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Research Article

Trace Metal Contamination Characteristics and Health Risks Assessment of *Commelina africana* L. and Psammitic Sandflats in the Niger Delta, Nigeria

Nsikak U. Benson,[1] Paul A. Enyong,[2] and Omowunmi H. Fred-Ahmadu[1]

[1] *Analytical and Environmental Chemistry Unit, Department of Chemistry, Covenant University, Km 10 Idiroko Road, Ota, Nigeria*
[2] *Department of Chemistry, University of Uyo, Uyo, Nigeria*

Correspondence should be addressed to Nsikak U. Benson; nbenson@covenantuniversity.edu.ng

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The purpose of this study was to investigate and quantify trace metal concentrations in *Commelina africana* L. and psammitic sandflats from an intertidal coastal ecosystem in Niger Delta, Nigeria, and to evaluate their spatial distribution, degree of contamination, and source apportionment. The environmental risks associated with soil contamination were elaborately assessed using potential ecological risk index, sediment quality guidelines, and enrichment relative to background levels. The mean concentrations of Cd, Cr, Ni, Pb, and Zn in sandflat soil samples are $0.76 \pm 9.0 \times 10^{-2}$, $7.39 \pm 8.7 \times 10^{-1}$, 2.28 ± 0.35, $0.024 \pm 4.0 \times 10^{-3}$, and 74.51 ± 2.55 mg/kg, respectively. Metal levels indicate strong variability with sampling sites. The order of trace metal concentrations in the *Commelina africana* L. samples is Zn > Ni > Cr > Pb > Cd. The concentrations varied with the sample locations; and the levels of Pb (0.05 to 0.08 mg/kg) at all locations are found to be significantly below permissible level of 0.3 mg/kg. Potential sources of metal loadings may be associated with localised or diffused anthropogenic activities. The average carcinogenic risks are below 1.0×10^{-6} threshold values, and the sandflat soils are not considered to pose significant health effects to children and adult males and females. However, the carcinogenicity and noncarcinogenicity risks ranking decrease following the order children > adult males > adult females. Comparatively, the hazard quotient and hazard index indicate that the psammitic sandflats might pose a health risk to children in future.

1. Introduction

Pollution investigations in coastal ecosystems of Niger Delta have revealed that human mediated activities can adversely alter the ecological integrity of fragile aquatic systems in the region, resulting in bioaccumulation of chemical contaminants by zoobenthos [1–4], sediment enrichment [5], and impact on species abundance and biomass [6, 7]. Most equatorial wetlands and ultisol systems in the Niger Delta serve as primary recipients of petroleum exploration-exploitation wastes and domestic and industrial wastes generated by multinational oil companies that are found in the region. Studies have indicated enhanced levels of trace metals in soil, surface water, sediments, and biota from aquatic ecosystems in the area [8–11]. In the wetlands and soil environment, trace metals are naturally ubiquitous [12, 13]. Although some trace metals are present as natural nutrient components of the soil environment, introduced through weathering processes, most, however, originate from a variety of human mediated activities [14–18]. In the Niger Delta, crude oil pollution and petrochemical activities have been identified as major anthropogenic activities that significantly promote the introduction of trace metals into both the terrestrial and aquatic environments [5, 19, 20].

Wetland soils act as both sinks and carriers for trace metals and could provide valuable information on the pollution pattern and history of such ecosystems [21, 22]. Trace metals present in the soil are capable of undergoing chemical transformation from solids to ionic species or through biomethylation into organometallic moieties [23]. Also, they

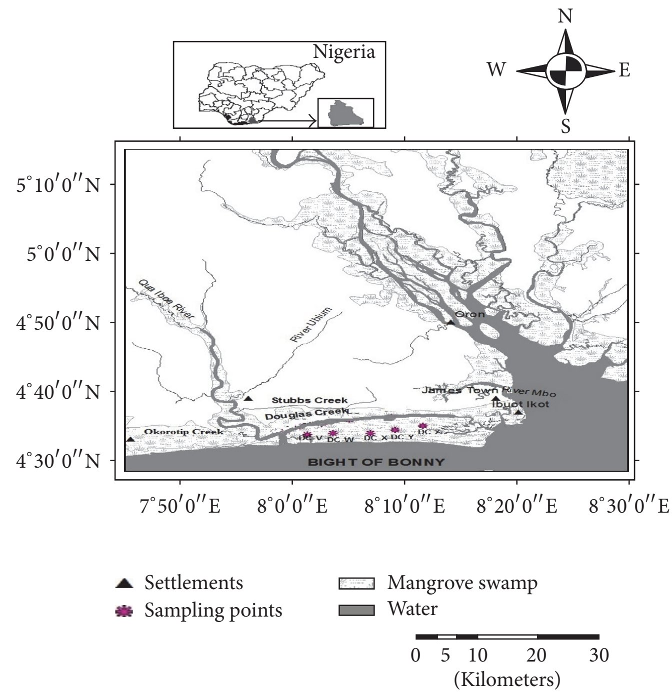

Figure 1: Qua Iboe Estuary mangrove ecosystem showing the sampling location along Douglas Creek. Insert: map of Nigeria showing the location of the study area.

could be released in both particulate and dissolved forms and are known to have high affinities for fine-grained sediment and soil particulates [24–27]. However, the fate, transport, and pollution characteristics of trace metals in the wetland soils have become an important problem due to their toxic effects, accumulation, and bioconcentration through the food chain [28, 29].

Trace metals introduced into the environment are capable of having toxicological implications on terrestrial invertebrates, humans, and the natural environment [30–32]. Adverse health effects, such as lung and skin cancer, prostatic proliferative lesions, peripheral neuropathy, kidney dysfunction, dermal lesions, and peripheral vascular disease, have been attributed to trace metals pollution. However, metal toxicity mainly depends on the metal speciation and bioavailability, as well as on the means of uptake, accumulation, and excretion rates of the organisms [24, 28, 33–35]. Therefore, elucidating the potential sources, ionic forms, ecosystem variability, pollution status, and environmental risks, assessment of trace metals in wetland soil environment is a critical tool in understanding the contamination characteristics of such ecosystems. It also provides expository information for environmental pollution prevention and control.

The present study was initiated with the following objectives: (a) to determine the levels of trace metals accumulation and distribution in coastal sandflats, flora, and fauna from an estuarine ecosystem, (b) to evaluate potential ecological risks from metal pollution using different indices such as metal pollution index (MPI) and transfer factors (TFs); (c) to assess the degree of trace metal pollution using contamination indices such as pollution load index (PLI), contamination factor (Cf), modified contamination degree (mCD), and geoaccumulation index (I_{geo}); (d) to evaluate the coastal soil quality and environmental risks of investigated trace metals by comparison with soil quality guidelines (SQGs); (e) to identify the possible sources of trace metal pollution and to assess their ecotoxicological significance; and (f) to assess potential noncarcinogenic and carcinogenic risks due to inhalation, dermal contact, and oral ingestion exposure pathways.

2. Materials and Methods

2.1. Study Area. The Douglas Creek is a major tributary of Qua Iboe Estuary (Figure 1). The estuary is characterized by shallow intertidal mudflats that are surrounded by mangroves and is perennially subjected to sediment deposition from Qua Iboe River and marine sand from the Atlantic Ocean. It is located close to several coastline settlements within an oil producing area in Southeastern Nigeria. The Qua Iboe Estuary and Douglas Creek lie within latitude 4°30′ to 4°45′N and longitude 7°30′ to 8°00′E. It serves as the receiving water body for residential, agricultural, and petrochemical wastes generated from multinational oil companies located in the oil producing communities. The estuary is characterized by fine sandy beaches fringed with mangrove swamps and tidal mudflats on which Nypa palm vegetation dominates. The study area is characterized by a humid tropical climate with an annual rainfall of about 4021 mm, average humidity of 80%, and mean minimum and maximum temperatures of 22°C and 30°C, respectively. There are two predominant seasons, dry and wet seasons. The wet season begins in March

Table 1: Reference (SRM 8704) concentration values, analytical results, and percentage recovery.

Metals	SRM 8704 reference values (mg/kg)	AAS results (mg/kg) ($n = 3$)	Accuracy (% recovery)
Cadmium	2.94 ± 0.29	3.03 ± 0.04	102.96
Chromium	121.90 ± 3.80	119.47 ± 1.64	98.01
Nickel	42.90 ± 3.70	40.86 ± 0.18	95.23
Lead	150.00 ± 17.00	156.04 ± 6.95	104.23
Zinc	408.00 ± 15.00	398.60 ± 10.54	97.67

or April and is usually characterized by heavy storms of short duration. The dry season, which normally lasts 3–5 months, is comparatively short, beginning in November and extending to February. Tidal currents are strong especially during the wet seasons along estuary upper reaches and creek and this plays an important role in sedimentation, biota distribution, trace metal laden, waste transportation, and industrial and domestic waste transportation.

2.2. Sampling. A total of 30 plant and soil samples were each collected from the study area along a marked transect. Plant and soil samples were collected during two separate trips from five designated grids: DC-V, DC-W, DC-X, DC-Y, and DC-Z mapped out along the stretch of Douglas Creek extending into Qua Iboe Estuary. At each sampling station, triplicates of the plants and soil samples were obtained and carefully transferred into clean polyethylene glass containers. A short core sampler was used to collect the soil from the top 0 to 15 cm of the soil surface and homogenized and the subsamples were stored in labeled black polythene bags. Plant samples were also handpicked along the tidal shores of Douglas Creek and thoroughly cleaned with fresh water to get rid of soil before transferring them into labeled aluminium foil. The samples were all stored in ice-packed coolers and transported to the laboratory. They were further refrigerated in the laboratory at 4°C to inhibit microbial activities and preserve the integrity of the samples prior to analysis.

2.3. Analytical Procedures for Sample Pretreatment and Chemical Analysis. The soil samples were air-dried by exposure to ambient air for 48 hours and manually sorted to remove stones, sticks, organic matter, and shells from the air-dried samples, pulverized using porcelain pestle and mortar, and sieved through a 2 mm mesh and sieved to collect less than 63 μm grain sizes. 2.0 g of each sample was digested with a solution of concentrated HCl (6.0 mL) and HNO_3 (0.3 mL) to near dryness and allowed to cool before 20 mL of 5.0 M HNO_3 solution was added. The digested soil sample solution was allowed to stay for about 12 hours before they were filtered. The filtrates were subsequently transferred into 100 mL volumetric flask and made up to the mark with 0.5 M HNO_3 prior to elemental analysis. A reagent blank was also prepared using a mixture of HCl and HNO_3 following the stepwise analytical procedure described for the sample preparation.

On the other hand, the plant samples were oven dried at 80°C for 24 hours to prevent microbial decomposition, pulverized into fine powder, and stored in well-labeled Ziploc bags. Precisely 1.0 g of each plant sample was accurately weighed into 10 mL conical flask and 1 mL $HClO_4$ and 7 mL of 40% HF were added and digested slowly for 2 hours using a modified method of Vaněk et al. [36]. After digestion, they were allowed to cool and later were heated and the content was evaporated until fumes of $HClO_4$ appeared. The residue was allowed to cool and 1 mL H_2SO_4 added and heated again to drive off $HClO_4$. After cooling, all samples were diluted with a little water and filtered into 25 mL volumetric flasks fitted with a glass funnel and Whatman number 1 filter paper. The filtrates were later made up to 25 mL mark with distilled water. Also blanks were prepared following the above procedure, with all reagents excluding the sample. The solutions were used for the determination of trace metals. Acid eluates desorbed from the filter, and 30 digested soil and plant sample solutions and the reagent blanks were analysed for the concentrations of Zn, Pb, Cd, Ni, and Cr using an atomic absorption spectrometer (S Series S4 AA System, Thermo Electron Corporation). In order to evaluate the precision of each method of digestion for soil and plant samples, the trace metal analyses were run in duplicates.

2.4. Quality Assurance. Buffalo River Sediment Reference Material (SRM 8704), sourced from National Institute of Standards and Technology (US), intended primarily for use in the analysis of sediments, soils, or materials of a similar matrix was analysed with the soil samples for quality assurance purposes. Reference values and the analytical results for the concentrations of five trace metals are given in Table 1. The recoveries of the AAS analytical results for Cd, Cr, Ni, Pb, and Zn ranged between 97.67 and 104.23%. The concentrations of certified materials SRM 8704 indicated results within the range of the reference values. Therefore, the method employed for this work is reliable and reproducible. Blanks were also monitored throughout the analysis of the soil samples and blank subtractions were employed to correct metal concentrations obtained for soil samples.

2.5. Statistical Analysis. The data were analysed using the XLSTAT-Pro software (AddinSoft, Inc., NY, USA). Pearson's correlation analysis and factor analysis were employed to explore the interrelationship among trace metals in soil samples and also attempt to identify their probable origin. The various statistical analyses were performed with a 95% confidence interval (significance $p < 0.05$).

2.6. Pollution Indicators. On the basis of observed data, the relative gradation of contamination levels by trace metals in ultisols can be achieved using pollution indices (PIs) and efficient risks assessment approaches. However, the evaluation of pollution loading status and the estimation of impacts associated with human induced events on coastal wetland soils could be attained through geochemical approaches such as geoaccumulation index and enrichment factor [16, 37].

2.7. Soil Contamination Indices and Potential Ecological Risks. The under listed contamination indices were adopted to evaluate trace metals contamination assessment in soil samples collected from the study area: (i) degree of contamination (CD); (ii) modified contamination degree (mCD); (iii) contamination factor (Cf); (iv) pollution load index (PLI); (v) pollution index (PI) and Nemerow integrated pollution index (NIPI); and (vi) geoaccumulation index (I_{geo}) [37]. The single metal and multimetal potential ecological risk indices were also calculated for Cd, Cr, Ni, Pb, and Zn.

The CD was calculated to assess the holistic impact of multimetals on the environment [22, 38]. The formula developed by Håkanson [39] was used for the calculation of CD:

$$\mathrm{CD} = \sum_{i=1}^{n} \mathrm{Cf}_i, \quad (1)$$

$$\mathrm{Cf}_i = \left[\frac{C^i_{\mathrm{mconc}}}{C^i_{\mathrm{bkg}}} \right], \quad (2)$$

where Cf_i is contamination factor of metal i, C^i_{mconc} is mean concentration, and C^i_{bkg} is background value of individual metal. The degree of contamination is classified into low degree of contamination (CD $\leq$ 6), moderate degree of contamination (6 $<$ CD $\leq$ 12), considerable degree of contamination (12 $<$ CD $\leq$ 24), and very high degree of contamination (CD $>$ 24). The Cf is derived by dividing the concentration of selected trace metal by the background value. The gradation of Cf is as follows: Cf $<$ 1 indicates low degree of contamination; 1 $\leq$ Cf $<$ 3 indicates moderate contamination; 3 $\leq$ Cf $<$ 6 indicates considerable contamination; and Cf $\geq$ 6 shows very high degree of contamination.

The mCD is an empirical assessment of the overall degree of contamination by pollutants in a designated ecosystem and is mathematically expressed as follows:

$$\mathrm{mCD} = \frac{\sum_{i=1}^{n} \mathrm{Cf}_i}{n}, \quad (3)$$

where Cf is contamination factor, n is the number of analysed trace metals, and i is ith metal.

The following classifications and descriptions are available for modified degree of contamination in soil: mCD $<$ 1.5 refers to nil to very low degree of contamination; 1.5 $\leq$ mCD $<$ 2 indicates low degree of contamination; 2 $\leq$ mCD $<$ 4 implies moderate degree of contamination; 4 $\leq$ mCD $<$ 8 indicates high degree of contamination; 8 $\leq$ mCD $<$ 16 means very high degree of contamination; 16 $\leq$ mCD $<$ 32 implies extremely high degree of contamination; and mCD $\geq$ 32 refers to ultrahigh degree of contamination.

PLI was evaluated using Tomlinson's pollution load index (PLI) [40] and is expressed as the nth root of the product of n Cf as

$$\mathrm{PLI} = \left[\mathrm{Cf}_1 \times \mathrm{Cf}_2 \times \cdots \times \mathrm{Cf}_n \right]^{1/n}, \quad (4)$$

where n is the number of metals and Cf_n is the Cf value of metal n. PLI is classified as follows according to the contamination degree: background concentration (PLI = 0), unpolluted (0 $<$ PLI $\leq$ 1), unpolluted to moderately polluted (1 $<$ PLI $\leq$ 2), moderately polluted (2 $<$ PLI $\leq$ 3), moderately to highly polluted (3 $<$ PLI $\leq$ 4), highly polluted (4 $<$ PLI $\leq$ 5), or very highly polluted (PLI $>$ 5) [16, 41].

Additionally, the pollution index (PI) was used to evaluate soil pollution by comparing the metal concentrations obtained in this study with Dutch soil guidelines [42]. According to Lee et al. [37], PI is expressed as

$$\mathrm{PI} = \frac{C_n}{T_n}, \quad (5)$$

where C_n is the concentration of an individual trace metal and T_n is the corresponding target concentration of Dutch soil guidelines, which consider different land-use types and are based on extensive studies of both the human and ecotoxicological effects of soil contaminants [43]. Nemerow integrated pollution index (NIPI) was also employed for the assessment of the overall pollution integrity of the investigated ecosystem [44]. The NIPI was calculated using the following equation:

$$\mathrm{NIPI} = \left[0.5 \times \left(I^2_{\mathrm{mean}} + I^2_{\mathrm{max}} \right) \right]^{1/2}, \quad (6)$$

where I_{mean} is the mean value of all pollution indices of the metals considered and I_{max} is the maximum value. According to Cheng et al. [45], the classification of NIPI is as follows: safe (NIPI $\leq$ 0.7), precaution (0.7 $<$ NIPI $\leq$ 1), slightly polluted (1 $<$ NIPI $\leq$ 2), moderately polluted (2 $<$ NIPI $\leq$ 3), or heavily polluted (NIPI $>$ 3).

The index of geoaccumulation (I_{geo}) is a common approach employed to estimate metals enrichment above background or baseline concentrations in soil or sediment. The I_{geo} values for the studied trace metals were calculated using the following equation developed by Müller [46]:

$$I_{\mathrm{geo}} = \log_2 \left(\frac{C_n}{1.5 B_n} \right), \quad (7)$$

where C_n is the measured concentration of selected metal (n) in the soil sample and B_n is the geochemical background in average shale of metal (n). In this study, the geochemical background soil concentrations of Cd, Cr, Ni, Pb, and Zn were 0.3, 90, 68, 20, and 95 mg/kg, respectively, and were used in calculating the I_{geo} values [47]. The coefficient 1.5 is used to detect variations in the background data due to lithogenic [48, 49] and anthropogenic influences [50]. I_{geo} consists of seven grades. According to Müller [46], I_{geo} consists of 7 classes. The corresponding relationships between I_{geo} and

Table 2: Summary statistics of trace metal concentrations (mg/kg) in sandflats and *Commelina africana* L. from the sandy beaches of Douglas Creek.

Trace metals		Min.	Max.	Mean	Std. deviation	CV%
Soil	Zn	71.43	77.850	74.51	2.553	3.42
	Pb	0.019	0.030	0.024	0.004	16.67
	Cd	0.695	0.900	0.759	0.090	11.84
	Ni	1.750	2.600	2.278	0.346	14.91
	Cr	6.100	8.120	7.392	0.875	11.77
C. africana L.	Zn	225.90	252.2	239.26	11.801	4.93
	Pb	0.050	0.080	0.058	0.013	22.41
	Cd	0.150	0.750	0.304	0.250	82.24
	Ni	10.65	26.750	19.152	7.289	38.07
	Cr	7.879	13.824	9.642	2.383	24.69

the degree of metal pollution level are as follows: unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately polluted ($1 < I_{geo} \leq 2$), moderately to heavily polluted ($2 < I_{geo} \leq 3$), heavily polluted ($3 < I_{geo} \leq 4$), heavily to extremely polluted ($4 < I_{geo} \leq 5$), or extremely polluted ($I_{geo} > 5$).

The overall toxicity and potential ecological hazards posed by metals in soil were assessed using a method proposed by Håkanson [39]. The potential ecological risk index (PERI) primarily evaluates the probable degree of trace metal contamination taking into consideration the relative toxicity of the overall metals and the short-to-long-term response of the environment. The risk index (R_I) is calculated based on the following equation:

$$E_f^i = \sum T_r^i \left(\frac{C_s^i}{C_n^i} \right), \qquad R_I = \sum E_f^i, \tag{8}$$

where R_I is the sum of individual risk factors for all trace metals; E_f^i is the monomial PERI for individual metal; C_s^i and C_n^i are the observed and background values of concentrations of metals, respectively; and T_r^i is the toxic response factor for a single trace metal. T_r^i for Cd, Cr, Ni, Pb, and Zn are 30, 2, 5, 5, and 1, respectively [39, 51]. The potential ecological risk R_I is classified as follows: $R_I < 95$ low risk; $95 \leq R_I < 190$ moderate risk; $190 \leq R_I < 380$ high risk; and $R_I \geq 380$ very high risk, while the potential ecological risk index associated with an individual metal E_f^i is ranked as follows: $E_f^i < 40$ low risk; $40 \leq E_f^i < 80$ moderate risk; $80 \leq E_f^i < 160$ considerable risk; $160 \leq E_f^i < 320$ high risk; and $E_f^i \geq 320$ very high risk [18, 52].

2.8. Assessment of Pollution and Bioaccumulation Index in Commelina africana L. Bioaccumulation index can be used to provide a relative evaluation of the degree of contamination through uptake or exposure. This is sometimes referred to as a plant uptake factor or transfer factors (TFs) of heavy metals from soil to plants. In this study, the transfer factor was determined using

$$\mathrm{TF}_p = \frac{C_p^i}{C_s^i}, \tag{9}$$

where C_p^i is the i metal concentration in the plant material (dry weight basis) and C_s^i is the total concentration of the i metal in the soil (dry weight basis) [53, 54]. In addition, metal pollution index (MPI) was employed as a means of comparing the total metal concentration of *Commelina africana* L. with the respective sampling sites. MPI is expressed according to the following equation [55, 56]:

$$\mathrm{MPI} = \left[C_1 \times C_2 \times C_3 \times \cdots \times C_n \right]^{1/n}, \tag{10}$$

where n is the number of metals and C_n is the concentration of metal n in *Commelina africana* L. on dry weight basis.

3. Results and Discussion

3.1. Trace Metal Content. Metal levels in the *Commelina africana* L. and soil samples have been assessed for zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), and chromium (Cr), and the results are presented in Table 2. The results show that mean concentration of most trace metals in the coastal sandflats exceeded the recommended guideline values. The mean concentrations of Cd, Cr, Ni, Pb, and Zn in sandflat soil samples were $0.76 \pm 9.0 \times 10^{-2}$, $7.39 \pm 8.7 \times 10^{-1}$, 2.28 ± 0.35, $0.024 \pm 4.0 \times 10^{-3}$, and 74.51 ± 2.55 mg/kg, respectively. Notably, the metal levels indicate strong variability with sampling sites. The observed variability and enhanced metal levels could have been influenced by changes in transport and sedimentation modes from surrounding intertidal ecosystem. Additionally, these variations may be attributed to differences in the rates of metal solubility in soils which is predominantly controlled by pH, amount of metals cations exchange capacity, organic carbon content, and oxidation state of the system [57]. The order of mean concentrations in the *C. africana* L. samples was Zn > Ni > Cr > Pb > Cd. However, Cd level (0.75 mg/kg) in *C. africana* L.

Table 3: Pollution indicators for trace metals in sandflats from Douglas Creek.

Pollution indices		Sample sites				
		DC-V	DC-W	DC-X	DC-Y	DC-Z
Cf	Zn	0.77	0.78	0.82	0.80	0.75
	Pb	0.001	0.001	0.001	0.001	0.001
	Cd	2.34	2.33	2.31	2.67	3.00
	Ni	0.03	0.03	0.04	0.03	0.04
	Cr	0.09	0.08	0.07	0.09	0.07
I_{geo}	Zn	0.512	0.520	0.546	0.535	0.508
	Pb	0.001	0.001	0.001	0.001	0.001
	Cd	1.558	1.556	1.544	1.778	2.000
	Ni	0.017	0.021	0.025	0.023	0.025
	Cr	0.059	0.059	0.051	0.060	0.045
Cd		3.219	3.234	3.251	3.595	3.859
mCD		0.644	0.647	0.650	0.719	0.772

from location DC-W was far above FAO/WHO maximum level of 0.2 mg/kg [58].

Although there is no authoritative reference detailing the regulated background values of trace metals in Nigeria, it is obvious that observed metal levels except Cd in sandflat soil samples did not exceed background values or regulatory standards of heavy metals from other parts of the world [59, 60]. Trace metals in soils have been shown to be very useful indicators of environmental pollution [61–63]. Thus, the environmental quality of this sandflat soil raises serious health concerns especially considering its usage as a recreational area, where people come into direct contact with contaminant soil and dust particles. Some of the dominant sources of trace metal loadings to the sandflat soil may be due to wastes deposited from localised or diffused sources such as crude oil spill, fuel combustion (gas flaring), wastes disposal, traffic emission, petrochemicals, fertilizers, and pesticides.

3.2. Evaluation of Soil Pollution Indices. The contamination factor values were calculated using (2) and are listed in Table 3. The mean Cf values calculated for studied trace metals in psammitic sandflat soil samples were in the following order: Cd (2.53) > Zn (0.78) > Cr (0.08) > Ni (0.03) > Pb (0.001) (Figure 2). Cf values less than 1 (one) and those between 1 and three are considered to pose low and moderate degree of contamination, respectively. Therefore, the results of the present study at the various sites showed that the soil samples taken from the beach of Douglas Creek were moderately contaminated by Cd whereas Cr, Ni, Pb, and Zn indicated low degree of contamination. Cadmium could be introduced to soil, air, and aquatic environment through anthropogenic inputs such as fossil fuel combustion, application of phosphate fertilizers, and waste dumping and incineration [43, 64]. Cd is a known carcinogen that can potentially cause adverse effects to human kidneys, lungs, and bones. Thus, the relatively high Cf value of Cd indicating moderate contamination is significant. However, considerable contamination is likely through uncontrolled

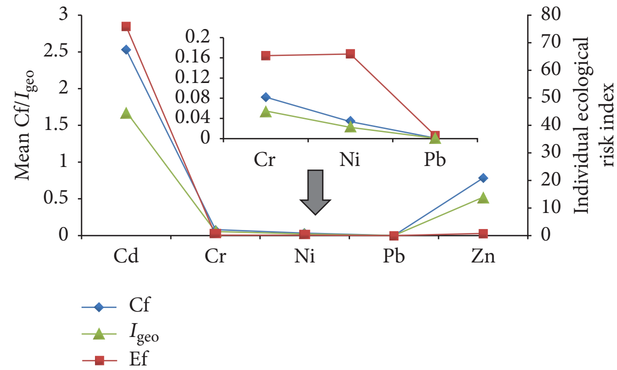

Figure 2: Individual ecological risk index and mean Cf/I_{geo} values of trace metals for sandflats soil samples of Douglas Creek.

fossil fuel combustion (excessive gas flaring) and untreated waste disposal, and carcinogenic risk associated with Cd is potentially of health and environmental concerns.

The degree of contamination (CD) and modified degree of contamination (mCD) were calculated using (1) and (3), respectively, and the derived contamination values are presented in Table 3. Results indicate that the CD and mCD at all sites generally showed low degree of contamination. Interestingly, both values did not exhibit correlative variability with the selected sites and may be considered to be in the range of unperturbed variability. This might be a function of the hydrodynamic conditions of the aquatic ecosystem at the period of obtaining the soil samples. However, the contamination ranking of trace metals on the basis of percent contribution to CD and mCD is Cd > Zn > Cr > Ni > Pb.

Table 3 shows the results of the calculated I_{geo} values and Figure 2 presents the mean I_{geo} values for each trace metal in the sandflats soil samples of the investigated sites. The I_{geo} values for Cr, Ni, Pb, and Zn indicated less variability among the sampling sites and were within $0 < I_{geo} \leq 1$ implying that the soil samples were unpolluted to moderately polluted. The calculated I_{geo} values for Cd showed that the soil samples were moderately polluted ($1 < I_{geo} \leq 2$) at all sites. It is imperative to emphasize that the average I_{geo} values for Cd were relatively higher than other trace metals, suggesting that the soil samples from the Douglas sandy beach must have been contaminated by Cd due to anthropogenic activities.

The pollution load index provides an integrated contamination assessment based on the Cf of each trace metal. The PLI values for Cd, Cr, Ni, Pb, and Zn are presented in Figure 3 and ranged between 0.086 and 0.097 at DC-W and DC-Z sites, respectively. As indicated by these PLI values, the sandflat samples of the present study are unpolluted, with PLI values between zero and one for all sites. However, it must be noted that the present day PLI values obtained for soil samples were dominated by individual contributions of Cd and Zn. The calculated pollution index (PI) and the Nemerow integrated pollution index (NIPI) values of trace metals in foreshore psammitic soil samples of Douglas Creek are presented in Table 4. Results indicate that the sandy beach of this aquatic ecosystem was not polluted but contamination ranking is precautionary ($0.7 < \text{NIPI} \leq 1$).

Table 4: Comparison of pollution indices (PIs) of trace metals in sandflat soils of Douglas Creek and other studies.

	Cd	Cr	Ni	Pb	Zn	I_{mean}	I_{max}	NIPI
Mean	0.76	7.39	2.28	0.02	74.51			
Target value[a]	0.8	100	35	85	140			
This study	0.95	0.074	0.065	0.0003	0.53	0.32	0.95	0.71
Odewande and Abimbola [76]	0.2	0.6	0.5	0.6	0.7	0.5	0.9	0.7

Dutch soil guidelines [42][a].

Table 5: Soil-to-plant transfer factors of studied trace metals.

Sample ID	Cd	Cr	Ni	Pb	Zn
DC-V	0.29	1.10	13.26	2.00	3.13
DC-W	1.07	1.09	10.85	2.63	3.05
DC-X	0.30	1.33	10.57	2.61	3.09
DC-Y	0.26	0.97	4.47	2.00	3.31
DC-Z	0.17	2.27	4.63	2.67	3.48

3.3. Evaluation of Pollution and Bioaccumulation Index. MPI results indicated that the calculated values varied with sampling sites and were a function of the total concentration of individual trace metals. The highest MPI value (4.42) was obtained at DC-W site followed by 3.75 at DC-X and then 3.46 at DC-Z site. The lowest MPI value of 2.95 for *Commelina africana* L. was recorded at downstream of the creek at DC-Y site. Moreover, transfer factor is one way through which the mobility of metal by plants can be assessed. The soil-to-plant transfer factor (TF) values recorded for different samples sites are presented in Table 5. The results revealed that Ni (13.26) in DC-V and Zn (3.48) in DC-Z soil had the highest transfer factor value while Cd (0.17) and Cr (0.97) in soils from DC-Z and DC-Y stations, respectively, reported the lowest transfer factor value in the study area. The metal bioavailability from soil to the plant as indicated by the transfer factor values for the five sample stations decreased in the order: $TF_{Ni} > TF_{Zn} > TF_{Pb} > TF_{Cr} > TF_{Cd}$. A higher value of transfer factor implies the tendency of more mobile and available metals [53]. Generally, Ni element exhibited higher valves of TF at all the sampling sites as shown on the table when compared with the results of other trace metals under investigation.

3.4. Evaluation of Potential Ecological Risks. The potential ecological risks assessment of trace metals in sandflat soil samples of the investigated ecosystem were calculated based on (8). Results of average potential ecological risk index of each trace metal are presented in Figure 2. Calculated E_f^i values for Cr (0.16), Ni (0.17), Pb (0.006), and Zn (0.78) indicated low degree of risk, while Cd E_f^i value indicated moderate risk ($40 \leq E_f^i < 80$). This result again highlights possible contamination concerns associated with Cd, which is likely due to fossil fuel burning in the region over the years. Interestingly, other researchers have reported that Cd contribution to potential ecological risk index of the environment is very significant [61, 65]. The contamination

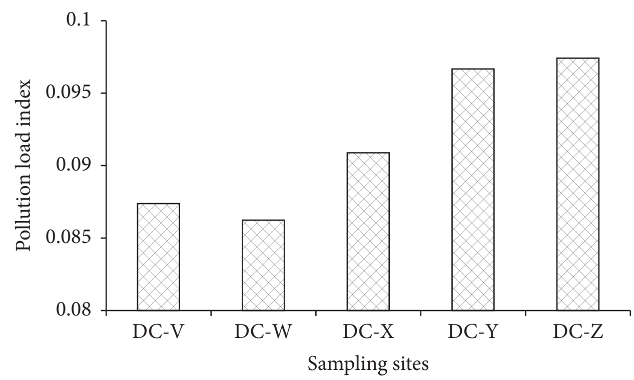

Figure 3: Pollution load index of metals at sampling sites of Douglas Creek.

ranking of trace metals in line with the mean PERIs for individual metal stressors is Cd > Zn > Ni > Cr > Pb. However, on the basis of the calculated R_I value ($R_I = 77$), a low ecological risk ($R_I < 95$ low risk) was indicated for the multielements considered in this study.

3.5. Principal Component Analysis (PCA). The principal component analysis (PCA) of variables was performed to extract significant principal components (PCs). The results of *n*-Pearson PCA performed further explored the relationships between the trace metals and also clarify their possible sources. Table 6 summarises the factor loadings of trace metals for sandflat and *Commelina africana* L., grouped into three principal component models. The loading plots of the PCs are presented in Figure 4. The Eigen values of PC1 and PC2 associated with sandflat soil were greater than 1 and in general accounted for 86.63% of the variability in concentrations of trace metals. PC1 indicated that 59.88% of the total variance was positively related to Cd, Pb, and Ni, with Cd and Pb showing relatively high factor loadings, while Cr indicated a strong negative relationship. On the other hand, PC2, which explained 26.76% of the total variance, indicated strong positive interrelationships for Ni and Zn.

It is worthy of note that the positive loading of Cd, Ni, and Pb with PC1 could possibly suggest that contamination of the sandflat soil samples might have been influenced by anthropogenic pollution sources. The Eigen values of PC1 and PC2 derived for *Commelina africana* L. samples indicate they were greater than 1 and accounted for 83.32% of the variability in trace metal levels. PC1 was the most significant principal component and was dominated by Cd, Cr, Ni, Pb, and Zn,

Table 6: PCA factor loadings of the concentrations of trace metals for sandflat soil and *C. africana* L. samples.

		Factor components		
		*F*1	*F*2	*F*3
Sandflat	Zn	−0.477	**0.830**	0.207
	Pb	**0.880**	−0.223	0.212
	Cd	**0.923**	−0.107	0.308
	Ni	0.663	**0.724**	0.038
	Cr	**−0.837**	−0.251	0.475
	Eigenvalue	2.994	1.338	0.410
	Variability (%)	59.879	26.755	8.207
	Cumulative %	59.879	86.634	94.841
C. africana L.	Zn	**0.833**	−0.470	0.037
	Pb	**0.849**	0.516	−0.021
	Cd	**−0.690**	0.304	0.637
	Ni	**−0.724**	0.430	−0.500
	Cr	**0.791**	0.600	0.083
	Eigenvalue	3.042	1.124	0.664
	Variability (%)	60.838	22.483	13.285
	Cumulative %	60.838	83.321	96.606

High factor loadings for each principle component are highlighted with bold type.

which accounted for 60.84% of the total variance. A very high loading of Cr (0.791), Pb (0.849), and Zn (0.833) in the PC1 component and the investigated trace metals indicated a significantly positive interrelationship. Additionally, the high loading of Cd (0.690) and Ni (0.724) on the first principal component indicated strong negative correlation.

3.6. Potential Health Risk Assessment. The health effects that might be attributed to noncarcinogenic trace metals in soil/sand/dust could be evaluated by comparing an exposure via oral ingestion over a specified time period with a reference dose (RfD) for each metal over a similar exposure period. This noncancer risk assessment ratio is termed target hazard quotient (THQ) [66]. The RfD is the toxicity threshold value, which is specific for each chemical contaminant. However, in order to evaluate the overall exposure potential for combined chronic effects caused by all the metal contaminants, a hazard index (HI) approach was adopted. The HI is equal to the arithmetic sum of individual metal THQs [66]. The estimated daily dose exposure through oral ingestion (EDD_{ing}), dermal (EDD_{dermal}) and inhalation absorption (EDD_{inh}), THQ, and HI is determined by the following equations, respectively [66–68]:

$$\mathrm{EDD}_{\mathrm{inh}} = \frac{C_{\mathrm{metal}} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{IR}_{\mathrm{inh}}}{\mathrm{Bw} \times \mathrm{AT} \times \mathrm{PEF}},$$

$$\mathrm{EDD}_{\mathrm{ing}} = \frac{C_{\mathrm{metal}} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{IR}_{\mathrm{ing}}}{\mathrm{Bw} \times \mathrm{AT}} \times 10^{-6},$$

$$\mathrm{EDD}_{\mathrm{dermal}} = \frac{C_{\mathrm{metal}} \times \mathrm{AF} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{SA} \times \mathrm{ABS}}{\mathrm{Bw} \times \mathrm{AT}} \times 10^{-6},$$

$$\mathrm{THQ}_i = \left[\frac{\mathrm{EDI}}{\mathrm{RfD}_i}\right],$$

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{THQ}_i, \tag{11}$$

where C_{metal} is the concentration (mg/kg) of trace metal in sandflat sample; EF is the exposure frequency (365 d/year); ED is the exposure duration equal to 6 y and 18 y for children aged between 1 and 6 years and 6 and 18 years, respectively, and 52.4 years for adults (World Bank 2013 estimate for average life expectancy in Nigeria) [69]; IR_{ing} is the ingestion rate (100 and 50 mg/day for children and adults, resp.); IR_{inh} is inhalation rate [70]; Bw is the average body weight (70, 48, and 19 kg for adults and children, resp.) and AT is the average exposure time for noncarcinogens (2190 d, age 1–6 y; 6570 d, age 6–18 y; 19162.5 d, adults); PEF is the particulate emission factor (m^3/kg) = 1.36×10^9; SA is the exposed skin surface area (cm^2); AF is the adherence factor (kg/cm^2-day); ABS is the dermal absorption factor; and RfD is the oral reference dose (mg kg^{-1} day^{-1}). The variable i denotes the ith trace metal. The RfDs for Cd, Cr, Ni, Pb, and Zn are 0.001, 0.003, 0.02, 0.0035, and 0.3 mg kg^{-1} d^{-1}, respectively [71]. However, target hazard quotient or hazard index ≤ 1 indicates that potential adverse health impacts from ingestion are unlikely, while THQ or HI > 1 suggests that adverse chronic effects are likely from direct oral ingestion of contaminated sandflats soil [66]. Moreover, to assess the carcinogenic effects, the average daily dose is multiplied by the corresponding slope factor (SF) to produce a level of cancer risk [16, 72]. However, the aggregate carcinogenic risk was evaluated as a summation of the individual cancer risk across inhalation exposure pathway as

$$\mathrm{Risk} = \sum \mathrm{EDD}_i \times \mathrm{SF}_i. \tag{12}$$

Tables 7 and 8 present the calculated results for noncarcinogenic hazard index for children and adults (males and females) in Nigeria, assessed by considering the exposure to trace metal contaminated sandflat soils via ingestion, inhalation, and dermal contact pathways. The potential risks in terms of the minimum, maximum, and average hazard indices of trace metals in sandflat soil samples for children and adult males and females were less than 1. Thus, these populations are unlikely to face any potential health risks [73].

As presented in Table 8, Cd, Cr, and Ni may pose relatively significant noncarcinogenic health risks to the selected population compared to Pb and Zn. For instance, considering the total hazard quotients (THQs) for inhalation of sandflat soils in children, Cd, Cr, and Ni accounted for 33.55%, 32.67%, and 33.56% of the calculated hazard index, respectively, while Pb and Zn contributed the relatively insignificant 0.22%.

Table 7: Noncarcinogenic effects due to oral ingestion exposure to sandflat soil trace metals.

		Cd	Cr	Ni	Pb	Zn
	Estimated daily dose (EDD_{ing})					
Children (1–6 years)	Min.	0.0035	0.0307	0.0088	0.0001	0.3756
	Max.	0.0045	0.041	0.0131	0.0002	0.3929
	Mean	0.0038	0.0373	0.0115	0.0003	0.3761
Children (6–18 years)	Min.	0.0014	0.0122	0.0035	0.00004	0.1487
	Max.	0.0018	0.0162	0.0052	0.00006	0.1555
	Mean	0.0015	0.0148	0.0046	0.00005	0.1489
Adults	Min.	0.0004	0.0043	0.0012	0.00001	0.0524
	Max.	0.0006	0.0057	0.0018	0.00002	0.0548
	Mean	0.0005	0.0052	0.0016	0.00002	0.0525
	Target hazard quotient (THQ)					
Children (1–6 years)	Min.	0.0035	0.0103	0.0004	0.00002	0.0012
	Max.	0.0045	0.0137	0.0007	0.00004	0.0013
	Mean	0.0038	0.0124	0.0006	0.00003	0.0012
Children (6–18 years)	Min.	0.0014	0.0041	0.0002	0.00001	0.0004
	Max.	0.0018	0.0054	0.0003	0.00002	0.0005
	Mean	0.0015	0.0049	0.0002	0.00001	0.0004
Adults	Min.	0.0005	0.0014	0.00006	0.000003	0.0002
	Max.	0.0006	0.0019	0.00009	$6.00E-06$	0.0002
	Mean	0.0005	0.0017	0.00008	$4.00E-06$	0.0002
	Hazard index (HI)	Min.	Max.	Mean		
	1–6 years	0.015	0.02	0.018		
	6–18 years	0.006	0.008	0.007		
	Adults	0.002	0.003	0.003		

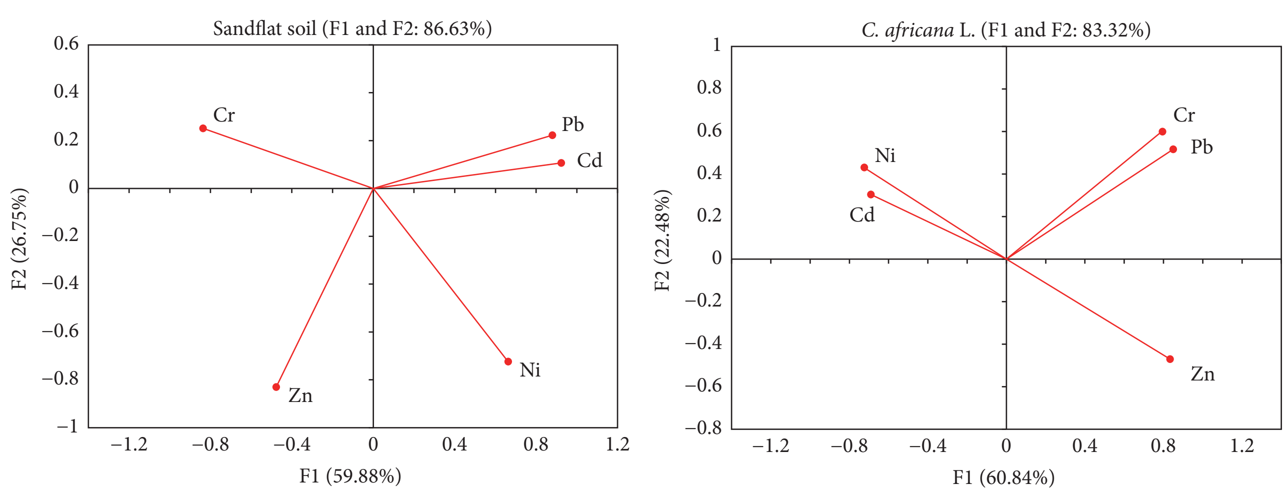

Figure 4: Factor loadings of principal components 1 and 2 for trace metals concentration in sandflat and *C. africana* L. samples showing the total variance explained by each component.

Results for potential exposure through dermal contact in children showed that Cd and Cr concentrations accounted for 73.31% and 25.49%, respectively, towards the total hazard index value, while Ni, Pb, and Zn represent about 1.19%. Previous studies on health risks assessment of soil trace metals indicated that Cd, Cr, and Ni exposure could pose relatively higher noncarcinogenic effects on children and adults due to their low RfD values or enhanced concentrations in soils [16]. Similarly, in adult females, the THQs of Cd and Cr represented 73.31% and 25.49% of the total hazard index (HI_{tot}) value for exposure due to inhalation, while both trace metals accounted for about 98.81% of the HI_{tot} value for risks

Table 8: Noncarcinogenic hazard index for children and adult for inhalation and dermal exposure pathways.

Metal	Conc. levels	Conc. (mg/kg)	Children (1–6 years) Inhalation EDD_{inh} (mg/kg-day)	Children (1–6 years) Inhalation THQ	Children (1–6 years) Dermal contact EDD_{dermal} (mg/m^3-day)	Children (1–6 years) Dermal contact THQ	Adult females Inhalation EDD_{inh} (mg/kg-day)	Adult females Inhalation THQ	Adult females Dermal contact EDD_{dermal} (mg/m^3-day)	Adult females Dermal contact THQ	Adult males Inhalation EDD_{inh} (mg/kg-day)	Adult males Inhalation THQ	Adult males Dermal contact EDD_{dermal} (mg/m^3-day)	Adult males Dermal contact THQ
Cd	Min.	0.69	1.97E − 10	1.97E − 09	1.12E − 08	1.57E − 01	7.91E − 11	7.91E − 08	5.01E − 06	5.01E − 01	1.09E − 10	1.09E − 07	4.19E − 06	4.19E − 01
	Max.	0.90	2.55E − 10	8.49E − 06	1.45E − 08	2.03E − 01	1.02E − 10	1.02E − 07	6.49E − 06	6.49E − 01	1.42E − 10	1.42E − 07	5.43E − 06	5.43E − 01
	Mean	0.76	2.15E − 10	7.17E − 06	1.23E − 08	1.72E − 01	8.64E − 11	8.64E − 08	5.47E − 06	5.47E − 01	1.20E − 10	1.20E − 07	4.58E − 06	4.58E − 01
Cr	Min.	6.10	1.73E − 09	5.76E − 07	9.85E − 08	4.93E − 02	6.94E − 10	2.31E − 07	9.41E − 06	1.57E − 01	9.94E − 10	3.21E − 07	7.88E − 06	1.31E − 01
	Max.	8.12	2.30E − 09	5.75E − 05	1.31E − 07	6.56E − 02	9.24E − 10	3.08E − 07	1.25E − 05	2.08E − 01	1.28E − 09	4.28E − 07	1.05E − 05	1.75E − 01
	Mean	7.39	2.09E − 09	6.98E − 06	1.19E − 07	5.97E − 02	8.41E − 10	2.80E − 07	1.14E − 05	1.90E − 01	1.17E − 09	3.89E − 07	9.55E − 06	1.59E − 01
Ni	Min.	1.75	4.96E − 10	1.84E − 05	9.89E − 06	1.83E − 03	1.99E − 10	9.96E − 09	3.15E − 05	5.83E − 03	2.77E − 10	1.38E − 08	2.64E − 05	4.88E − 03
	Max.	2.60	7.36E − 10	2.48E − 08	1.47E − 05	2.72E − 03	2.96E − 10	1.48E − 08	4.68E − 05	8.67E − 03	4.11E − 10	2.06E − 08	3.92E − 05	7.26E − 03
	Mean	2.28	6.45E − 10	7.17E − 06	1.29E − 06	2.38E − 03	2.59E − 10	1.29E − 08	4.10E − 05	7.60E − 03	2.59E − 10	1.80E − 08	3.43E − 05	6.35E − 03
Pb	Min.	0.02	5.38E − 12	1.54E − 09	1.84E − 09	3.51E − 06	2.16E − 12	6.18E − 10	5.87E − 09	1.12E − 05	3.60E − 12	8.58E − 10	4.90E − 09	9.35E − 06
	Max.	0.03	8.49E − 12	2.43E − 09	2.91E − 09	5.54E − 06	3.41E − 12	9.76E − 10	9.26E − 09	1.76E − 05	3.00E − 12	1.36E − 09	7.75E − 09	1.48E − 05
	Mean	0.02	6.91E − 12	1.97E − 09	2.36E − 09	4.50E − 06	2.78E − 12	7.93E − 10	7.54E − 09	1.44E − 05	4.74E − 12	1.10E − 09	6.31E − 09	1.20E − 05
Zn	Min.	74.43	2.10E − 08	7.02E − 08	2.40E − 05	4.00E − 04	8.47E − 09	2.82E − 08	7.66E − 05	1.27E − 03	1.18E − 08	3.92E − 08	6.41E − 05	1.06E − 03
	Max.	77.85	2.20E − 08	1.10E − 04	2.51E − 05	4.19E − 04	8.86E − 09	2.95E − 08	8.01E − 05	1.33E − 03	1.23E − 08	4.10E − 08	6.71E − 05	1.12E − 03
	Mean	74.51	2.11E − 08	4.40E − 08	2.41E − 05	4.01E − 04	8.48E − 09	2.82E − 08	7.67E − 05	1.28E − 03	1.18E − 08	3.93E − 08	6.42E − 05	1.07E − 03
Cumulative risk for min. values			2.34E − 08		3.84E − 05		9.45E − 09		1.23E − 04		1.31E − 08		1.03E − 04	
Cumulative risk for max. values			2.53E − 08		4.58E − 05		1.02E − 08		1.46E − 04		1.42E − 08		1.22E − 04	
Cumulative risk for mean values			2.40E − 08		4.22E − 05		9.67E − 09		1.34E − 04		1.34E − 08		1.13E − 04	
HI min. value				8.69E − 07		2.07E − 01		3.49E − 07		6.65E − 01		4.85E − 07		5.56E − 01
HI max. value				1.94E − 04		2.72E − 01		4.56E − 07		8.67E − 01		6.33E − 07		7.25E − 01
HI mean value				2.14E − 05		2.34E − 01		4.09E − 07		7.46E − 01		5.68E − 07		6.24E − 01

associated with dermal contact. The total hazard quotients of Cd and Cr indicated a relatively high percentage contribution of 89.72% and 98.81% of the overall HI_{tot} for adult males exposed to sandflat soils via inhalation and dermal contact pathways, respectively. However, the THQs of trace metals for children, adult males, and adult females decreased in the order of Cd > Cr > Ni > Zn > Pb for exposure due to dermal contact, while the risks ranking following inhalation pathway decreased in the order Cr > Cd > Ni > Zn > Pb and Cd > Ni > Cr > Zn > Pb for adult (males and females) and children, respectively. In general, the probability that noncarcinogenic effect may likely occur varied according to the three groups considered in this study. The ranking followed the decreasing order children > adult males > adult females, indicating that children are the most vulnerable group to noncarcinogenic risks. Comparatively, the hazard quotient and hazard index indicated that the sandflats might pose a health risk to children. Similar conclusion by Olawoyin et al. [11] on the vulnerability of Niger Delta children has been reported.

In this study, the carcinogenic risks associated with oral ingestion and dermal contact exposures were not considered due to unavailability of corresponding carcinogenicity slope factors for Cd, Cr, Ni, Pb, and Zn. However, the carcinogenic risks for Cd, Cr, and Ni were estimated only through inhalation pathways, while Pb and Zn were not considered due to lack of unit risk values [74]. Results for the average carcinogenic risk values were 8.98×10^{-8}, 5.01×10^{-8}, and 3.61×10^{-8} for children, adult males, and adult females, respectively. The 25% percentile of carcinogenic risks for children, adult males, and adult female was 7.42×10^{-8}, 4.14×10^{-8}, and 2.98×10^{-8}, respectively, while the 75% percentile of cancer risk values for children, adult males, and adult females was estimated as 9.88×10^{-8}, 5.52×10^{-8}, and 3.97×10^{-8}, respectively. According to Hu et al. [75], estimated carcinogenic risk values less than 1.0×10^{-8} are not considered as capable of posing adverse health effects, and risks above 1.0×10^{-4} are identified as unacceptable. In this study, the calculated carcinogenic risks were below 1.0×10^{-6}, and the sandflat soils are not considered to pose significant health effects to the three groups. However, the carcinogenicity ranking obtained in the present study decreased following the order children > adult males > adult females.

4. Conclusion

The present study confirms the occurrence and variability in the levels of carcinogenic trace metals in sandflat soils and *C. africana* L. of an important coastal ecosystem in Niger Delta, Nigeria. Results provide qualitative information on the pollution status of Cd, Cr, Pb, Ni, and Zn using pollution indices and ecological and health risks approaches. Based on the pollution indicators employed, the trace metals were considered to pose low to moderate degree of contamination. Available assessments indicate that anthropogenic activities such as petrochemical operations, fuel combustion, and industrial wastes dump are very likely sources of metal burden to the *C. africana* L. and sandflat soils. Results of the present study confirmed the dominant role of Cd in potential toxicity and in potential ecological risk. Noncarcinogenic and carcinogenic health risks assessments of soil trace metals may pose no adverse effects to children and adults. However, long-term health risks to children, being the most vulnerable population in the region, raise a lot of concern. Therefore, stringent measures should be put in place to limit children exposure risks to trace metals. In addition, frequent monitoring study by relevant government agencies, independent researchers, and health safety and environment departments of multinational oil companies operating in the Niger Delta region is recommended. Also, safe disposal of domestic sewage and industrial effluents should be practiced and where possible recycled to minimize the level of metals introduced into coastal water ecosystems.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] N. U. Benson and J. P. Essien, “Petroleum hydrocarbons contamination of sediments and accumulation in Tympanotonus fuscatus var. radula from the Qua Iboe Mangrove Ecosystem, Nigeria,” *Current Science*, vol. 96, no. 2, pp. 238–244, 2009.

[2] N. U. Benson, W. U. Anake, J. P. Essien, P. A. Enyong, and A. A. Olajire, “Distribution and risk assessment of trace metals in *Leptodius exarata*, surface water and sediments from Douglas Creek, Qua Iboe estuary,” *Journal of Taibah University For Science*, 2016.

[3] J. P. Essien, N. U. Benson, and S. P. Antai, “Seasonal dynamics of physicochemical properties and heavy metal burdens in Mangrove sediments and surface water of the brackish Qua Iboe Estuary, Nigeria,” *Toxicological and Environmental Chemistry*, vol. 90, no. 2, pp. 259–273, 2008.

[4] N. U. Benson, J. P. Essien, A. B. Williams, and D. E. Bassey, “Mercury accumulation in fishes from tropical aquatic ecosystems in the Niger Delta of Nigeria,” *Current Science*, vol. 96, no. 2, pp. 781–785, 2007.

[5] N. U. Benson, E. D. Udosen, and O. Akpabio, “Interseasonal distribution and partitioning of heavy metals in subtidal sediment of Qua Iboe Estuary and associated Creeks, Niger Delta (Nigeria),” *Environmental Monitoring and Assessment*, vol. 146, no. 1–3, pp. 253–265, 2008.

[6] J. P. Essien, S. P. Antai, and N. U. Benson, “Microalgae biodiversity and biomass status in Qua Iboe Estuary Mangrove Swamp, Nigeria,” *Aquatic Ecology*, vol. 42, no. 1, pp. 71–81, 2008.

[7] J. Liu, H. Wu, J. Feng, Z. Li, and G. Lin, “Heavy metal contamination and ecological risk assessments in the sediments and zoobenthos of selected mangrove ecosystems, South China,” *Catena*, vol. 119, pp. 136–142, 2014.

[8] N. U. Benson and U. M. Etesin, “Metal contamination of surface water, sediment and *Tympanotonus fuscatus var. radula* of Iko River and environmental impact due to Utapete gas flare station, Nigeria,” *Environmentalist*, vol. 28, no. 3, pp. 195–202, 2008.

[9] J. P. Essien, V. Essien, and A. A. Olajire, “Heavy metal burdens in patches of asphyxiated swamp areas within the Qua Iboe estuary mangrove ecosystem,” *Environmental Research*, vol. 109, no. 6, pp. 690–696, 2009.

[10] E. D. Udosen and N. U. Benson, "Spatio-temporal distribution of heavy metals in sediments and surface water in Stubbs Creek, Nigeria," *Trends in Applied Sciences Research*, vol. 1, no. 3, pp. 292–300, 2006.

[11] R. Olawoyin, S. A. Oyewole, and R. L. Grayson, "Potential risk effect from elevated levels of soil heavy metals on human health in the Niger delta," *Ecotoxicology and Environmental Safety*, vol. 85, pp. 120–130, 2012.

[12] N. U. Benson, "Lead, nickel, vanadium, cobalt, copper and manganese distributions in intensely cultivated floodplain ultisol of Cross River, Nigeria," *International Journal of Soil Science*, vol. 1, no. 2, pp. 140–145, 2006.

[13] Y. Hu and H. Cheng, "Application of stochastic models in identification and apportionment of heavy metal pollution sources in the surface soils of a large-scale region," *Environmental Science and Technology*, vol. 47, no. 8, pp. 3752–3760, 2013.

[14] E. D. Udosen, N. U. Benson, J. P. Essien, and G. A. Ebong, "Relation between aqua-regia extractable heavy metals in soil and manihot utilissima within a municipal dumpsite," *International Journal of Soil Science*, vol. 1, no. 1, pp. 27–32, 2006.

[15] J. O. Nriagu, "A history of global metal pollution," *Science*, vol. 272, no. 5259, pp. 223–224, 1996.

[16] H. Chen, Y. Teng, S. Lu, Y. Wang, and J. Wang, "Contamination features and health risk of soil heavy metals in China," *Science of the Total Environment*, vol. 512-513, pp. 143–153, 2015.

[17] X.-W. Fu, D.-G. Wang, X.-H. Ren, and Z.-J. Cui, "Spatial distribution patterns and potential sources of heavy metals in soils of a crude oil-polluted region in China," *Pedosphere*, vol. 24, no. 4, pp. 508–515, 2014.

[18] X. Yang, X. Yuan, A. Zhang et al., "Spatial distribution and sources of heavy metals and petroleum hydrocarbon in the sand flats of Shuangtaizi Estuary, Bohai Sea of China," *Marine Pollution Bulletin*, vol. 95, no. 1, pp. 503–512, 2015.

[19] L. C. Osuji and C. M. Onojake, "Field reconnaissance and estimation of petroleum hydrocarbon and heavy metal contents of soils affected by the Ebocha-8 oil spillage in Niger Delta, Nigeria," *Journal of Environmental Management*, vol. 79, no. 2, pp. 133–139, 2006.

[20] M. C. Onojake and O. Frank, "Assessment of heavy metals in a soil contaminated by oil spill: a case study in Nigeria," *Chemistry and Ecology*, vol. 29, no. 3, pp. 246–254, 2013.

[21] M. A. Addo, H. A. Affum, B. O. Botwe et al., "Assessment of water quality and heavy metal levels in water and bottom sediment samples from Mokwé Lagoon, Accra, Ghana," *Research Journal of Environmental and Earth Sciences*, vol. 4, no. 2, pp. 119–130, 2012.

[22] X. Li, L. Liu, Y. Wang et al., "Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China," *Geoderma*, vol. 192, no. 1, pp. 50–58, 2013.

[23] L. Madrid, E. Díaz-Barrientos, and F. Madrid, "Distribution of heavy metal contents of urban soils in parks of Seville," *Chemosphere*, vol. 49, no. 10, pp. 1301–1308, 2002.

[24] N. U. Benson, W. U. Anake, and I. O. Olanrewaju, "Analytical relevance of trace metal speciation in environmental and biophysicochemical systems," *American Journal of Analytical Chemistry*, vol. 04, no. 11, pp. 633–641, 2013.

[25] C. Mario, D. Valeria, H. Georg, and P. Stefano, "Guidance for sediment and biota monitoring under the Common Implementation Strategy for the Water Framework Directive," *TrAC Trends in Analytical Chemistry*, vol. 36, pp. 15–24, 2012.

[26] J. J. Vicente-Martorell, M. D. Galindo-Riaño, M. García-Vargas, and M. D. Granado-Castro, "Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary," *Journal of Hazardous Materials*, vol. 162, no. 2-3, pp. 823–836, 2009.

[27] S. Qiao, Z. Yang, Y. Pan, and Z. Guo, "Metals in suspended sediments from the Changjiang (Yangtze River) and Huanghe (Yellow River) to the sea, and their comparison," *Estuarine, Coastal and Shelf Science*, vol. 74, no. 3, pp. 539–548, 2007.

[28] S. Götze, A. Bose, I. M. Sokolova, D. Abele, and R. Saborowski, "The proteasomes of two marine decapod crustaceans, European lobster (*Homarus gammarus*) and Edible crab (*Cancer pagurus*), are differently impaired by heavy metals," *Comparative Biochemistry and Physiology C: Toxicology and Pharmacology*, vol. 162, no. 1, pp. 62–69, 2014.

[29] S. Rahmanpour, N. F. Ghorghani, and S. M. Lotfi Ashtiyani, "Heavy metal in water and aquatic organisms from different intertidal ecosystems, Persian Gulf," *Environmental Monitoring and Assessment*, vol. 186, no. 9, pp. 5401–5409, 2014.

[30] J. P. Essien, S. P. Antai, and N. U. Benson, "Microbial population dynamics as a function of sediment salinity gradients in the Qua Iboe Estuary Mangrove Swamp (Nigeria)," *Research Journal of Microbiology*, vol. 1, no. 3, pp. 255–265, 2006.

[31] M. Nummelin, M. Lodenius, E. Tulisalo, H. Hirvonen, and T. Alanko, "Predatory insects as bioindicators of heavy metal pollution," *Environmental Pollution*, vol. 145, no. 1, pp. 339–347, 2007.

[32] F. Talarico, P. Brandmayr, P. G. Giulianini et al., "Effects of metal pollution on survival and physiological responses in *Carabus* (*Chaetocarabus*) *lefebvrei* (Coleoptera, Carabidae)," *European Journal of Soil Biology*, vol. 61, pp. 80–89, 2014.

[33] N. Alkan, M. Aktaş, and K. Gedik, "Comparison of metal accumulation in fish species from the Southeastern Black Sea," *Bulletin of Environmental Contamination and Toxicology*, vol. 88, no. 6, pp. 807–812, 2012.

[34] M. E. Goher, H. I. Farhat, M. H. Abdo, and S. G. Salem, "Metal pollution assessment in the surface sediment of Lake Nasser, Egypt," *Egyptian Journal of Aquatic Research*, vol. 40, no. 3, pp. 213–224, 2014.

[35] P. Vrhovnik, J. P. Arrebola, T. Serafimovski et al., "Potentially toxic contamination of sediments, water and two animal species in Lake Kalimanci, FYR Macedonia: relevance to human health," *Environmental Pollution*, vol. 180, pp. 92–100, 2013.

[36] A. Vaněk, L. Borůvka, O. Drábek, M. Mihaljevič, and M. Komárek, "Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry," *Plant, Soil and Environment*, vol. 51, no. 7, pp. 316–321, 2005.

[37] C. S.-L. Lee, X. Li, W. Shi, S. C.-N. Cheung, and I. Thornton, "Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics," *Science of the Total Environment*, vol. 356, no. 1–3, pp. 45–61, 2006.

[38] G. Qingjie, D. Jun, X. Yunchuan, W. Qingfei, and Y. Liqiang, "Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing," *Journal of China University of Geosciences*, vol. 19, no. 3, pp. 230–241, 2008.

[39] L. Håkanson, "Ecological risk index for aquatic pollution control. A sedimentological approach," *Water Research*, vol. 14, pp. 975–1001, 1980.

[40] D. C. Tomlinson, J. G. Wilson, C. R. Harris, and D. W. Jeffrey, "Problems in the assessment of heavy metals levels

in estuaries and the formation of pollution index," *Helgoland Marine Research*, vol. 33, pp. 566–575, 1980.

[41] C. Zhang, Q. Qiao, J. D. A. Piper, and B. Huang, "Assessment of heavy metal pollution from a Fe-smelting plant in urban river sediments using environmental magnetic and geochemical methods," *Environmental Pollution*, vol. 159, no. 10, pp. 3057–3070, 2011.

[42] VROM, *Circular on Target Values and Intervention Values for Soil Remediation. Annex A*, Dutch Ministry of Housing Spatial Planning and Environment (VROM), The Hague, The Netherlands, 2000.

[43] G. Suresh, V. Ramasamy, M. Sundarrajan, and K. Paramasivam, "Spatial and vertical distributions of heavy metals and their potential toxicity levels in various beach sediments from high-background-radiation area, Kerala, India," *Marine Pollution Bulletin*, vol. 91, no. 1, pp. 389–400, 2015.

[44] N. L. Nemerow, *Stream, Lake, Estuary, and Ocean Pollution*, Van Nostrand Reinhold Publishing, New York, NY, USA, 1985.

[45] H. Cheng, M. Li, C. Zhao et al., "Overview of trace metals in the urban soil of 31 metropolises in China," *Journal of Geochemical Exploration*, vol. 139, pp. 31–52, 2014.

[46] G. Müller, "Index of geoaccumulation in sediments of the Rhine River," *GeoJournal*, vol. 2, pp. 108–118, 1969.

[47] K. K. Turekian and K. H. Wedepohl, "Distribution of the elements in some major units of the earth's crust," *Geological Society of America Bulletin*, vol. 72, no. 2, pp. 175–192, 1961.

[48] N. U. Benson, F. E. Asuquo, A. B. Williams et al., "Source evaluation and trace metal contamination in benthic sediments from equatorial ecosystems using multivariate statistical techniques," *PLoS ONE*, vol. 11, no. 6, Article ID e0156485, 2016.

[49] W. Zhuang and X. Gao, "Integrated assessment of heavy metal pollution in the surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China: comparison among typical marine sediment quality indices," *PLoS ONE*, vol. 9, no. 4, Article ID e94145, 2014.

[50] K. Loska, D. Wiechulła, and I. Korus, "Metal contamination of farming soils affected by industry," *Environment International*, vol. 30, no. 2, pp. 159–165, 2004.

[51] Y. Wang, L. Yang, L. Kong, E. Liu, L. Wang, and J. Zhu, "Spatial distribution, ecological risk assessment and source identification for heavy metals in surface sediments from Dongping Lake, Shandong, East China," *CATENA*, vol. 125, pp. 200–205, 2015.

[52] S. Wu, S. Peng, X. Zhang et al., "Levels and health risk assessments of heavy metals in urban soils in Dongguan, China," *Journal of Geochemical Exploration*, vol. 148, pp. 71–78, 2015.

[53] M. Intawongse and J. R. Dean, "Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract," *Food Additives and Contaminants*, vol. 23, no. 1, pp. 36–48, 2006.

[54] E. T. Idowu, N. H. Amaeze, P. I. Adie, and O. A. Otubanjo, "Heavy metal bioaccumulation and biomarkers of oxidative stress in the wild African tiger frog, *Hoplobatrachus occipitalis*," *African Journal of Environmental Science and Technology*, vol. 8, no. 1, pp. 6–15, 2014.

[55] A. Khaled, A. Hessein, A. M. Abdel-Halim, and F. M. Morsy, "Distribution of heavy metals in seaweeds collected along Marsa-Matrouh beaches, Egyptian Mediterranean Sea," *Egyptian Journal of Aquatic Research*, vol. 40, no. 4, pp. 363–371, 2014.

[56] J. Usero, E. González-Regalado, and I. Gracia, "Trace metals in the bivalve molluscs *Ruditapes decussatus* and *Ruditapes philippinarum* from the Atlantic Coast of Southern Spain," *Environment International*, vol. 23, no. 3, pp. 291–298, 1997.

[57] M. Ghosh and S. P. Singh, "A review on phytoremediation of heavy metals and utilization of its byproducts," *Applied Ecology and Environmental Research*, vol. 3, no. 1, pp. 1–18, 2005.

[58] FAO/WHO, "Report of the sixth session of the Codex Committee on contaminants in foods," Tech. Rep. CF/6 INF/1, Codex Alimentarius Commission, The Hague, The Netherlands, 2012.

[59] State Environmental Protection Administration of China (SEPAC), "Environmental quality standard for soils," Tech. Rep. GB15618-1996, State Environmental Protection Administration of China (SEPAC), Beijing, China, 1995.

[60] United States Environmental Protection Agency (USEPA), *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites*, Office of Solid Waste and Emergency Response, Washington, DC, USA, 2002.

[61] X.-S. Luo, S. Yu, Y.-G. Zhu, and X.-D. Li, "Trace metal contamination in urban soils of China," *Science of the Total Environment*, vol. 421-422, pp. 17–30, 2012.

[62] Y. Sun, Q. Zhou, X. Xie, and R. Liu, "Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China," *Journal of Hazardous Materials*, vol. 174, no. 1–3, pp. 455–462, 2010.

[63] Z. P. Yang, W. X. Lu, Y. Q. Long, X. H. Bao, and Q. C. Yang, "Assessment of heavy metals contamination in urban topsoil from Changchun City, China," *Journal of Geochemical Exploration*, vol. 108, no. 1, pp. 27–38, 2011.

[64] Agency for Toxic Substances and Disease Registry (ATSDR), Division of Toxicology and Environmental Medicine/Applied Toxicology Branch, 2012, http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=48&tid=15.

[65] X. Qing, Z. Yutong, and L. Shenggao, "Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China," *Ecotoxicology and Environmental Safety*, vol. 120, pp. 377–385, 2015.

[66] USEPA (United States Environmental Protection Agency), *Risk Assessment Guidance for Superfund. Human Health Evaluation Manual, (Part A)*, vol. 1, Office of Emergency and Remedial Response, Washington, DC, USA, 1989, EPA/540/1-89/002.

[67] A. O. W. Leung, N. S. Duzgoren-Aydin, K. C. Cheung, and M. H. Wong, "Heavy metals concentrations of surface dust from e-waste recycling and its human health implications in southeast China," *Environmental Science and Technology*, vol. 42, no. 7, pp. 2674–2680, 2008.

[68] P. Li, C. Lin, H. Cheng, X. Duan, and K. Lei, "Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China," *Ecotoxicology and Environmental Safety*, vol. 113, pp. 391–399, 2015.

[69] World Bank Data Catalogue, *Life Expectancy at Birth, Total (Years)*, 2015, http://data.worldbank.org/indicator/SP.DYN.LE00.IN/countries/NG?display=graph.

[70] United States Environmental Protection Agency (USEPA), *Exposure Factors Handbook: 2011 Edition*, EPA/600/R-090/052F, 2011.

[71] United States Environmental Protection Agency (USEPA), *Integrated Risk Information System (IRIS)*, 2014.

[72] L. Ferreira-Baptista and E. De Miguel, "Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban

environment," *Atmospheric Environment*, vol. 39, no. 25, pp. 4501–4512, 2005.

[73] USEPA (United States Environmental Protection Agency), "Supplemental guidance for developing soil screening levels for superfund sites," OSWER 9355.4-24, Office of Solid Waste and Emergency Response, Washington, DC, USA, 2001.

[74] USEPA (United States, Environmental Protection Agency), Integrated Risk Information System, 2007, https://cfpub.epa.gov/ncea/iris2/atoz.cfm.

[75] X. Hu, Y. Zhang, Z. Ding et al., "Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and $PM_{2.5}$ in Nanjing, China," *Atmospheric Environment*, vol. 57, pp. 146–152, 2012.

[76] A. A. Odewande and A. F. Abimbola, "Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria," *Environmental Geochemistry and Health*, vol. 30, no. 3, pp. 243–254, 2008.