class	Value	Levels of contamination
4	$3 < I_{géo} < 4$	Severely contaminated
5	$4 < I_{géo} < 5$	Severely contaminated to extremely contaminated
6	$5 < I_{géo}$	Extremely contaminated

3.4. Pollution Loading Index

Equation (6) was used to calculate the Pollution Loading Index (PLI). This index is calculated from the Contamination Factor (CF).

$$PLI=(CF_1\times CF_2\times CF_3\times\ldots\ldots\ldots\times CF_n)^{1/n} \quad (6)$$

Where n is the number of sediments; CF is the contamination factor.

The pollution loading index gives cumulative information on metal pollution in soils or sediments. For PLI = 0, there is no deterioration; for PLI = 1, only baseline levels of pollutants are present, and PLI value > 1 indicates progressive deterioration of the sediments [37].

3.5. Degree of Contamination, Cd

The degree of contamination also called the contamination index is calculated from the equation 2

$$C_d = \sum_{i=1}^{n} C_F^i \quad (7)$$

Where C_F^i = the individual contamination factors for the metals and n is the number of the CF examined for specific element. The (C_d) is computed separately for each sampling site as a sum of contamination factors (C_f) of individual elements exceeding the permissible limits. Hakanson [27] proposed the classification of the degree of contamination (mCd) in sediments as:

Cd<6 Low degree of contamination

6<Cd<12 Moderate degree of contamination

12<Cd<24 Considerable degree of contamination

Cd> 24 High degree of contamination

3.6. Modified Degree of Contamination (mCd)

The modified degree of contamination (mCd) is a generalized tool for determining the overall degree of contamination of a particular site based on the contamination factor (CF) of each heavy metals within the sediment.

The mCd is calculated using the Eq. (8)

$$mCd = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (8)$$

Where, Cf is the contamination factor, i represents the "ith" metal, and n is the number of metals evaluated. The mCd is classified into contamination grades: uncontaminated to very low contamination grade (mCd ≤ 1.5), low contamination grade (1. 5 < mCd ≤ 2), moderate contamination grade (2 < mCd ≤ 4), high contamination grade (4 < mCd ≤ 8), very high contamination grade 8 < mCd ≤ 16), extremely high contamination grade (16 < mCd ≤ 32), and ultra-high contamination grade (mCd > 32).

3.7. Evaluation of Ecological Risk Indices (Er and RI)

The ecological risk indices employed in this study include the monomial potential ecological factor (Er) which expresses the potential ecological risk of individual heavy metals in the riverine sediment. It is expressed in equation 9 [49];

$$Er = Tr \times CF \quad (9)$$

Where Tr is the toxic-response factor of the heavy metals as presented in Table 6 and CF is the contamination factor.

And the comprehensive potential ecological risk index (RI), which is the sum of all Er values was used to express the potential ecological risk for a given environment.

$$RI = \Sigma Er \quad (10)$$

The different grades for Er and RI of heavy metals as classified by Hakanson and co-workers [27] and used by Mackmannuel and co-workers [4] are presented in table 5.

Table 5. *Grades of the Environment by Potential Ecological Risk Index.*

Er values	Grades of Er of single element	RI values	Grades of potential RI of the environment
Er<40	Low risk	RI<95	Low risk
40≤Er<80	Moderate risk	95≤RI<190	Moderate risk
80 ≤ Er<160	Considerable risk	190≤RI<380	Considerable risk
160 ≤ Er<320	High risk	RI>380	High risk
Er ≥ 320	Very high risk		

Table 6. *Toxic response factors (mg/kg) for the heavy metals investigated and the reference metal (Fe) (Hakanson, 980).*

Metals	Ni	Zn	Cr	Pb	Cu	Co	Cd	As	Fe
Toxic response factors (mg/kg)	5	1	2	5	5	5	30	10	1

3.8. Statistical Evaluation of Experimental Data

The statistical analyses (mean value, minimum, maximum, standard deviation, analysis of variance and Pearson's correlation) were carried out with the STATISTICA 2005 software (version 7.1). Analysis of variance (one-way ANOVA) was used to assess the difference between the sampling sites. The difference was considered significant at P

< 0.05.

4. Results and Discussion

Heavy Metals Concentrations in Riverine Sediment of Maa-Dee-Tai River: The concentration of each heavy metal increases in the water medium due to re-suspension adsorption-desorption, reduction-oxidation processes and the action of organisms degrading the metals into the water component at a certain period when the interface between the surface of the water and sediment is distorted [50]. This is the negative impact of trace metal concentrations in sediments of any water system on the environment [51]. The summary of the magnitude of trace element in sediments from Maa-Dee-Tai River are given in table 1.

Table 7. *Concentration of metals (mg/Kg) in sediments from Maa-Dee-Tai River in comparison with standards.*

Metals	Dee-Tai	Barawansah	Werri	AMCS	DPR/FEPA	Shale value
Ni	3.52±0.58	4.04±1.04	5.07±1.14	4.21	35	19
Zn	3.25±0.54	3.55±0.44	3.88±0.68	3.56	140	95
Cr	3.14±0.09	3.87±0.16	3.01±0.72	3.35	100	45
Pb	3.26±0.79	4.17±0.67	2.32±0.85	3.25	85	20
Cu	1.48±0.57	0.94±0.21	2.35±0.63	1.59	36	45
Co	0.08±0.05	0.56±0.51	1.76±0.81	0.80	20	19
Cd	0.24±0.38	0.04±0.01	0.09±0.03	0.12	0.8	0.3
As	0.24±0.08	0.09±0.02	0.03±0.02	0.12	1	13

Note (n=12), values are mean ± SD. AMCS-average means concentration of the sampling stations. [52] DPR-Department of Petroleum Resources (2002) or [53] FEPA-Federal Environmental Protection Agency (2003) national limits in Nigeria. Shale values from [54] Turekian and Wedepohl (1961).

4.1. Distribution of Heavy Metals in Riverine Sediments of the Sampling Stations

The order of abundance of the metals in the sediments is Ni>Zn>Cr>Pb>Cu>Co>As>Cd. In all the stations examined, Nickel (Ni) was the most abundant metal and ranged from 3.52±0.58 to 5.07±1.14 mg/Kg. The average figures recorded for the three stations are 3.52±0.58, 4.04±1.04 and 5.07±1.14mg/Kg for Dee-Tai, Barawansah and Werri respectively. The mean value for the three stations is 4.21±0.92mg/Kg. Among the three stations examined, Werri had the maximum magnitude of nickel (Ni) among the three stations assess. The maximum and minimum magnitudes were observed at Werri and Dee-Tai respectively. This assessment revealed that the concentration of Ni is below those in New Calabar River, Rivers State of Nigeria, where its value is 4.537±0.427mg/Kg but above those of Bodo Creek [50, 51]. However, Maa-Dee-River shows no significant difference with other rivers within Niger Delta [55, 56]. It is lower than the permissive limit for Ni set by DPR.

Zinc (Zn) mean concentrations in this study ranged from 3.25±0.54 to 3.88±0.68mg/Kg and the mean values within the three stations were 3.23±0.54, 3.55±0.44 and 3.88±0.68mg/Kg for Dee-Tai, Barawansah and Werri respectively. Mean concentration for the three stations is 3.56±0.55mg/Kg. The average maximum and minimum magnitudes were revealed at Werri and Dee-Tai respectively. The values of Zinc (Zn) assess in this investigation were below those obtained in New Calabar and Okrika Rivers, both in Niger Delta, Nigeria, where their mean concentration is 5.49±2.01mg/Kg and 245.49±0.52mg/Kg respectively [57]. It is still lower than the value of permissive limit set for Zinc by DPR. The magnitude of Cr obtained in this assessment ranged from 3.01±0.72 – 3.87±0.16mg/Kg and the mean concentration values in the three stations were 3.14±0.09, 3.87±0.16 and 3.01±0.72 for Dee-Tai, Barawansah and Werri respectively. For the three stations, the mean concentration is 3.5±0.32mg/Kg. The lowest and highest mean concentrations (3.01±0.72 and 3.87±0.16) were observed within Werri and Barawansah stations respectively. In this study, the mean concentrations for Cr observed is higher than those from Ekulu River in Enugu and Owan River in Edo State, Nigeria where the value is 0.214-0.267 and 0.12-8.08mg/kg respectively [58, 59]. But it does not show much variation when compared with those from Warri River, Delta State, Nigeria [60]. The range of mean concentration values of Pb within the sampling locations is 2.32±0.85-4.17±0.67mg/Kg but the mean concentration in each of the stations was 3.26±0.79, 4’17±0.67 and 2.32±0.85mg/Kg for Dee-Tai, Barawansah and Werri respectively. The mean value for the three locations is 3.25±0.77mg/Kg and the highest and lowest mean values (4.17±0.67 and 2.32±0.85) mg/Kg are observed at Barawansah and Werri respectively. In this study, the concentrations of Pb when compared with other literature revealed higher values than those obtained in samples from Ikpoba River, Edo State, Nigeria [61] but fall within values obtained in samples from New Calabar River [51] Bonny River, Rivers State, Nigeria [34] and by far lower than the values observed in sediments from beach area in Lagos, Nigeria [35].

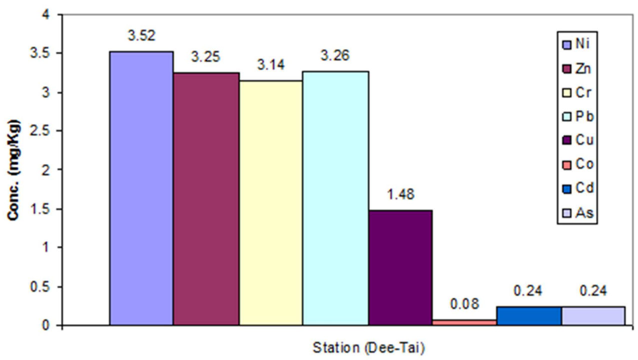

Figure 2. *Distribution of heavy metals concentration (mg/Kg) in sediment from Dee-tai station.*

The average concentration values of Copper (Cu) in the sample stations varied from 0.94±0.21-2.35±0.63mg/Kg while for the three locations such as Dee-Tai, Barawansah and Werri, the mean values were 1.48±0.57, 0.94±0.21 and 2.35±0.63mg/Kg. The mean value for the three locations is 1.59±0.47. The lowest and highest mean values obtained are 0.94±0.21 and 2.35±0.63mg/Kg for Werri and Barawansah respectively. When the magnitudes of copper in this assessment were compared with other literatures on sediments in Niger Delta region, it was observed that the values were lower than those observed in sediments from Bodo creeks, Owan River, and Andoni River respectively [50, 59, 62]. But the mean value is higher than those from Orashi River [63].

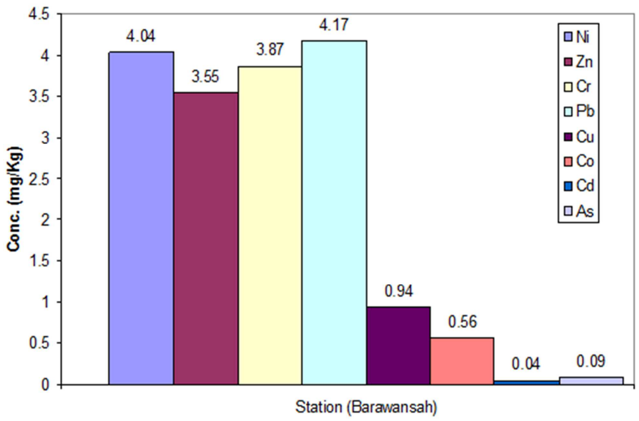

Figure 3. *Distribution of heavy metals concentration (mg/Kg) in sediment from Barawansah station.*

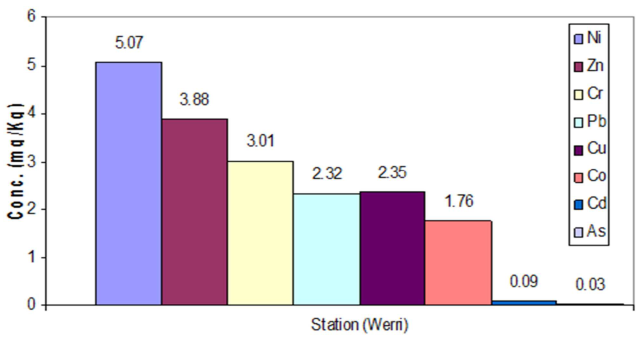

Figure 4. *Distribution of heavy metals concentration (mg/Kg) in sediment from Werri station.*

Cobalt (Co) mean concentration values in the experimental work ranged from 0.08±0.05-1.76±0.81mg/Kg whereas for the three stations, the mean values were 0.08±0.05, 0.56±0.51 and 1.76±0.81mg/Kg for Dee-Tai, Barawansah and Werri respectively. 0.8±0.46mg/Kg is the total mean value for the three locations while the lowest and highest mean values observed are 0.08±0.05 and 1.76±0.81mg/Kg for Dee-Tai and Werri respectively. In this present study, the mean values obtained were compared with other research findings and was observed to be lower than those from New Calabar River [2] but slightly higher than those in sediments from Bodo creeks and Bonny/New Calabar River respectively [51, 64]. As and Cd almost have the same mean concentration values which ranges from 0.03±0.02-0.24±0.08 and 0.04±0.01-0.24±0.38 mg/Kg respectively. The highest mean concentration value was observed in Dee-Tai station for both of them. They have similar variation with those observed in sediments from Andoni River [62]. The sources of heavy metals in the river investigated resulted from agricultural runoff, domestic waste, atmospheric deposition and natural means like weathering of rocks and erosion.

4.2. Evaluation of Pollution Indices of Maa-Dee-Tai River

Recognizing the pollution characteristics and potential risks of trace metals in sediments are important to protect water ecosystem safety. In the present study, a systematic investigation was performed to assess the pollution and risk level of trace metals in river sediments located in the greatest gold production base in China. The geo-accumulation index was used to assess the contamination degree. The sediment quality guidelines and potential ecological risk index were employed to complete an ecological risk assessment. A non-carcinogenic health risk assessment was also carried out to evaluate potential adverse health risks. Correlations and principal component analyses were applied to check relationships among trace metals and ascertain potential pollution sources. The results suggested that the sediments in the river were most polluted by As, Cd, and Hg followed by Cu, Pb, and Zn. The assessment of potential human health risk revealed that there was no significant non-carcinogenic risk to the inhabitants. Gold mining and smelting activities and the long-term excessive application of fertilizers and agrochemicals were identified as the main anthropogenic releases. This study contributed an understanding that possible sources, contamination degree, and ecological risk level of trace metals in riverine surface sediments in a gold mining area.

Contamination factor of trace metals: The contamination factors of the individual trace elements are presented in Table 2. The contamination values obtained from the different stations (Dee-Tai, Barawansah and Werri) in the Maa-Dee-Tai River were reported according to the contamination intervals postulated by Muller [65].

Table 8. *Contamination Factor (CF) Analysis of Heavy Metals in Sediments from the Different Stations in Dee-Tai River.*

Metals	Dee-Tai	Barawansah	Werri
Ni	0.185	0.213	0.267
Zn	0.034	0.037	0.041
Cr	0.0698	0.086	0.067
Cu	0.033	0.0209	0.052
Co	0.0042	0.0295	0.093
As	0.018	0.0069	0.0023
Cd	0.80	0.0133	0.3
Pb	0.162	0.209	0.116

The contamination factor of the metals investigated showed that Ni ranged from 0.185 – 0.267 in the stations with the highest and lowest values occurring at Werri and Dee-Tai accordingly. Low contamination of the sediment samples was recorded for Ni because it falls CF<1. The contamination factor for Zinc varied between 0.034– 0.041in the stations showing highest and lowest factors occurring at Werri and Dee-Tai respectively. These values indicated very low contamination of the sediment with Zn, As and Cd have the contamination factor that varied between 0.0023-0.018 and 0.133-0.80 respectively. Their highest values occur at Dee-Tai while lowest values at Barawansah for Cd and Werri for As. They fall between low contaminations indicating lack of pollution to the river investigated. Pb, Cu, Cr and Co had values that completely represents low contamination because they fall within range of contamination factor less than one (CF<1).

4.3. Pollution Load Index (PLI), Contamination Degree (CD) and Modified Contamination Degree (Mcd)

The magnitude of pollution load index, degree of contamination and modified degree of contamination of sediments from the several locations in Maa-Dee-Tai are presented in Table 3. The results of pollution load index obtained from the three locations when compared with the intervals of pollution load index assessment postulated by Bonnail and Co-workers [68] signified Dee-Tai, Barawansah and Werri from Maa-Dee-Tai River are free from the selected heavy metals pollution. This is because the results examined fall within the category of PLI <1 indicating no pollution, which signified that the Maa-Dee-Tai River located in Sogho Community is unpolluted with the trace elements selected for this investigation. Evaluation of contamination degree of the selected trace metals in sediment samples as proposed by Hakanson [27] revealed that all the stations showed low contamination degree. Also, modified contamination degree evaluation revealed that the figures showed obtained in sediment samples from Maa-Dee-Tai River in the various stations assessed varied within the category of Nil to extreme low degree of contamination (mCD< 1.5) [51].

Table 9. *Pollution Index (PLI), Contamination Degree (CD) and Modified Contamination Degree (Mcd) of Sediments from Dee-Tai River.*

Assessment Indices	Dee-Tai	Barawansah	Werri
PLI	0.059	0.041	0.064
CD	1.307	0.735	0.938
Mcd	0.163	0.092	0.117

4.4. Geo-Accumulation Index for the Selected Heavy Metals in Sediment Samples

The index of geo-accumulation for the selected trace elements is presented in table 4.

Table 10. *Geoaccumulation index of heavy metals in sediment samples from Maa-Dee-Tai River.*

		Igeo		
Metals	**Dee-Tai**	**Barawansah**	**Werri**	**AMCS**
Ni	0.049929	0.057305	0.071915	0.059716
Zn	0.032338	0.035323	0.038607	0.035423
Cr	0.022754	0.028043	0.021812	0.024275
Pb	0.127843	0.163529	0.09098	0.127451
Cu	0.035238	0.022381	0.055952	0.037857
Co	0.004444	0.031111	0.097778	0.044444
Cd	1.777778	0.296296	0.666667	0.888889
As	0.033333	0.0125	0.004167	0.016667

The geo-accumulation index for Co, Pb, Cd, As, Cr, Cu, Ni and Zn studied have negative values indicating that the river under investigation is unpolluted (Igeo < 0) [65]. This observation is certain because the river does not receive any industrial effluents except runoff from the locality and agricultural farmland. Therefore, there is low anthropogenic input that greatly affects water bodies and makes it unfit for consumption and other human utilizations. The index of geo-accumulation in this research agreed with the reports by [66] and partially with those reported by [67].

4.5. Evaluation of Ecological Risk Indices

Ecological risk assessment was assessed using the monomial potential ecological factor (Er) which expresses the potential ecological risk of individual heavy metals in the riverine sediment and the comprehensive potential ecological risk index (RI) which is the sum of all Er values, which was used to express the potential ecological risk (PERI, or RI) for the Maa-Dee-Tai riverine sediment.

Table 11. *Potential ecological risk indices (Er) and the comprehensive ecological risk index (RI) was of heavy metals in sediment samples from Maa-Dee-Tai River.*

Metals	Dee-Tai	Barawansah	Werri	AMCS
Ni	0.37447	0.42979	0.539362	0.447872
Zn	0.04851	0.05299	0.05791	0.053134
Cr	0.06826	0.08413	0.065435	0.072826
Pb	0.95882	1.22647	0.682353	0.955882
Cu	0.26429	0.16786	0.419643	0.283929
Co	0.03333	0.23333	0.733333	0.333333
Cd	80	13.3333	30	40
As	0.5	0.1875	0.0625	0.25
RI	82.24768	15.7154	32.56054	42.32415

The Er values and RI value of the studied metals from all sampling stations of the riverine sediments are presented in table 11. Going by the heavy metals investigated in the riverine sediments, Er for Cd is higher than other metals indicating the potential risk of Cd contamination as 80 in Dee-Tai; 13.33 in Barawansah and 30 in Werri with an average of 40 for the studied environment. This level be a potential Cd toxicity with adverse effect organisms. The other elements have low risk of pollution in the riverine sediments as Er<40.

5. Conclusions

In the present work, the results showed that the riverine sediment in the Maa-Dee-Tai River contain no significant amount of the heavy metals (Pb, Cd, Co, Zn, Cu, Ni, As and Cr) because the levels are lower than the standard permissible or allowable limits recommended by regulatory authorities. Finally, all the pollution indices revealed that the sediment is unpolluted with heavy metals at the moment with a concern on Cd.

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Conflicts of Interest

The author declares no conflict of interests.

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