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EVALUATION STUDY ON THE SEQUENTIAL EXTRACTION AND ECO-TOXICOLOGICAL PROFILE OF HEAVY METALS IN SEDIMENT ALONG THE COASTLINE OF NIGERIA

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ABSTRACT. Evaluation study of sediment samples collected from the coastline of Nigeria was investigated in order to assess the ecological impact of anthropogenic activities in the studied area. Sequential extraction, digestion and quantification were done using standard methods. The eco-toxicological assessment of heavy metals was performed using risk assessment indices, sediment quality guideline, fractionation study and total concentration of heavy metals. The risk assessment indices revealed that amid the analyzed heavy metals, Cu has the least probability of been toxic to the environment, however the fractionation study revealed that the mobility and bioavailability of the heavy metals followed the order: Cr > Cd > Pb > Ni > Cu. The sediment quality guidelines posited the analyzed heavy metals to be 8% toxic to the environment. Finally, the total concentration of heavy metals fell below the maximum permissible limit of USEPA.

1. INTRODUCTION

The heavy metals occurrence resulting in the contamination of aquatic ecological system has been postulated to be a global predicament in the present century resulting from the non-degradable along with toxic impact of heavy metals on living systems [1]. From the series of environmental pollutants, the category of heavy metals has been posited to be of severe concern which has been linked to their potential toxic effect and bioaccumulative capability in various water bodies and the ecological surrounding [2-3]. Heavy metals emerging from anthropogenic sources

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Keywords. Risk, sediment, bioavailability, extraction, anthropogenic, fractionation

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that include agricultural runoff, burning of fossil fuels, geochemical activities, industrial along with domestic effluents are regarded as the most dangerous environmental pollutants because of their environmental toxicity, persistence nature and accumulative tendency in both aquatic and terrestrial environment and this results in heavy metal toxicity to plants, animals and humans through water and food chain transport [4-9]. Substantial quantities of fertilizers are often applied to soils in intensive farming operations in order to provide sufficient phosphorus, nitrogen and potassium required for the healthy growth of plant. The chemical compounds employed to make these essential elements available contain trace amount of heavy metals that include Cd and Pb as impurities, which may significantly increase heavy metal concentration in the soil as a consequence of continuous fertilizer application [10-11].

Certain heavy metals that include Zn, Cu, Mn and Fe are needed in trace amounts for plants but higher concentration of these metals in the ecosystem may lead to an excessive accumulation of these metals, which may be toxic to plants and cause possible health problems to animals and humans. Heavy metal contaminated soils could lead to human health hazard and also limit the area available for agriculture activities [12-13]. Heavy metals are identified as problematic pollutants of the environment, with well-known toxic effects on living organisms. Nevertheless, because of certain desirable chemical and physical properties, heavy metals which include cadmium, lead and mercury are intentionally incorporated into certain consumer and industrial commodities for instance batteries, circuit boards, switches, and certain pigments. Sometimes during the normal life cycle of product, there is a partial release of heavy metals into the ecological environment. In other cases, heavy metals may be contained during product life cycle, however poor management or discarded products may lead to significant release of heavy metals into the environmental system [14].

The bioavailability of metal to plants is majorly controlled by the concentration of heavy metal in the soil. Previous studies showed that the use of wastewater contaminated with heavy metals for irrigation over long period of time increases the heavy metal contents of soils above the permissible limit [15-16]. This eventually increases heavy metal concentration in soil and the plant's uptake of heavy metals; however, this depends on factors such as plant growth stages, plant species and the type of soil. Heavy metals exert adverse effect on soil ecology, quality of agricultural production, surface, and ground water quality, this will eventually cause harm to the health status of living organism via the food chain and water column. These undesirable effects are linked with the biological availability of heavy metals, which is controlled by the speciation of metal ions in the soil. The concentration of free metal ion does not solely depend on the total concentration of metals but also on the species of metal which determines the activity and impact of trace metals in aquatic systems [15-17].

A crucial aspect of heavy metals in aquatic system is the ability of metals to bind with both suspended and dissolved components. The metals display significant affinity and capacity to bind to organic compounds which have their origin linked to natural process that include vegetative decay or organic discharge from industrial and municipal sources. This organic species-metal association alters the reactivity of metals in the aquatic ecological system [18]. Heavy metals are ecologically important to be investigated, due to aggregation behavior and their toxicity, which results in the reduction of biodiversity in marine ecosystem. Previous research on the coastline of Nigeria focused on satellite-based mitigation and adaptation scenarios for sea level rise in Niger Delta, coastal erosion in addition to the environmental devastation, economic poverty, and constant conflict in the studied area [19-22]. This research work is aimed at investigating the eco-toxicological assessment of heavy metals as an outcome of the anthropogenic activities in the coastline of Nigeria.

2. MATERIALS AND METHODS

2.1. The study area

The coastline of Nigeria is a crude oil producing area which is made up of four major coastal areas (Barrier Lagoon coast, Mahin Mud coast, Niger Delta and Strand coast). The Nigerian coastline consists of a narrow strip of land bordered by the Gulf of Guinea of the central eastern Atlantic Ocean. Nigeria coastal area is characterized by a tropical climate with relative humidity higher than 60% throughout the year, it also consists of rainy season (April to October) and dry season (November to March). The map of the study area is depicted in Figure 1.

2.2. Sampling and analytical method

Sediment samples from locations exposed to anthropogenic activities were collected from each of the coastal zone within six sampling sites by using a soil auger and stored in a polythene bag. A total of 3 subsurface sediment samples were collected from each of the sampling sites, these sediment samples were air dried for 2 weeks and pulverized using laboratory mortar and pestle, then the sediment samples were sieved using a 2mm mesh size.

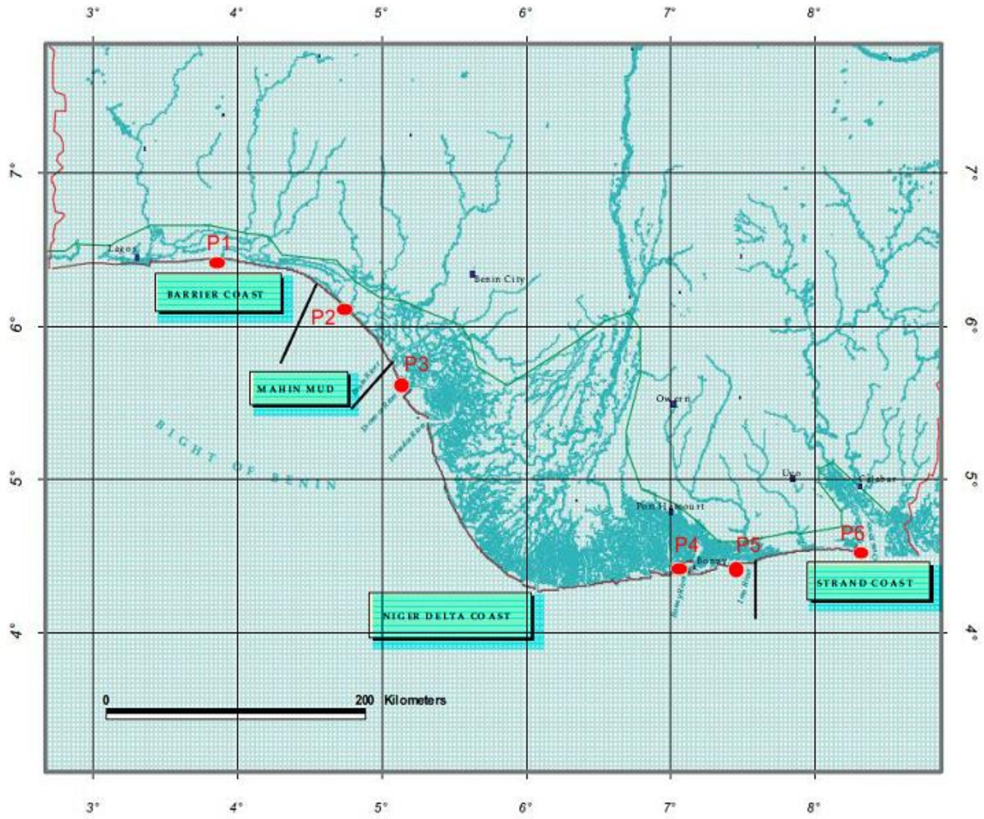

FIGURE 1. Map of the Nigerian coastline showing the sampling locations.

2.2.1. Total concentration of heavy metals

The total concentration of heavy metals was determined by digesting 1g of the sediment samples with a combination of 5ml conc. Nitric acid (HNO_3, 65% w/w), 10ml of hydrofluoric acid (HF, 40% w/w) and 10ml of perchloric acid ($HClO_4$, 70% w/w).

2.2.2. Extraction and fractionation of heavy metals

The sequential extraction procedure proposed by Tessier *et al.* (1979) was used for the chemical fractionation analysis of heavy metals in the sediment samples collected from the sampling sites [4, 23].

Fraction 1 (Exchangeable fraction): The sediment samples was extracted with 8 ml 1 M $MgCl_2$ for 1 h at room temperature with continuous agitation using a centrifuge (Uniscope laboratory centrifuge model SM112).

Fraction 2 (Carbonate fractions): The residues obtained from fraction 1 (F_1) was leached for 5 h with 8 ml 1 M sodium acetate regulated to pH 5.0 with acetic acid, at ambient temperature and with nonstop agitation using a centrifuge (Uniscope laboratory centrifuge model SM112).

Fraction 3 (reducible fraction): The residues collected from fraction 2 (F_2) was extracted using 20 ml of 0.04 M hydroxylamine hydrochloride in 25% acetic acid for 5 h in boiling water bath shaker (BBI-OSCAR WBS11 Model) and with periodic agitation.

Fraction 4 (oxidizable fraction): The residue obtained from fraction 3 (F_3) was extracted with 3 ml 0.02M HNO_3 and 8 ml 30% H_2O_2 regulated to pH 2.0 with HNO_3 for 5 h at 85 ^{0}C with sporadic agitation and then at ambient temperature with 5 ml 3.2 M ammonium acetate in 20% HNO_3.

Fraction 5 (Residual fraction): the residue from fraction 4 (F_4) was oven dried at 105 ^{0}C. Digestion was carried out with a mixture of 5ml conc. HNO_3 (HNO_3, 65 % w/w), 10ml of hydrofluoric acid (HF, 40% w/w) and 10ml of perchloric acid ($HClO_4$, 70 % w/w).

After each extraction step, the sample was subjected to centrifugation at 4,000 rpm and the supernatants were decanted from the residue to ensure selective dissolution and to prevent possible interface mixing between the extractants. The extracts and digestate from the sediment samples were quantified for heavy metals using atomic absorption spectrometer (AAS, Perkin Elmer Model-A Analyst 200 Model). The chemicals including sodium acetate (99.0%), hydroxylamine hydrochloride (99.0%), ammonium acetate (98.0%), sodium hydroxide (99.0%), acetic acid (98.0%) were purchased from Merck, Germany, while magnesium chloride (98.0%), hydrogen peroxide (30%), Nitric acid (65%), hydrofluoric acid (40%) and perchloric acid (70%) were purchased from Sigma-Aldrich, U.S.A. These chemicals were used for the analysis of heavy metals in the sediment samples and blanks were also used for the correction of background and other source of error.

2.2.3. Eco-toxicological assessment

Eight (8) risk assessment indices, fractionation study and comparative analysis of the total concentration of the analyzed heavy metal with USEPA maximum permissible limit, TEL (threshold effects level) and PEL (probable effects level), which were proved to be effective sediment quality guidelines (SQGs) were carried out in order to access the contamination levels of heavy metals in the sediment samples. For the purpose of effective comparison with the background values of the analyzed heavy metals in this research, the average shale concentration of heavy metals given by Turekian and Wedepohl was adopted [24- 25].

2.2.3.1. Fractionation study

The experimental data obtained from the speciation and fractionation study was used in assessing the eco-toxicological impact of heavy metals in the study area. Moreover, the mobility and bioavailability of the analyzed heavy metals was calculated from the chemical fractionation data in the easily leached fractions of F_1 and F_2 (the acid soluble portion) using the formula given below.

$$\frac{F1+F2}{F1+F2+F3+F4+F5} \text{ x } 100\% \qquad (2.1)$$

where F = fraction

This is because unlike the other fractions, the F_1 and F_2 are the respective fractions of heavy metals in ionic form that can be easily drained by water and the easily extractable form that can be accumulated by plants. Moreover, F_1 and F_2 also regarded as the acid soluble portion does not require extreme conditions such as strong reduction and oxidation reactions in order to release heavy metals into the environment to become harmful to the ecosystem.

2.2.3.2. Risk assessment code (RAC)

The total concentration of heavy metals in soil and sediment matrixes is inadequate to provide information on the toxicity of heavy metals in the environment because the mobility and bioavailability which is a function of the toxicity of heavy metals depends on the chemical speciation of heavy metals. RAC determines the availability of heavy metals in sediments by applying a scale to the percentage of heavy metals in the exchangeable and carbonate fractions [26]. RAC is expressed as:

$$\mathrm{RAC} = \mathrm{Exc}\% + \mathrm{Carb}\% \tag{2.2}$$

Exc% and Carb% are percentages of metals in exchangeable and carbonate fractions respectively (i.e., acid soluble fractions in the present study). According to RAC values, each sample falls into one of the five categories: (i) $\mathrm{RAC} \leq 1\%$ (no risk); (ii) $1\% < \mathrm{RAC} \leq 10\%$ (low risk); (iii) $10\% < \mathrm{RAC} \leq 30\%$ (medium risk); (iv) $30\% < \mathrm{RAC} \leq 50\%$ (high risk); (v) $50\% \leq \mathrm{RAC}$ (very high risk).

2.2.3.3. Contamination factor (CF), contamination degree (CD) and pollution load index (PLI)

The contamination level of a particular toxic substance can be illustrated by using the contamination factor (CF). The pollution load index (PLI) and contamination degree (CD) depend on the values obtained from the contamination factor. The PLI and CD complement each other; therefore, they could be used individually or in combination as an effective analytical instrument for accessing the environmental geochemistry of soil and sediment samples. Moreover, they can be used to convey vital information on the pollution levels and the remediation need for the environment. High PLI and CD indicate anthropogenic effect on the ecological environment while low PLI and CD indicate no considerable anthropogenic effect on the ecological surrounding [27]. The Pollution Load Index (PLI) of heavy metals in the sediment can be mathematical calculated by obtaining the n^{th} root from the n number of the obtained contamination factors (CF) of the heavy metals. The mathematical expression of CF, CD and PLI can be written as follows:

$$\mathrm{CF} = {}^{Co}/_{Cb} \tag{2.3}$$

where C_o = concentration of metal in sediment, C_b = background concentration of metal

$$\mathrm{CD} = \sum_{i=1}^{n} CF \tag{2.4}$$

where n= number of heavy metals.

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF1\ x\ CF2\ x \ldots\ldots x\ CFn}} \tag{2.5}$$

CF <1 (low CF), $1 \leq$ CF < 3 (moderate CF), $3 \leq$ CF < 6 (considerable CF), CF $\geq$ 6 (very high CF), while CD < 6 (low CD), $6 \leq$ CD < 12 (moderate CD), $12 \leq$ CD < 24 (considerable CF), CD $\geq$ 24 (very high CD indicating alarming anthropogenic contamination).

The world average shale value was employed to represent the average background value of the analyzed heavy metals. PLI is an indicative summary of the toxicity extent of heavy metals in the environment, because it indicates the number of times the concentration of heavy metals in the sediment surpasses the natural background concentration of the analyzed heavy metal [24, 28 - 29].

TABLE 1. Categorization of PLI.

Pollution load index (PLI) value	Soil pollution level
8-10	Extremely polluted
6-8	Strongly polluted
4-6	Significantly polluted
2-4	Moderately polluted
0-2	Unpolluted to slightly polluted

2.2.3.4. Ecological risk index (RI)

Potential ecological risk index postulated by Hakanson from a sedimentology perspective is used to access the characteristic and environmental behaviour (toxicology) of heavy metal contaminants in soil as well as sediment matrixes [30]. The potential risk index approach gives a relationship between the heavy metal concentration in the sample and the average background value of the analyzed heavy metals. Ecological risk index comprises a single contamination coefficient system, as well as a comprehensive contamination measurement, in addition to the toxic response factor for heavy metals, and the potential ecological risk index [30-31]. The mathematical expression of Risk Index can be shown as:

$$E_i = T_i \text{ x } \frac{Ci}{Co} \tag{2.6}$$

$$RI = \sum_{i=1}^{n} (Ti \; x \; Ci/Co) \tag{2.7}$$

where, n is the number of heavy metals, RI is the risk index, T_i is the toxic response factor for a given substance (e.g., Cd = 30, Cr = 2, As= 10, Cu = Pb = Ni = 5, Hg= 40, Zn = 1), C_i indicates metal concentration in soil and C_0 is the regional background value of heavy metals. By reason of the unavailability of the regional background values of measured heavy metals, the concentration of metals for the world shale average were selected as the average background value [26, 32-33].

TABLE 2. Categorization of ecological risk index.

E_i	Ecological risk for single metal	RI	Ecological risk for all metals
$E \leq 40$	Low (slightly)	$RI < 150$	Low (slightly)
$40 \leq E_i < 80$	Moderately	$150 \leq RI < 300$	Moderately
$80 \leq E_i < 160$	Strongly	$300 \leq RI < 600$	Strongly
$160 \leq E_i < 320$	Very strongly	$600 \leq RI$	Very strongly
$320 \leq E_i$	Extremely		

2.2.3.5. Geoaccumulation index (I_{geo})

The geoaccumulation Index (I_{geo}) is a widely used empirical relationship for evaluating the degree of metal contamination or pollution in soil or sediment of terrestrial or aquatic environments [34-35]. The geoaccumulation index can be mathematically expressed as follows:

$$I_{\text{geo}} = \log_2\left(\frac{Cn}{1.5Bn}\right) \quad (2.8)$$

where C_n is the measured concentration of heavy metal (n) in sediment, Bn is the geochemical background value of heavy metal (n), and 1.5 is the background matrix correction factor as a consequence of lithogenic effects. In this study, B_n was selected from the world shale average of heavy metals [26, 32-33].

TABLE 3. Categorization of geoaccumulation index (I_{geo}).

Geoaccumulation index (I_{geo}) value	Classification	Ecological pollution level
< 0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to extremely polluted
> 5	6	Extremely polluted

2.2.3.6. Enrichment factor (EF)

The enrichment factor (EF) is an analytical measure of geochemical trends of heavy metals; it is a useful contamination index in determining the degree of anthropogenic heavy metal pollution. The enrichment factor of heavy metals in soil and sediment matrixes helps to understand whether certain heavy metals were present in high concentrations relative to the concentrations in the earth's crust using the equation from Sposito *et al.* (1982) [36-39]. In this study, iron was considered as a reference element for geochemical normalization, the background value was selected from the world shale average of heavy metals [26, 32-33]. The EF for each of the heavy metals was calculated in order to evaluate the anthropogenic influence on heavy metals in the sediment using the formula:

$$EF = \frac{\left[\frac{Cx}{CFe}\right] sample}{\left[\frac{Cx}{CFe}\right] background} \tag{2.9}$$

where C_X = Concentration of heavy metals, C_{FE} = Concentration of iron.

TABLE 4. Categorization of enrichment factor (EF).

Enrichment factor (EF) value	EF Class	Enrichment level
< 0.5	0	Enrichment from point and non-point source
0.5 – 1.5	1	Enrichment entirely from crustal materials
1.5 – 2	2	Minimal enrichment
2 -5	3	Moderately enrichment
5- 20	4	Significant enrichment
20 – 40	5	Very high enrichment
> 40	6	Extremely high enrichment

2.2.3.7. Pollution index (PI)

In this research, PI was employed to determine the extent of pollution of the analyzed heavy metals in the research area by comparing the concentration of heavy metals in the sediment samples to the regulatory (maximum permissible) limit. When PI is greater than one (PI > 1), it indicates that the soil or plant is contaminated by the metal, when PI = 1, it indicates a critical state and when PI < 1, there is no pollution [40-42]. PI can be mathematically expressed as:

$$PI = C_{sediment/plant}/C_{usepa\text{-}standard} \tag{2.10}$$

where PI is the individual pollution index of studied metal; $C_{sediment}$ is the concentration of metal in sediment; $C_{usepa\text{-}standard}$ is the maximum permissible limit by USEPA. The overall pollution indices in the sediment can be written as:

$$PI_{sediment} = \sqrt{\frac{(PIave)2 +((PImax)2}{2}}(2.11)$$

where $PI_{sediment}$ is the Pollution Index of the soil or sediment, PI_{ave} is the average Pollution indices while PI_{max} is the maximum PI recorded. $PI_{sediment}$ is the overall soil pollution status [43-44].

2.2.3.8. Sediment quality guidelines (SQGs)

Threshold effects level (TEL) can be defined as the concentration below which adverse biological effects rarely occur, while Probable effects level (PEL) can be defined as the concentration beyond which adverse biological effects frequently occur. It has been posited that heavy metals occur in soil and sediments, based on this fact the mean PEL quotient method has been constructively utilized to determine the possibility for biological effect from combined toxic groups by calculation of the mean quotients for a broad range of contaminants employing the formula [37, 45].

$$\text{Mean PEL quotient} = \sum (Cx/PELx)/n(2.12)$$

where C_x is the concentration of component x in sediment, PEL_x is the PEL for the compound x and n represent the sum of components. Premised on the analysis of matching chemical and toxicity data from over 1000 sediment samples from the USA estuaries, the mean PEL quotients of 0.1 have an 8% probability of being toxic, the mean PEL quotients of 0.11–1.5 have a 21% probability of being toxic, the mean PEL quotients of 1.51–2.3 have a 49% probability of being toxic, and the mean PEL quotients of 2.3 have a 73% probability of being toxic [37, 46].

2.3. Statistical analysis

Statistical analyses were conducted by employing Microsoft Excel and SPSS 20.0 statistical software on a personal computer, and the results included maximum, minimum, mean and correlation values.

3. RESULTS AND DISCUSSION

3.1. Risk assessment premised on the levels of heavy metals in the sediments

A significant scientific report on the analyzed heavy metals can be posited from Table 5, the results obtained from the total heavy metal concentration in the sediment samples showed that the concentration of the analyzed heavy metals was below the maximum permissible limit (MPL) of USEPA. This is an indication that the aquatic environment is not polluted with the analyzed heavy metals, this result agreed with the report on comparison of levels of heavy metals in water and sediment from Challawa George Dam, Nigeria [47]. The correlation matrix for the analyzed heavy metals has shown in Table 6 revealed that there is a strong positive correlation between the analyzed heavy metals while Cr exhibited the strongest correlation with Ni (1.000). The analyzed heavy metals are strongly correlated and are significant at probability level of 0.01. This pointed out that the sources of the analyzed heavy metals are probably of a common origin and this result is in agreement with the report on the assessment of heavy metal pollution on marine sediments [37].

TABLE 5. Total concentration (mg/kg) of heavy metals in sediment samples.

Metals/Sites	Cd	Cu	Ni	Pb	Cr	Fe
Site 1	0.79 ±0.01	2.19 ±0.01	2.39 ±0.01	2.52 ±0.02	5.61 ±0.03	25.42 ±0.03
Site 2	0.41 ±0.01	3.05 ±0.02	3.03 ±0.01	3.01 ±0.02	4.88 ±0.01	21.27 ±0.03
Site 3	0.76 ±0.02	2.15 ±0.01	2.44 ±0.02	2.96 ±0.01	5.59 ±0.03	26.07 ±0.01
Site 4	0.43 ±0.01	2.17 ±0.01	2.41 ±0.01	2.51 ±0.01	4.89 ±0.02	22.89 ±0.03
Site 5	0.39 ±0.01	3.08 ±0.01	3.07 ±0.01	2.95 ±0.01	5.63 ±0.01	19.65 ±0.03
Site 6	0.75 ±0.03	3.07 ±0.02	3.05 ±0.02	2.50 ±0.02	4.91 ±0.01	25.07 ±0.02
MPL	3	50	50	300	400	NL

MPL = Maximum permissible unit (USEPA) [48]. NL = No limit

TABLE 6. Pearson correlation matrix for heavy metal concentrations (mg/kg) in sediment samples.

	Cd	Cu	Ni	Pb	Cr
Cd	1	0.998*	0.993**	0.988**	0.995**
Cu		1	0.997**	0.994**	0.999**
Ni			1	0.994**	1.000**
Pb				1	0.994**
Cr					1

**. Correlation is significant at the 0.01 level (2-tailed).

3.2. Risk assessment on the basis of sediment quality guidelines (SQGs)

The concentration of the analyzed heavy metals was mathematically compared with the PEL, and TEL guidelines and the result is revealed in Table 7. It was observed that the concentration of the analyzed heavy metals from the sampling sites fell below the PEL. Similarly, the concentration of the analyzed heavy metals fell below the TEL, except Cd which exceeded the value of TEL by 50%, as a consequence of the level of Cd concentration recorded as 0.79, 0.76 and 0.75 mg/kg as shown in Table 5 which exceeded the TEL guideline of 0.68 in Table 7. The mean PEL quotient (m-PEL-Q) of the analyzed heavy metals was calculated to have a value of zero (0), which is less than 0.1; this means that the combination of the analyzed heavy metals has 8% probability of being toxic to the aquatic environment. This result is in coherent with the values obtained for the total concentration of the analyzed heavy metals which fell below the maximum permissible limit of USEPA.

TABLE 7. Comparative analysis of the SQGs with mean values of heavy metal concentration (mg/kg) in sediment samples.

Index/metals	Cd	Cu	Ni	Pb	Cr
TEL guideline	0.68	18.70	15.90	30.20	52.30
PEL guideline	4.20	108	42.80	112	160
Average levels of heavy metals in the study area	0.59	2.62	2.73	2.74	5.25
% samples which exceeded TEL	50	0	0	0	0
% samples which exceeded PEL	0	0	0	0	0

Threshold effect level (TEL) and Probable effect level (PEL) guidelines [49].

3.3. Risk assessment premised on chemical fractionation of heavy metals

The results of the chemical fractionation of heavy metals in sediment samples collected from Nigerian coastline have been presented in the Table 8.

TABLE 8. Mean of heavy metals concentrations (mg/kg) in fractions in sediment samples.

Fraction/heavy metals	Cd		Cu		Ni		Pb		Cr	
	Max	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*
F1	0.02	0.01	0.05	0.03	0.26	0.14	0.23	0.17	0.73	0.69
F2	0.14	0.06	0.16	0.09	0.27	0.21	0.27	0.21	0.84	0.64
F3	0.19	0.12	0.08	0.02	0.31	0.26	0.53	0.46	0.96	0.72
F4	0.18	0.07	1.26	0.97	0.42	0.37	0.64	0.52	1.22	1.13
F5	0.23	0.15	1.52	1.06	1.79	1.43	1.28	1.15	1.86	1.71

F= fraction

The speciation and fractionation study as depicted in Figure 2 revealed that the analyzed heavy metals in sediment samples were all detected in the five fractions of the sequential extraction procedure by Tessier *et al.* (1979) [23]. The relative partitioning of Cd in the sediment samples revealed that a significant concentration of Cd was observed in the residual (32%), reducible (27%) and oxidizable (21%) fractions. However, a lower concentration was observed in the carbonate fraction, while the least concentration of Cd was observed in the exchangeable fraction. This result showed that Cd in the sediment samples is associated with the non-bioavailable fractions; this result is in agreement with the report on chemical fractionations and bioavailability of Cd to Cole grown in multi-metals contaminated soil [50].

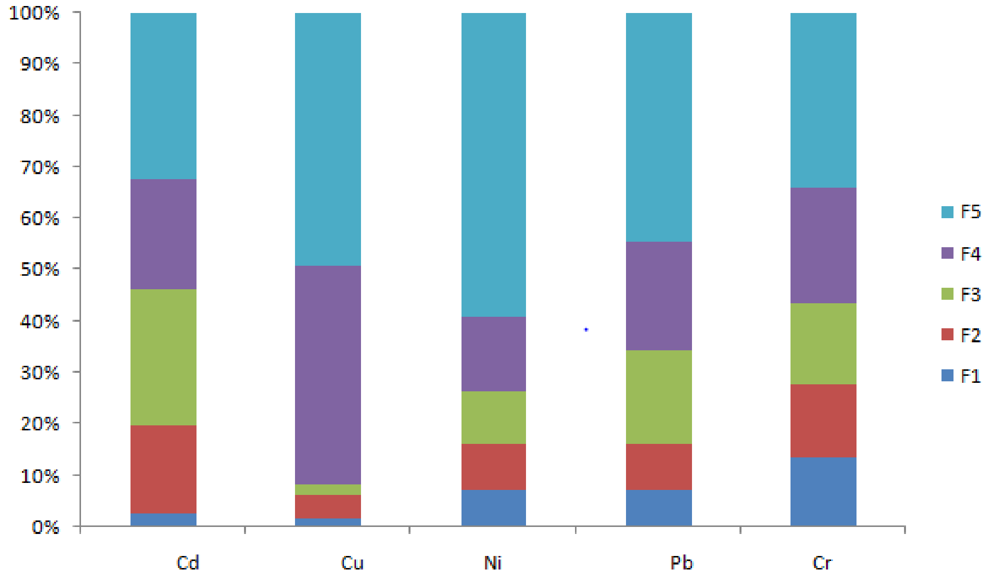

FIGURE 2. Relative partitioning of heavy metals in sediment samples (F=fraction).

The relative partitioning of Cu in the sediment samples showed that the maximum concentration of Cu was reported in the residual fraction, Cu also had a high concentration in the oxidizable fraction. This is probably subsequent to the association of Cu with organic matter, while a low concentration of Cu was observed in the exchangeable, carbonate and reducible fractions. This result is in concord with the report on the speciation of heavy metals in sediment [51].

The relative partitioning of Ni revealed the highest concentration (59%) of Ni in the residual fraction; this is probably due to the association of Ni with silicate matrices in soil and sediment. However, a significant concentration of Ni was found in the oxidizable fraction. Conversely, it was observed that a lower concentrations of Ni was detected in the exchangeable, carbonate and reducible fractions. This result is in agreement with the report on metal speciation of the surface sediments of the Vigo Ria [52].

The relative partitioning of Pb revealed the highest concentration of Pb in the residual fraction, a high concentration of Pb was observed in the reducible and oxidizable fractions, while lower concentrations was observed in the exchangeable and carbonate fractions, this result in concord with the report on the speciation of heavy metals in sediments of rivers in different regions in Ondo State, Nigeria [4, 53].

The relative partitioning of Cr in the sediment samples revealed that Cr displayed the highest concentration in the residual fraction (34%), however a lesser concentration was detected in the oxidizable fraction, while the concentrations of Cr was observed in a very close range in the reducible, exchangeable and carbonate fractions with both exchangeable and carbonate fractions displaying 14% concentration individually along with the reducible fraction displaying 16% concentration. This result agreed with the report on speciation and geochemical behaviour of heavy metals [54].

The mobility and bioavailability of the analyzed heavy metals was observed to follow the following order: Cr > Cd > Pb > Ni > Cu. This result indicated that Cu is the least mobile and bioavailable metal among the analyzed heavy metals in the sediment samples.

3.4. Risk assessment according to risk indices

The maximum and minimum values for the risk assessment of the analyzed heavy metals in the sediment samples collected from Nigerian coastline is depicted in Table 9. From the result obtained in Table 9, the calculated RAC values for the analyzed heavy metals are at a medium risk category to the environment, except Cu which occurred at a low-risk category to the environment. The total concentration of the analyzed heavy metals in the sediment is reportedly lower than the USEPA maximum permissible limit. Nevertheless, the acid soluble portion (exchangeable and carbonate fractions) of the sediment samples is relatively high for the analyzed heavy metals except for Cu. However, according to speciation studies using the exchangeable and carbonate fractions as an indicator for metal mobility and bioavailability in the environment, Cu is less likely to be leached into the aquatic environment because it has the least RAC value. This result is in concord with the report on ecological risk assessment of the heavy metals in sediment of Xiawan port [55].

The result of the ecological risk index of the heavy metals has been presented in Table 9; it was posited that the ecological risk index values were below 40, which indicated that the analyzed heavy metals are at a low ecological risk level to the aquatic environment. Conversely, the ecological risk index for Cd was above 40, thereby indicating a moderate level. This result is in concord with the report on potential ecological risk of heavy metals in sediment from Mediterranean coast, Egypt [25].

The geoaccumulation index (I_{geo}) which shows the quality of sediment in regard to heavy metal distribution and pollution level has been presented in Table 9. it was noted that the analyzed heavy metals fell in the class 0, expect Cd which occurred in class 1, this result confirmed that the aquatic environment is unpolluted with the analyzed heavy metals and this result is in agreement with the report on characteristics of heavy metals and Pb isotopic composition in sediment collected from three Gorges reservoirs in China [56].

The values of the contamination factor (CF) of the analyzed heavy metals as shown in Table 9 was observed to be less than 1 except Cd (1.36 and 1.93). The pollution load index (PLI) of the studied heavy metals was calculated to be less than 2 (occurring between 1.17 and 1.10), thereby pointing out that the aquatic environment is unpolluted with the analyzed heavy metals. Moreover, the contamination degree (CD) of the analyzed heavy metals was calculated to be below 6 (occurring between 2.27 and 1.62), thereby indicating a low contamination degree of the analyzed heavy metals in the aquatic environment.

The pollution index (PI) of heavy metals in the study area was observed to be less than 1, which indicated that there is no pollution in the study area. This result revealed that the study area is not contaminated with the analyzed heavy metals and this result is in concord with the report on distribution, enrichment, and ecological risk assessment of element in bed sediments of a tropical river [27]. The values of the enrichment factor (EF) of the heavy metals in the sediment as shown in Table 9 revealed EF values greater than 40 for all the heavy metals, thereby suggesting an EF Class 6, with a remark of extremely high enrichment of the analyzed heavy metals. This result on the enrichment factor of the analyzed heavy metals in sediments from Nigerian coastline is in concord with scientific reports on the analysis of enrichment factor of heavy metals in aquatic environment from different region of the world [26, 57].

TABLE 9. Pollution indices for the analyzed heavy metals in the sediment samples.

Pollution index/ heavy metals		RAC (%)	RI	I_{geo}	CF	EF	PI
Cd	*Max*	28.25	57	0.05	1.93	3461.11	0.20
	Min	17.07	41	0.02	1.36	3036.33	
Cu	*Max*	6.84	0.34	-0.67	0.07	125	0.05
	Min	5.53	0.22	-0.73	0.05	106.99	
Ni	*Max*	17.38	0.24	-0.76	0.06	82.95	0.06
	Min	14.52	0.20	-0.79	0.03	78.65	
Pb	*Max*	16.95	0.74	-0.48	0.15	272.82	0.01
	Min	15.4	0.65	-0.54	0.13	278.48	
Cr	*Max*	27.99	0.13	-0.69	0.06	115.27	0.01
	Min	27.20	0.25	-0.73	0.05	120.57	

RAC = Risk assessment code, RI = Risk index, I_{geo} = Geoaccumulation index, CF = Contamination Factor, EF = Enrichment factor, Max= maximum, Min= minimum, PI = Pollution index.

The values of PI (Cd = 0.20, Cu = 0.05, Ni = 0.06, Cr = 0.01, Pb = 0.01) and $PI_{sediment}$ (0.15) of the analyzed heavy metals were found to be less than 1 as reported in Table 9, this indicated that the sediment is not polluted with the analyzed heavy metals.

4. CONCLUSION

This study investigated the geochemical fractionation and risk assessment of heavy metals in sediments collected from 6 sampling sites in the Nigerian coastline, the observations of the results obtained from the elemental analysis on the basis of pollution indices, geochemical fractionation, total concentration of heavy metals and sediment quality guidelines can be summarized as stated below:

1. Risk assessment based on the total concentration of heavy metals in the sediments revealed that the total concentration of the analyzed heavy metals fell below the maximum permissible limit

of USEPA, which indicated that the sediment collected from the study area is not polluted with the analyzed heavy metals. Also, it was observed that there is a strong correlation between the analyzed heavy metals thereby suggesting a common source of origin.

2. Risk assessment on the basis of speciation and chemical fractionation study of the investigated heavy metals revealed that the analyzed heavy metals were detected in the five (5) fractions of chemical speciation study. It also reveals that Ni had the maximum concentration in the residual fraction, while Cu had a high concentration in both the residual and oxidizable fractions but the least concentration in the exchangeable fraction, thereby pointing out that Ni and Cu do not pose a high risk to the aquatic environment in the investigated area. The chemical speciation of the heavy metals suggested the order of mobility and bioavailability of the analyzed heavy metals in the following order: Cr > Cd > Pb > Ni > Cu.
3. Risk assessment on the basis of risk assessment indices is stated as follows:
   (a) According to RAC, the analyzed heavy metals fell in the category of medium risk except Cu which fell in the category of low risk, thereby suggesting that Cu has the least probability of posing risk to the environment due to its low percentages in both exchangeable and carbonate fractions.
   (b) As a result of the ecological risk index, the investigated heavy metals are at a low risk to the environment because the risk index values of the investigated heavy metals are less than 40.
   (c) According to geoaccumulation index, the study area is unpolluted with the investigated heavy metals except Cd which fell in the category of unpolluted to moderately polluted, thereby suggesting that Cd has the highest probability of posing risk to the environment.
   (d) According to contamination factor, the analyzed heavy metals had a low contamination factor, except Cd which had a moderately contamination factor, suggesting that Cd has a higher probability of posing risk to the environment. Also, the contamination degree and pollution load index showed a similar result as the contamination factor. Thereby, indicating

that the study area is unpolluted with a low contamination degree.

(e) According to enrichment factor, the analyzed heavy metals fell in EF class 6, thereby suggesting that there is an extremely high enrichment of the analyzed heavy metals in the study area.

(f) According to pollution index, the values of the individual and overall pollution index were observed to be less than one, thereby suggesting that the sediment is not polluted with the analyzed heavy metals.

4. Risk assessment on the premise of sediment quality guidelines (SQGs) revealed that there is a low possibility for an adverse biological effect in the study area as a result of the analyzed heavy metals because the analyzed heavy metals fell below probable effect level (PEL). The eco-toxicological index expressed as the mean quotients (m-PEL-Q) suggested that the combination of Cd, Cr, Pb, Ni and Cu showed only 8% probability of being toxic due to the combination of the analyzed heavy metals.

List of abbreviation

PELProbable effect level
TELThreshold effect level
SQGsSediment quality guidelines
m-PEL-QMean quotient probable effect level
EFEnrichment factor
I*geo*Geoaccumulation index
RIRisk index
RACRisk assessment code
FFraction
MPLMaximum permissible limit
USEPAUnited state environmental protection agency
PIPollution index
CDContamination degree
CFContamination factor
PLIPollution load index
MaxMaximum
MinMinimum

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