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Original Research

Geochemical fractionation and ecological risks assessment of benthic sediment-bound heavy metals from coastal ecosystems off the Equatorial Atlantic Ocean

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ABSTRACT

This study determines the pollution, fractionation, and ecological risks of sediment-bound heavy metals from coastal ecosystems off the Equatorial Atlantic Ocean. Contamination Factor (CF), pollution load index (PLI), and geoaccumulation index (*Igeo*) were used to assess the extent of the heavy metal pollution, while the potential ecological risk was evaluated using the risks assessment code (RAC) and Håkanson potential ecological risk. The analysis revealed concentrations (mg/g, dw) of the cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) in sediments for wet and dry seasons vary from 4.40–5.08, 14.80–21.09, 35.03–44.8, 2.14–2.28, and 172.24–196.39, respectively. The results also showed that the metal fractionation percentages in the residual, oxidizable, and reducible fractions are the most significant, while the exchangeable and carbonate bound trace metals are relatively low. The RAC values indicate no risk for Cd and Ni and low risk for other metals at all the studied sites during both seasons. Potential ecological risk analysis of the heavy metal concentrations indicates that Cd had high individual potential ecological risk, while the other metals have low risk at all investigated sites. The multi-elemental potential ecological risk indices (R_1) indicate high ecological risk in all the ecosystems.

1. Introduction

Over the past two decades, investigations into anthropogenic heavy metals loadings, deposition, accumulation, and cycling in estuarine and marine ecosystems have become the prime focus for the coastal environment (Benson et al., 2009, 2016a, 2017; Benson & Etesin, 2008; Gao & Chen, 2012; Huang et al., 2013; Leung et al., 2014; Li et al., 2012; Lin et al., 2013; Maanan et al., 2013; MacDonald et al., 1996; Usman et al., 2013; Yuan et al., 2011; Zahra et al., 2014). Heavy metals are usually present as micro-pollutants at ultra-trace levels as part of the natural aquatic constituents. However, enhanced concentrations of heavy metals observed in many ecosystem compartments such as sediment, water, flora, and fauna may be associated with human-mediated inputs such as industrial, domestic, and agricultural activities rather than natural enrichment (Benson et al., 2016b, 2017). In aquatic ecosystems, heavy metals are regarded as toxicants, depending on dose, time of exposure, specific resistance of organisms, and co-presence of other factors; and their relative magnitude of contamination has been attributed to their sedimentary binding strength, biogeochemical characteristics of the aquatic system, and sediment pH (Goher et al., 2014; Uzairu et al., 2009). Sediments in coastal ecosystems are known repositories as well as sources of several inorganic contaminants including toxic heavy metals (Benson et al., 2015, 2016a, 2017; Hill et al., 2013; Huang et al., 2013; Tessier et al., 1979; Usman et al., 2013). Sediments are significantly important in the uptake, storage, release, and transfer of metal toxicants between the various compartments of the aquatic ecosystem. It is generally recognized that sediment-bound metals are easily remobilized, transformed, and released to the overlying aqueous column thereby making them readily bioavailable and

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more hazardous to aquatic plants, organisms, and the environment (Gao et al., 2010; Morelli & Massimo, 2014).

Quantifying heavy metal toxicity and its potential to bioaccumulate using the total metal content in sediment and biological systems can be misleading (Benson et al., 2013, 2016b, 2017; Kalloul et al., 2012). Although the concept of the total metal level is useful as an index for expressing the degree of elemental load in environmental samples, applying a chemical fractionation procedure is considered significant and widely applicable in characterizing the chemical species of metals present in environmental matrices, including sediment (Li et al., 2012; Morelli & Massimo, 2014; Tessier et al., 1979). Fractionation also provides requisite information associated with the origin, occurrence, mobility, bioactivity, bioavailability, transport, and the risk posed by sediment-bound metals (Benson et al., 2013; Passos et al., 2010). Several fractionation schemes have been developed and applied for analysis and characterization of sediment-bound elements (Li et al., 2012; Tessier et al., 1979). A classical multi-step phase-selective extraction scheme delineates heavy metal species sequentially into four or more fractions.

A variety of quantitative tools, indices, and guidelines have been proposed and applied in assessing the sediment-associated elemental contamination degree, enrichment, and risks (Bastami et al., 2014; Buccolieri et al., 2006; Håkanson, 1980; MacDonald et al., 2000; Müller, 1979; Tomlinson et al., 1980). The present study was conducted to ascertain the level of elemental contamination and the ecological risk status of the five major coastal aqua-systems impacted by crude oil exploration and exploitation in the Niger Delta of Nigeria. The research was specifically designed to: (a) determine and explain the sequential chemical fractionations and spatio-temporal trends of heavy metals in benthic sediments; (b) estimate the mobility, bioavailability, and toxicity of sediment-bound heavy metals considering differentiation in binding strengths; and (c) evaluate the degree of contamination and risks using existing indices.

2. Materials and methods

2.1. Study locations, sediment collection and pretreatment

In this study, a mix of five meso-tidal and intertidal coastal water systems was considered. The aquatic ecosystems include Douglas Creek (DOU), Okorotip Creek (OKT), Stubbs Creek (STB), Qua Iboe Estuary (QUE), and Qua Iboe River (QUR) (Fig. 1). Details of the study sites have been previously reported (Benson et al., 2009, 2016a; Williams & Benson, 2010). Sediment sampling was conducted monthly during the wet (June–August) and dry (November–January) seasons. In each ecosystem, three sites were designated at a distance approximately 300–400 m apart and three benthic sediment subsamples were collected with a grab sampler (van Veen 0.1 m^2). A total of 90 samples were obtained, stored in well-labeled PTFE bottles and preserved in ice-packed coolers to inhibit microbial activities prior to analysis. In the laboratory, the sediment samples were oven dried at 100–110 °C and then gently homogenized and comminuted manually with a mortar. Disaggregated samples were sieved through a 2-mm sieve before subjecting the composites to chemical digestion (Radojevic & Bashkin, 1999). The coning and quartering method was used to obtain subsamples from the respective representative samples.

2.2. Analytical procedure for chemical extraction and metal determination

Sediment samples were subjected to Tessier's sequential extraction method for the analytical differentiations of sediment-bound heavy metals into five fractions: the exchangeable (F1), carbonate bound (F2), reducible (F3), oxidizable (F4), and residual (F5) fractions (Tessier et al., 1979). Detail of the selective extraction procedure is presented in Table S1. The total metal concentration in sediment samples was determined by the wet digestion method (Benson et al., 2009, 2016a). Reagent blanks were prepared following the sequence of steps outlined for sample preparation. Analyses were done in triplicate to ascertain the precision/reproducibility of the extraction method. Heavy metals concentrations of sediment samples were analyzed using inductively coupled plasma-atomic emission spectrometer (ICP-AES). Calibration standards were prepared by appropriate dilutions of commercially available stock solutions of the heavy metals analyzed (1000 μg/ml BDH Grade).

2.3. Evaluation of heavy metal contamination in benthic sediment

The degree of metal contamination on and risk assessment for sediments were evaluated by several empirical approaches including the determination of the pollution load index (PLI), contamination factor (CF), geoaccumulation index (I_{geo}), and potential ecological risk index (PERI).

2.3.1. Contamination factor and pollution load index

The CF is a pollution indicator expressed as the ratio of the concentration of an individual heavy metal to the background level (Håkanson, 1980):

$$CF = \frac{C_{metal}}{C_{bkg}} \tag{1}$$

where C_{metal} = metal concentration in the sediment and C_{bkg} = background value of the metal. Ideally, the background concentration should be predetermined values in an environmental matrix that is free of any human induced pollution. In this study area, there are no standard background values for sediments. More so, despite the low concentrations of metals obtained in this study, using the levels as background values in preference to shale standard values could be misleading. Rather, the results should be considered as baseline values against future research within these ecosystems. Therefore, the concept of background concentration in the present study refers to pre-anthropogenic (preindustrial) concentrations of trace elements in shale sediments as reported by Turekian and Wedepohl (1961). The degrees of sediment contamination by metals are listed in Table 1.

However, the sediment quality was also assessed based on Tomlison's pollution load index (PLI) for the determined heavy metals (Bastami et al., 2014; Suresh et al., 2011; Tomlinson et al., 1980). The PLI is calculated according to the equation:

$$PLI = [CF_1\ x\ CF_2\ x\ CF_3\ x\ CF_4\ x ...... x\ CF_n]^{1/n} \tag{2}$$

where n = the number of metals (n=5); CF_n = the contamination factor of metal n. The PLI represents the number of times by which the metal content in the sediment exceeds the natural background concentration of the metals, and gives a cumulative indication of the overall level of heavy metal toxicity in a sample.

2.3.2. Geoaccumulation index (I_{geo})

The I_{geo} is a common technique applied for assessing the magnitude of heavy metal contamination in environmental samples. The I_{geo} values for the five metals were computed using the equation developed by Müller (1979):

$$I_{geo} = \log_2(C_n)/1.5(C_{bkg}) \tag{3}$$

where C_n is the n^{th} heavy metal concentration in the subtidal sediment sample, C_{bkg} is the geochemical background value of

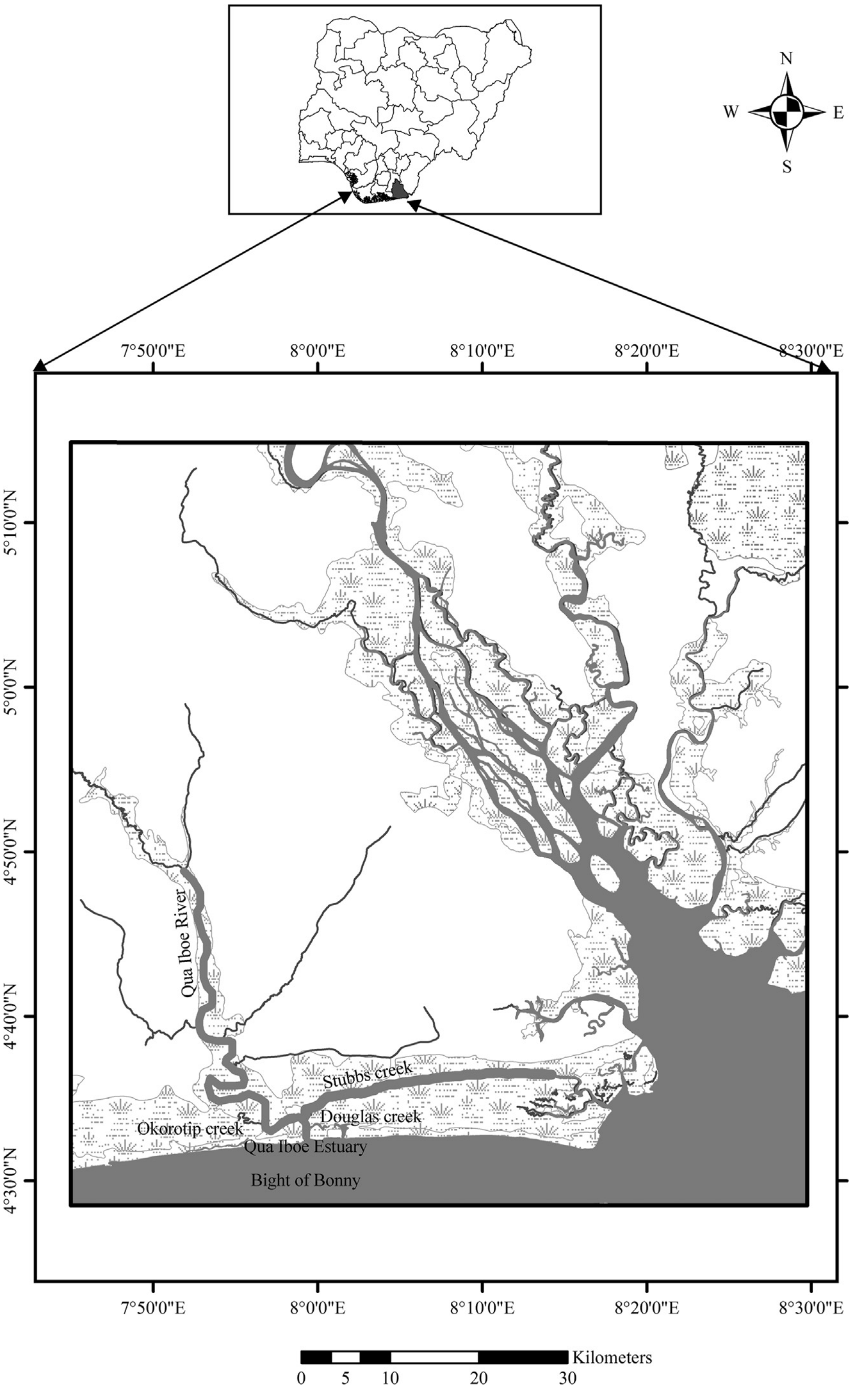

Fig. 1. Map of the study location showing the estuarine and freshwater ecosystems in the Niger Delta region of Nigeria. (Inset: Map of Nigeria).

metal n in reference average shale (Turekian & Wedepohl, 1961), and 1.5 is a factor used to address the possible deviations in the background concentrations of the metals, which may be associated with lithogenic (Rahman & Ishiga, 2012; Yu et al., 2011; Zhuang & Gao, 2014), and anthropogenic (Goher et al., 2014; Gong et al., 2008; Varol, 2011) effects. According to Müller's geoaccumulation indices, the magnitude of contamination with respect to individual element concentration is categorized as listed in Table 1.

2.4. Risk assessment code and environmental implications

The bioactivity, environmental toxicity, and bioavailability of metal species in aquatic ecosystems are better constrained in terms of their binding strengths in various fractionation phases (Benson et al., 2013; Saleem et al., 2015). The risk assessment code (RAC) is widely used for ecological risks assessment of the correlative effects that sediment-bound heavy metals pose to aquatic plants and animals (Nemati et al., 2011; Perin et al., 1985; Sundaray et al., 2011). In this study, the RAC was computed as a function of the bioavailable metal concentrations in terms of percent contribution in the exchangeable (F1) and carbonate (F2) geochemical fractions. It is expressed using the equation:

$$RAC_i = (\%F_{exc} + \%F_{carb})_i \tag{4}$$

where the $\%F_{exc}$ and $\%F_{carb}$ = percentages of heavy metal concentrations in exchangeable (F1) and carbonate bound (F2) fractions, respectively. The grades of sediments are categorized as indicated in Table 2.

Table 1
Categories of pollution load index, contamination factor and geoaccumulation index.

I_{geo}[a]			CF[b]		PLI[c]	
I_{geo} index	I_{geo} class	Degree of contamination	CF value	Degree of contamination	PLI grade	Degree of contamination
≤ 0	0	Uncontaminated	$CF < 1$	Low	0	Perfection
$0 < - \leq 1$	1	Uncontaminated to moderately contaminated	$1 \leq CF < 3$	Moderate	< 1	Unpolluted
$1 < - \leq 2$	2	Moderately contaminated	$3 \leq CF < 6$	Considerable	> 1	Polluted
$2 < - \leq 3$	3	Moderately to highly contaminated	$CF \geq 6$	Very high		
$3 < - \leq 4$	4	Highly contaminated				
$4 < - \leq 5$	5	Highly to extremely contaminated				
> 5	6	Extremely contaminated				

PLI = pollution load index, CF = contamination factor, I_{geo} = geoaccumulation Index

[a] Buccolieri et al. (2006).
[b] Gong et al. (2008).
[c] Tomlinson et al. (1980).

Table 2
Potential ecological risk indices, grades, and toxic response factors of metals.

Risk assessment code		Ecological risk index		Multi-elemental potential ecological risk index	
RAC	Degree of risk	E_f^i	Degree of risk	R_I	Degree of risk
RAC ≤ 1%	No risk	$E_f^i < 40$	Low risk	$R_I < 95$	Low risk
1% < RAC ≤ 10%	Low risk	$40 \leq E_f^i < 80$	Moderate risk	$95 \leq R_I < 190$	Moderate risk
10% < RAC ≤ 30%	Medium risk	$80 \leq E_f^i < 160$	Considerable risk	$190 \leq R_I < 380$	High risk
30% < RAC ≤ 50%	High risk	$160 \leq E_f^i < 320$	High risk	$R_I \geq 380$	Very high risk
50% > RAC	Very high risk	$E_f^i \geq 320$	Very high risk		

RAC = Risk assessment code; R_I = Multi-elemental potential ecological risk index; E_f^i = Potential ecological risk index of each metal

Sediment-bound metals are primarily associated with different fractions and they are known to exhibit varied bonding strength, which governs their bioavailability in aquatic ecosystems and their attendant ecological risk (Bacon & Davidson, 2008; Benson et al., 2013). In this study, the RAC was evaluated on the basis of the percentages of the metal concentrations that were present in bioavailable sediment fractions (exchangeable + carbonates bound), where the metal-sediment bonding strength is weak. The categories into which RAC is put hold that a percentage less than 1% indicates the sediment poses no risk to the aquatic environment. RAC percentages of 1–10%, 11–30%, 31–50% and > 50% reflect low risk, medium risk, high risk, and very high risk, respectively (Jain, 2004; Passos et al., 2010).

2.5. Håkanson potential ecological risks

Håkanson (1980) developed a methodology to assess ecological risks for aquatic pollution control. This method is based on the assumption that the sensitivity of the aquatic system depends on its primary productivity. The potential ecological risk index (PERI) primarily assesses the probable degree of heavy metal contamination in benthic sediments, taking into perspective the relative toxicity of the overall metals and the short- to long-term response of the environment. It is a comprehensive method that incorporates the toxicity, bioavailability, and discrepancy of regional background reference concentrations of heavy metals (Horst, 1997; Li et al., 2013). The risk index (R_I) equals the summation of the PERI (E_f^i) and generally indicates the sensitivity of the biota to hazardous metals and represents the ecological risks associated with aggregate heavy metals contamination. The R_I is calculated based on the equation:

$$R_I = \sum E_f^i \tag{5}$$

$$E_f^i = \sum T_r^i \left(\frac{C_s^i}{C_{bkg}^i}\right) \tag{6}$$

where R_I = aggregate risks factor computed considering all individual sediment-bound elements, E_f^i = the PERI for each single element i, C_s^i = the observed concentration of metal i in sediment samples, C_{bkg}^i = the background values of metal i, and T_r^i = the toxic response factor for a selected metal i. The T_r^i for cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) are 30, 2, 5, 5, and 5, respectively (Håkanson, 1980; Maanan et al., 2013; Wang et al., 2015). The terminology used to describe the risk factors E_f^i and R_I is listed in Table 2 (Håkanson, 1980).

3. Results and discussion

3.1. Fractionation characteristics of the heavy metals

The sequential extraction method (SEM) applied in this study presents heavy metals in five sediment geochemical fractions (exchangeable + carbonate bound + reducible + oxidizable + residual) (Fig. 2). Results obtained for heavy metals in the environmentally mobile and bioavailable fractions (exchangeable + carbonate bound + reducible + oxidizable) and the nonbioavailable (residual) fraction are listed in Tables 3a–3e. In the labile fractions, the order of the most to the least bioavailable heavy metal during the wet season was: Cu > Cr > Ni > Cd > Pb for the DOU ecosystem, while the trend obtained for sites OKT and STB were: Cu > Cr > Ni > Cd > Pb and Cr > Cu > Ni > Cd > Pb, respectively. In the Qua Iboe estuary and river ecosystems, the selectivity order during the wet season followed: Cu > Cr > Ni > Cd > Pb and Cr > Cu > Ni > Cd > Pb, respectively. Results indicate that the wet season mobility trend followed the order Cu > Cr > Ni > Cd > Pb at sites DOU, OKT, and QUE and Cr > Cu > Ni > Cd > Pb at sites STB and QUR. During the dry season, the mobility sequence at site DOU was: Cr > Cu > Ni > Cd > Pb. Generally, the selectivity order during the dry season was: Cu > Cr > Ni > Cd > Pb for all the sites except at DOU site. The results indicate that Cu, Cr, and Ni show the greatest percent concentrations in the bioavailable fractions while

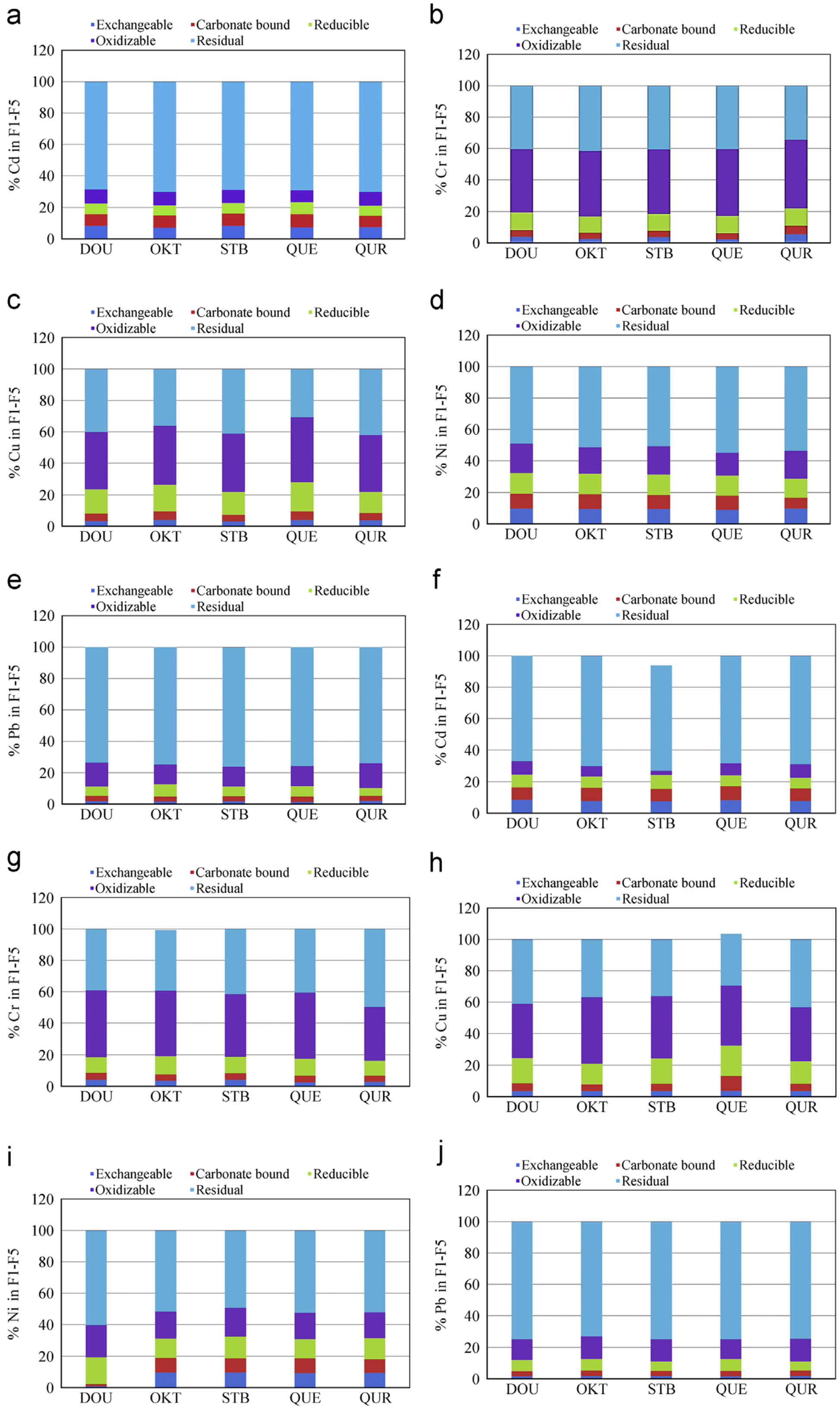

Fig. 2. a: Heavy metals distribution in different geochemical phases in the benthic sediments during the wet season (June–August). **b:** Heavy metals distribution in different geochemical phases in the benthic sediments during the dry season (November–January).

Cd and Pb had relatively low percentages. Heavy metals in the exchangeable geochemical fraction are considered to be unstable and weakly bound to sediment (Passos et al., 2010; Tessier et al., 2011). The extractability percent order of heavy metals in the residual fraction followed the trend Pb > Cd > Ni > Cr > Cu. The elevated percentages of total residual fractions in relation to nonresidual fractions of Pb and Cd indicate that high proportions of these metals are strongly bound to the sediments.

The partitioning of heavy metals according to the chemical fractions previously listed could be predominantly influenced by the bonding strengths of the elements, their latent reactivity, and sediment properties (Soon & Bates, 1982). It is generally accepted that the partitioning of heavy metals in environmental matrices provides an indirect assessment of their mobility, bioavailability, and the inherent health and environmental risks. This order offers only qualitative insights about chemical partitioning of heavy metals viz-à-viz their bioavailability in the labile fractions (exchangeable and carbonate bound). Furthermore, it can be asserted that heavy metals in the mobile or "direct effects" (non-residual) fractions are considered to be more bioavailable compared to those found in the residual fraction. These bioavailable heavy metals, due to their toxicity, have serious environmental implications on the water column and portend great risks to organisms living in the water column.

3.2. *Total heavy metal distribution*

Table 4 lists the range, mean, and standard deviation of heavy metals in sediments of the studied ecosystems. Among all the metals studied, Pb shows the highest mean concentration in the sediment for both seasons, followed by Cu. The maximum mean concentration values for Cd (5.3 mg kg^{-1}), Cr (22.1 mg kg^{-1}), Cu (42.8 mg kg^{-1}), Ni (3.2 mg kg^{-1}), and Pb (200.5 mg kg^{-1}) were obtained in sediment collected during the wet season. Intensive fishing activities, sewage drainage from the mainland, and other industrial activities are possible potential sources for the enrichment of these elements, especially Pb and Cu in both seasons. In general, the mean concentrations of Cd, Cu, and Pb in the five studied locations are higher than the sediment quality guidelines for moderately polluted sediments. Mean concentrations of heavy metals in sediment samples is in order: Pb > Cu > Cr > Cd > Ni. The variation in the concentration of these metals between the two seasons may also be attributed to increased absorption, sedimentation and flocculation dynamics that take place in the ecosystem (Matagi et al., 1998).

3.3. *Pollution indices*

3.3.1. *Contamination factor and pollution load index*

The contamination factor values of sediments of all the study sites during the wet and dry seasons are graphically depicted in Fig. 3. The *CF* values recorded for Cu, Cr, and Ni were less than 1 at

Table 3a

Cadmium concentrations (mean ± standard deviation, n = 3 months) and relative abundance in sediment fractions from aquatic ecosystems.

Fraction	Samples (mg kg^{-1})				
	DOU	STB	OKT	QUE	QUR
F_{1W}	0.38 ± 0.02	0.40 ± 0.04	0.37 ± 0.03	0.34 ± 0.01	0.38 ± 0.03
F_{1D}	0.41 ± 0.01	0.33 ± 0.02	0.37 ± 0.01	0.39 ± 0.04	0.36 ± 0.05
F_{2W}	0.35 ± 0.06	0.39 ± 0.02	0.40 ± 0.02	0.39 ± 0.02	0.36 ± 0.02
F_{2D}	0.39 ± 0.02	0.34 ± 0.03	0.41 ± 0.01	0.41 ± 0.01	0.38 ± 0.02
F_{3W}	0.32 ± 0.03	0.33 ± 0.01	0.32 ± 0.04	0.36 ± 0.05	0.33 ± 0.03
F_{3D}	0.38 ± 0.03	0.39 ± 0.02	0.35 ± 0.06	0.33 ± 0.02	0.33 ± 0.04
F_{4W}	0.42 ± 0.06	0.42 ± 0.09	0.43 ± 0.09	0.35 ± 0.06	0.45 ± 0.06
F_{4D}	0.42 ± 0.05	0.39 ± 0.06	0.32 ± 0.01	0.37 ± 0.04	0.41 ± 0.03
F_{5W}	3.20 ± 0.11	3.41 ± 0.01	3.54 ± 0.18	3.24 ± 0.26	3.56 ± 0.51
F_{5D}	3.28 ± 0.15	2.95 ± 0.06	3.40 ± 0.35	3.23 ± 0.09	3.27 ± 0.16
$\sum_{i=1}^{i=5} F_i$	4.67 ± 0.14	4.95 ± 0.10	5.06 ± 0.21	5.05 ± 0.27	5.08 ± 0.52
	4.88 ± 0.16	4.40 ± 0.09	4.85 ± 0.36	4.73 ± 0.11	4.75 ± 0.18
NR, %	31.48	31.11	30.04	35.84	29.92
	32.79	32.95	29.90	31.71	31.16
R, %	68.52	68.89	69.96	64.16	70.08
	67.21	67.05	70.10	68.29	68.84

F_W = wet season; F_D = dry season, NR = non-residual, R = residual; DOU=Douglas Creek; OKT=Okorotip Creek; STB=Stubbs Creek; QUE=Qua Iboe Estuary; QUR=Qua Iboe River

Table 3b

Chromium concentrations (mean ± standard deviation, n = 3 months) and relative abundance in sediment fractions from aquatic ecosystems.

Fraction	Samples (mg kg^{-1})				
	DOU	STB	OKT	QUE	QUR
F_{1W}	0.75 ± 0.07	0.73 ± 0.01	0.53 ± 0.01	0.44 ± 0.07	0.79 ± 0.04
F_{1D}	0.79 ± 0.03	0.76 ± 0.01	0.77 ± 0.11	0.51 ± 0.12	0.60 ± 0.32
F_{2W}	0.82 ± 0.05	0.80 ± 0.01	0.84 ± 0.02	0.79 ± 0.06	0.83 ± 0.00
F_{2D}	0.84 ± 0.08	0.82 ± 0.01	0.80 ± 0.07	0.82 ± 0.08	0.81 ± 0.07
F_{3W}	2.09 ± 0.15	2.14 ± 0.23	2.14 ± 0.08	2.13 ± 0.05	1.63 ± 0.49
F_{3D}	1.98 ± 0.04	2.03 ± 0.04	2.22 ± 0.13	2.10 ± 0.05	2.03 ± 0.17
F_{4W}	7.72 ± 0.87	8.36 ± 0.42	8.83 ± 0.14	8.49 ± 0.58	6.47 ± 2.15
F_{4D}	8.37 ± 0.20	7.85 ± 0.76	8.11 ± 0.48	8.43 ± 0.40	7.31 ± 0.57
F_{5W}	7.67 ± 0.55	8.17 ± 0.16	8.71 ± 0.27	7.94 ± 0.22	5.08 ± 0.41
F_{5D}	7.67 ± 0.49	8.09 ± 0.58	7.46 ± 0.64	8.10 ± 0.54	10.58 ± 0.58
$\sum_{i=1}^{i=5} F_i$	19.05 ± 1.04	20.20 ± 0.50	21.05 ± 0.32	19.79 ± 0.63	14.80 ± 0.66
	19.65 ± 0.54	19.55 ± 0.96	19.36 ± 0.82	19.96 ± 0.69	21.33 ± 0.89
NR, %	59.74	59.55	58.62	59.88	65.68
	60.97	58.62	61.47	59.42	50.40
R, %	40.26	40.45	41.38	40.12	34.32
	39.03	41.38	38.53	40.58	49.60

Table 3c
Copper concentrations (mean ± standard deviation, n = 3 months) and relative abundance in sediment fractions from aquatic ecosystems.

Fraction	Samples (mg kg^{-1})				
	DOU	STB	OKT	QUE	QUR
F_{1W}	1.27 ± 0.07	1.21 ± 0.22	1.31 ± 0.01	1.44 ± 0.07	1.43 ± 0.20
F_{1D}	1.29 ± 0.07	1.32 ± 0.10	1.37 ± 0.11	1.34 ± 0.02	1.42 ± 0.01
F_{2W}	1.76 ± 0.17	1.82 ± 0.12	1.88 ± 0.02	1.87 ± 0.08	1.84 ± 0.11
F_{2D}	1.85 ± 0.09	1.81 ± 0.17	1.80 ± 0.07	1.92 ± 0.04	1.85 ± 0.08
F_{3W}	6.03 ± 0.39	6.05 ± 0.35	5.75 ± 0.08	6.65 ± 0.11	5.28 ± 1.77
F_{3D}	6.09 ± 0.38	6.19 ± 0.46	5.25 ± 0.13	6.77 ± 0.12	5.73 ± 0.76
F_{4W}	14.06 ± 0.68	15.68 ± 0.52	12.79 ± 0.14	14.75 ± 1.91	14.16 ± 3.07
F_{4D}	13.05 ± 1.42	15.36 ± 0.77	17.31 ± 0.48	13.34 ± 1.23	13.77 ± 0.19
F_{5W}	15.45 ± 1.49	17.23 ± 2.52	12.26 ± 0.27	10.93 ± 1.94	16.42 ± 2.88
F_{5D}	15.43 ± 0.23	13.91 ± 0.55	15.01 ± 0.64	11.65 ± 2.51	17.28 ± 1.23
$\sum_{i=1}^{i=5} F_i$	38.57 ± 1.69	41.99 ± 2.61	33.99 ± 0.32	35.64 ± 2.73	39.13 ± 4.57
	37.71 ± 1.49	38.59 ± 1.07	40.74 ± 0.82	35.02 ± 2.80	40.05 ± 1.46
NR, %	59.94	58.97	63.93	69.33	58.04
	59.08	63.95	63.16	66.73	56.85
R, %	40.06	41.03	36.07	30.67	41.96
	40.92	36.05	36.84	33.27	43.15

Table 3d
Nickel concentrations (mean ± standard deviation, n = 3 months) and relative abundance in sediment fractions from aquatic ecosystems.

Fraction	Samples (mg kg^{-1})				
	DOU	STB	OKT	QUE	QUR
F_{1W}	0.21 ± 0.00	0.21 ± 0.00	0.20 ± 0.01	0.20 ± 0.01	0.21 ± 0.01
F_{1D}	0.20 ± 0.01	0.21 ± 0.00	0.21 ± 0.01	0.21 ± 0.00	0.21 ± 0.01
F_{2W}	0.20 ± 0.01	0.20 ± 0.01	0.20 ± 0.01	0.20 ± 0.01	0.15 ± 0.02
F_{2D}	0.20 ± 0.01	0.20 ± 0.02	0.20 ± 0.01	0.21 ± 0.00	0.19 ± 0.02
F_{3W}	0.29 ± 0.01	0.29 ± 0.01	0.28 ± 0.01	0.29 ± 0.02	0.26 ± 0.07
F_{3D}	0.32 ± 0.04	0.30 ± 0.01	0.27 ± 0.02	0.28 ± 0.00	0.30 ± 0.01
F_{4W}	0.41 ± 0.01	0.40 ± 0.02	0.36 ± 0.04	0.33 ± 0.04	0.39 ± 0.05
F_{4D}	0.39 ± 0.02	0.41 ± 0.01	0.38 ± 0.06	0.38 ± 0.02	0.37 ± 0.05
F_{5W}	1.06 ± 0.06	1.13 ± 0.05	1.10 ± 0.05	1.24 ± 0.29	1.16 ± 0.02
F_{5D}	1.13 ± 0.04	1.08 ± 0.07	1.13 ± 0.01	1.19 ± 0.03	1.16 ± 0.01
$\sum_{i=1}^{i=5} F_i$	2.17 ± 0.06	2.23 ± 0.06	2.14 ± 0.07	2.26 ± 0.29	2.17 ± 0.09
	2.24 ± 0.06	2.20 ± 0.07	2.19 ± 0.06	2.27 ± 0.04	2.23 ± 0.06
NR, %	51.15	49.33	48.60	45.13	46.54
	49.55	50.91	48.40	47.58	47.98
R, %	48.85	50.67	51.40	54.87	53.46
	50.45	49.09	51.60	52.42	52.02

Table 3e
Lead concentrations (mean ± standard deviation, n = 3 months) and relative abundance in sediment fractions from aquatic ecosystems.

Fraction	Samples (mg kg^{-1})				
	DOU	STB	OKT	QUE	QUR
F_{1W}	3.02 ± 0.34	3.18 ± 0.22	2.81 ± 0.12	2.80 ± 0.30	3.44 ± 0.11
F_{1D}	2.89 ± 0.05	3.04 ± 0.08	3.02 ± 0.33	2.95 ± 0.34	3.27 ± 0.29
F_{2W}	6.31 ± 0.12	6.09 ± 0.29	5.89 ± 0.26	6.26 ± 0.43	5.71 ± 0.21
F_{2D}	5.95 ± 0.39	5.85 ± 0.18	5.94 ± 0.26	6.34 ± 0.20	6.02 ± 0.34
F_{3W}	10.17 ± 1.16	11.05 ± 1.15	14.15 ± 0.25	13.18 ± 1.86	8.57 ± 1.54
F_{3D}	13.05 ± 2.27	10.76 ± 1.77	13.11 ± 1.62	14.03 ± 0.56	10.31 ± 1.89
F_{4W}	26.46 ± 0.32	22.87 ± 2.97	22.66 ± 4.18	25.08 ± 4.08	27.39 ± 0.97
F_{4D}	24.34 ± 2.50	25.55 ± 1.68	25.09 ± 4.94	23.25 ± 1.12	26.12 ± 0.68
F_{5W}	126.35 ± 4.60	138.06 ± 2.05	134.98 ± 9.80	149.06 ± 29.30	127.51 ± 9.20
F_{5D}	138.20 ± 2.97	133.69 ± 3.99	128,28 ± 8.45	139.18 ± 11.72	133.38 ± 2.71
$\sum_{i=1}^{i=5} F_i$	172.31 ± 4.77	181.25 ± 3.80	180.49 ± 10.66	196.38 ± 29.64	172.62 ± 9.38
	184.43 ± 4.51	178.89 ± 4.68	175.44 ± 9.93	185.75 ± 11.79	179.10 ± 3.40
NR, %	26.67	23.83	25.21	24.10	26.13
	25.07	25.27	26.88	25.07	25.53
R, %	73.33	76.17	74.79	75.90	73.87
	74.93	74.73	73.12	74.93	74.47

Table 4
Ranges (mean ± standard deviation, n = 3) of heavy metal concentrations (mg/kg dry weight) in sediment for the studied ecosystems.

Metal	Wet season (June – August)					Dry season (December – January)				
	DOU	STB	OKT	QUE	QUR	DOU	STB	OKT	QUE	QUR
Cd	2.34–6.10 (4.8 ± 0.8)	4.16–7.32 (5.1 ± 0.6)	2.96–6.54 (5.3 ± 0.4)	1.78–6.41 (4.9 ± 0.5)	2.22–7.10 (5.1 ± 0.4)	3.21–6.99 (5.0 ± 0.6)	2.11–5.33 (4.7 ± 0.2)	3.15–7.10 (4.4 ± 0.7)	1.11–6.30 (5.4 ± 0.4)	2.90–6.61 (4.9 ± 0.6)
Cr	15.7–25.4 (20.1 ± 1.2)	18.6–24.8 (21.2 ± 1.5)	13.7–23.9 (22.1 ± 2.0)	16.1–27.3 (20.3 ± 1.8)	10.7–20.4 (15.3 ± 0.9)	14.9–28.4 (21.6 ± 1.6)	17.4–24.1 (19.4 ± 1.3)	11.6–25.1 (18.9 ± 1.7)	16.4–24.8 (19.1 ± 1.8)	18.9–27.8 (22.4 ± 2.1)
Cu	32.8–57.9 (40.6 ± 2.5)	27.9–63.1 (42.8 ± 1.9)	23.6–49.4 (34.6 ± 2.2)	31.6–60.5 (36.9 ± 1.5)	22.9–74.6 (40.5 ± 2.7)	34.6–49.4 (37.3 ± 1.6)	30.7–56.4 (38.9 ± 2.1)	36.8–64.9 (41.2 ± 1.8)	27.8–46.7 (35.3 ± 1.4)	38.1–73.4 (44.8 ± 2.3)
Ni	0.7–3.1 (2.3 ± 0.6)	0.5–2.5 (2.0 ± 0.4)	1.1–3.4 (2.7 ± 0.8)	1.5–4.7 (3.2 ± 0.5)	1.3–3.9 (2.0 ± 0.2)	0.4–2.9 (2.1 ± 0.2)	0.7–3.9 (2.1 ± 0.5)	0.2–4.6 (2.5 ± 0.4)	0.5–5.1 (2.8 ± 0.7)	0.9–3.8 (2.4 ± 0.5)
Pb	140.1–210.6 (182.1 ± 8.9)	127.6–198.1 (184.2 ± 11.4)	150.7–208.9 (180.1 ± 14.2)	178.6–220.1 (200.5 ± 18.7)	115.4–203.5 (178.1 ± 16.9)	170.5–220.1 (190.4 ± 18.1)	148.9–199.6 (179.4 ± 21.1)	134.8–200.4 (176.4 ± 17.4)	157.4–210.1 (192.6 ± 20.2)	133.5–208.5 (181.6 ± 15.1)

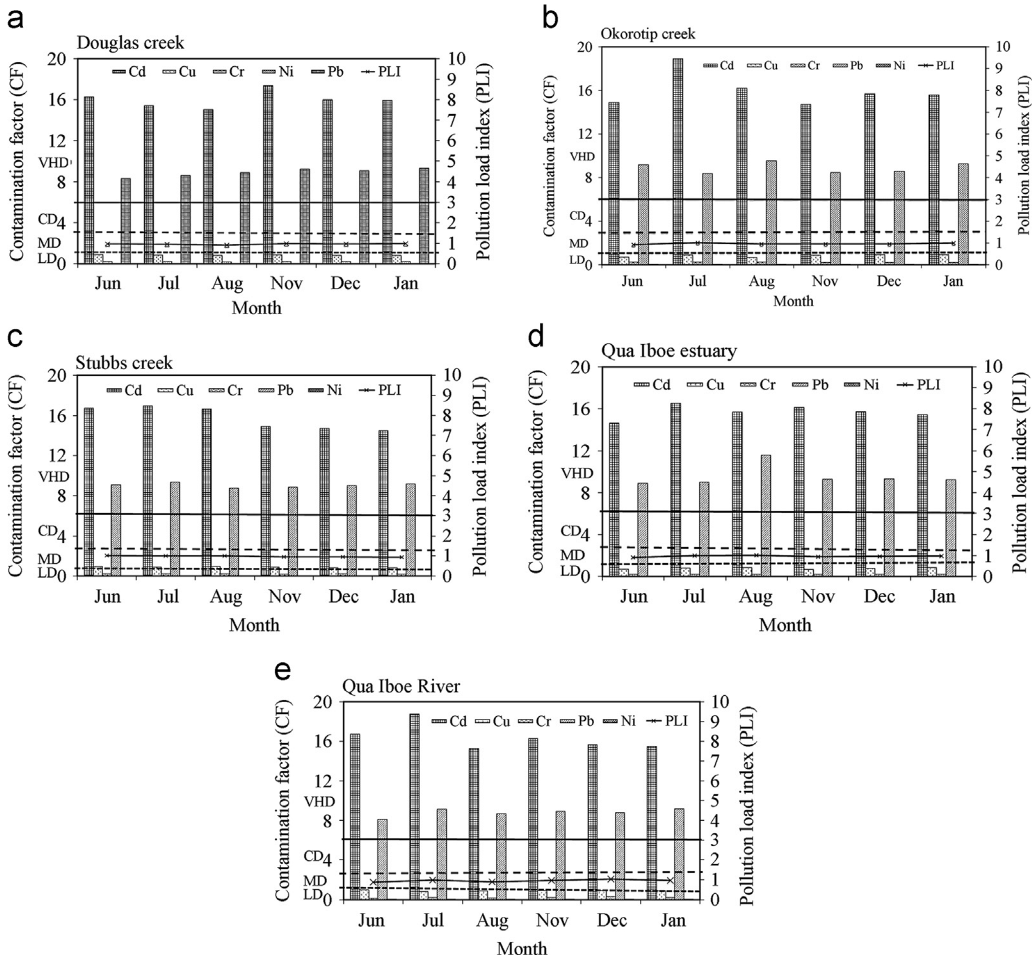

Fig. 3. Description of monthly contamination factors and pollution load index at different study sites. The horizontal square dot, dash and solid lines represent *CF* values of 1.0, 3.0, and 6.0, respectively. (LD = low contamination; MD = moderate contamination; CD =considerable contamination; VHD = very high contamination).

all the studied sites indicating the low degree of sediment contamination with respect to these heavy metals. However, a very high degree of heavy metal pollution arising from Cd and Pb was recorded at all sites during the wet and dry seasons, with Cd having a relatively higher *CF* in the wet season than the dry season. These results could possibly point to significant heavy metals inputs from municipal and agricultural runoff, and industrial discharges. In this study, Ni had the lowest *CF* values among the five studied metals, while Cd recorded the highest *CF* values at all sites. The *CFs* for heavy metals investigated generally followed the trend Cd > Pb > Cu > Cr > Ni. The pollution load indices computed for all the sites are shown in Fig. 3. The PLI values obtained for sites DOU, OKT, STB, QUE and QUR ranged between 0.8 and 1.0 with mean seasonal PLI values less than 1, except during the wet season at site STB, where the mean seasonal PLI value was slightly greater than 1. Again these findings reinforce possible influences of human mediated activities that might have contributed to sediment contamination, and should be of concern in view of various anthropogenic activities that are prevalent in the region.

3.3.2. Geoaccumulation index (I_{geo})

The calculated geoaccumulation index (I_{geo}) values of benthic sedimentary metals are listed in Table 5. As indicated in the

Table 5
Geoaccumulation indices (I_{geo}) of heavy metals for benthic sediments at all investigated sites.

Sites	Metals	Wet season			Dry season		
		Min.	Max.	Mean ± SD	Min.	Max.	Mean ± S.D
DOU	Cd	3.32	3.36	3.36 ± 0.05 [b]	3.40	3.53	3.45 ± 0.07 [b]
	Cr	-2.95	-2.83	-2.83 ± 0.11	-2.83	-2.75	-2.78 ± 0.04
	Cu	-0.89	-0.73	-0.81 ± 0.08	-0.88	-0.78	-0.84 ± 0.05
	Ni	-5.51	2.24	-2.95 ± 4.49	-5.56	-5.49	-5.52 ± 0.03
	Pb	2.47	2.57	2.52 ± 0.04[a]	2.59	2.64	2.62 ± 0.02 [a]
OKT	Cd	3.31	3.66	3.46 ± 0.17 [b]	3.29	3.38	3.35 ± 0.05 [b]
	Cr	-2.70	-2.65	-2.67 ± 0.02	-2.87	-2.75	-2.80 ± 0.06
	Cu	-1.15	-0.73	-1.01 ± 0.24	-0.77	-0.68	-0.72 ± 0.04
	Ni	-5.64	-5.53	-5.57 ± 0.05	-5.60	-5.49	-5.54 ± 0.06
	Pb	2.48	2.67	2.59 ± 0.09 [a]	2.49	2.63	2.55 ± 0.07 [a]
STB	Cd	3.47	3.49	3.48 ± 0.01 [b]	3.26	3.31	3.29 ± 0.02 [b]
	Cr	-2.76	-2.72	-2.74 ± 0.02	-2.85	-2.70	-2.79 ± 0.07
	Cu	-0.76	-0.64	-0.69 ± 0.06	-0.85	-0.74	-0.81 ± 0.06
	Ni	-5.54	-5.50	-5.51 ± 0.02	-5.58	-5.52	-5.54 ± 0.03
	Pb	2.55	2.64	2.59 ± 0.04 [a]	2.55	2.61	2.58 ± 0.02 [a]
QUE	Cd	3.28	3.46	3.38 ± 0.09 [b]	3.36	3.43	3.39 ± 0.03 [b]
	Cr	-2.73	-2.83	-2.77 ± 0.06	-2.86	-2.71	-2.76 ± 0.08
	Cu	-1.09	-0.89	-0.93 ± 0.15	-1.12	-0.82	-0.95 ± 0.15
	Ni	-5.63	-5.29	-5.49 ± 0.17	-5.50	-5.49	-5.49 ± 0.01
	Pb	2.57	2.95	2.69 ± 0.22 [a]	2.62	3.64	2.63 ± 0.01 [a]
QUR	Cd	3.35	3.65	3.49 ± 0.15 [b]	3.37	3.44	3.39 ± 0.03 [b]
	Cr	-3.60	-2.89	-3.22 ± 0.35	-2.98	-2.24	-2.70 ± 0.39
	Cu	-0.94	-0.63	-0.79 ± 0.16	-0.78	-0.71	-0.75 ± 0.03
	Ni	-5.65	-5.51	-5.57 ± 0.07	-5.56	-5.48	-5.51 ± 0.04
	Pb	2.43	2.60	2.52 ± 0.09 [a]	2.55	2.61	2.58 ± 0.03 [a]

[a] Moderate to high contamination.
[b] High contamination based on Müller's (1979) classification.

Table 6
Comparative assessment of RAC levels (%) in benthic sediments for the studied sites inboth wet (and dry) seasons.

Metal	Douglas Creek	Okorotip Creek	Stubbs Creek	Qua Iboe Estuary	Qua Iboe River
Cd	M[a](M)[b]	M (M)	M (M)	M (M)	M (M)
Cr	L (L)	L (L)	L (L)	L (L)	M (L)
Cu	L (L)	L (L)	L (L)	L (M)	L (L)
Ni	M (L)	M (M)	M (M)	M (M)	M (M)
Pb	L (L)	L (L)	L (L)	L (L)	L (L)

L: Low risk; M: Medium risk
[a] wet season
[b] dry season

results, the I_{geo} values for the metals were characterized as uncontaminated by Cr and Cu at all sites during the wet and dry seasons. The sediments were uncontaminated by Ni at all sites except DOU where it exhibited a moderate contamination during the wet season. The I_{geo} values also indicate that benthic sediments were moderately to highly contaminated by Pb at all sites, and highly contaminated (I_{geo} class 4) by Cd in both seasons at the investigated sites.

3.4. *Risk assessment code and environmental implications*

The distributions of the RAC levels (%) in benthic sediments at the five investigated sites are listed in Table S2. A comparative assessment of the RAC values indicates medium risk ($10\% < \text{RAC} \leq 30\%$) for Cd and Ni at all studied sites during the wet and dry seasons (Table 6). However, Pb, Cr, and Cu recorded low risk at all investigated sites for both wet and dry seasons except at site QUR. The value of RAC at QUR was characterized by medium risk for Cr during the wet season. Risk associated with Cu and Pb in the benthic sediments was low at all sites. Moreover, Cu at site QUE indicates a medium risk. Sedimentary Ni at all sites during the wet and dry seasons indicates medium risk except at site DOU, which has a low risk. In general, the RAC values indicated that the sedimentary metals, especially Cd and Ni, were moderately bioavailable with a substantial risk of heavy metal mobilization from benthic sediments in the studied ecosystems to aquatic flora and fauna. The decreasing order of RAC of these five metals in both wet and dry seasons is as follows:

$$\text{Ni} > \text{Cd} > \text{Cu} \approx \text{Cr} > \text{Pb}$$

3.5. *Potential ecological risks (E_f^i)*

Using Eqs. (5) and (6), the potential ecological risk indices E_f^i and R_I for each site were obtained. The calculated R_I for the studied sites is shown in Fig. 4. Also, the percentage contributions of each metal to the net ecological risk index are listed in Table 7. According to these data, Cd poses a very high ecological risk at site QUE in the dry season and a high risk at other sites in both seasons. Additionally, Pb also poses moderate ecological risk at site QUE in the wet season and low risk at other sites in both seasons. The high ecological risks of these two heavy metals in coastal ecosystems are consequences of their high toxic-response factors. The potential ecological risk indices for single regulators (E_f^i)

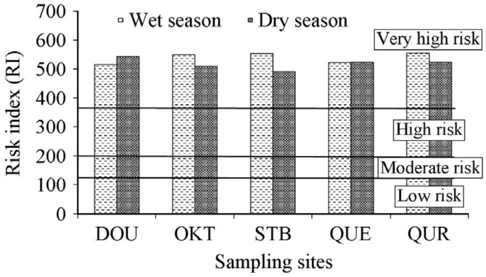

Fig. 4. Multi-elemental potential ecological risk index (R_I) in benthic sediments at the studied sites.

Table 7
Percent contributions of individual heavy metals to overall risk index (R_I).

	DOU		OKT		STB		QUE		QUR	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Cd	90.70	90.64	90.98	90.37	90.86	89.83	89.72	90.27	89.72	90.27
Cr	0.08	0.08	0.09	0.08	0.08	0.09	0.08	0.08	0.08	0.08
Cu	0.83	0.77	0.68	0.89	0.84	0.87	0.75	0.74	0.75	0.74
Ni	0.03	0.03	0.02	0.03	0.02	0.032	0.03	0.03	0.03	0.03
Pb	8.36	8.48	8.21	8.62	8.19	9.18	9.40	8.87	9.40	8.87

indicate that the severity of pollution of the five heavy metals decreased in the following sequence: Cd > Pb > Cu > Cr > Ni.

The sensitivity of various biological communities to toxic substances and the potential ecological risk caused by heavy metals are represented by R_I. The spatial distribution values for Cd single potential ecological risk contribution to the overall potential risk index are substantially above 80% (Table 7). Similar findings indicating significant contribution by Cd to R_I have been reported by Maanan et al. (2013). However, the individual potential ecological risk factors for Cr, Cu, and Ni at all sites were very low with less than a 1% contribution to the general risk indices (R_I), indicating low potential ecological risk. More so, the E_f^i values for Pb were generally greater than 40 ($40 < E_f^i < 80$), with between 8 and 10% contribution to the overall potential ecological risk index. This implies that Pb caused moderate ecological risk.

The multi-elemental potential ecological risk indices at all sampling sites during the wet and dry seasons exceeded 450 (Fig. 4), indicating very high ecological risk. However, the severity of contamination by percentage contribution to the overall potential ecological risk index followed the sequence: Cd > Pb > Cu > Cr > Ni. This trend agrees with the contamination sequence obtained for other risk assessment indices used in this study and other reports (Benson et al., 2016a; Hou et al., 2013; Maanan et al., 2013; Ruiz et al., 2006).

4. Conclusions

Heavy metal pollution is an important issue in the Niger Delta ecosystem. The aim of this paper was to study the regional impacts of heavy metals (Cd, Cr, Cu, Pb, and Ni) in the benthic sediments of the major aquatic ecosystems. On the basis of investigations at five locations within the area, heavy metal concentrations in the benthic sediments were measured, and pollution indices and potential ecological risk indices were calculated. In general, the mean concentrations of Cd, Cu, and Pb at the five studied locations are higher than the sediment quality guidelines for moderately polluted sediments. The geoaccumulation Index (*Igeo*) and Contamination Factor (CF) values of these heavy metals reveal that sediment samples are moderately to strongly polluted by Cd and Pb at all sites during the wet and dry seasons. The RAC values indicate moderate risk for Cd and Ni and low risk for Cr, Cu, and Pb at all studied sites during the wet and dry seasons. Analysis of the potential ecological risk of sediment heavy metal concentrations shows that all the sample sites experienced a relatively high ecological risk for Cd and low risk for other metals in both seasons. The order of potential ecological risk generally followed the pattern Cd > Pb > Cu > Cr > Ni, in which the potential ecological risks of Cd, Pb, and Cu are in accordance with their overall accumulations in the study area. Multi-elemental potential ecological risk indices indicate high ecological risk at all sampling sites during both seasons.

Authors' contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of interest

The authors declare no competing interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ijsrc.2017.07.007.

References

Bacon, J. R., & Davidson, C. M. (2008). Is there a future for sequential chemical extraction? *Analyst*, *133*, 25–46.

Bastami, K. D., Bagheri, H., Kheirabadi, V., Zaferani, G. G., Teymori, M. B., Hamzehpoor, A., & Ganji, S. (2014). Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. *Marine Pollution Bulletin*, *81*, 262–267.

Benson, N. U., Adedapo, A. E., Eritobor, A. L., & Udosen, E. D. (2015). Total dissolved inorganic carbon and physicochemical characteristics of surface microlayer and upper mixed layer water from Lagos Lagoon, Nigeria. *Global NEST Journal*, *17*(2), 334–343.

Benson, N. U., Anake, W. U., Essien, J. P., Enyong, P. A., & Olajire, A. A. (2017). 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*, *11*(3), 434–449. http://dx.doi.org/10.1016/j.jtusci.2016.08.004.

Benson, N. U., Anake, W. U., & Olanrewaju, I. O. (2013). Analytical relevance of trace metal speciation in environmental and biophysicochemical systems. *American Journal of Analytical Chemistry*, *4*, 633–641.

Benson, N. U., Asuquo, F. E., Williams, A. B., Essien, J. P., Ekong, C. I., Akpabio, O., & Olajire, A. A. (2016a). Source evaluation and trace metal contamination in benthic 1 sediments from equatorial ecosystems using multivariate statistical techniques. *PLoS One*, *11*(6), 1–19. http://dx.doi.org/10.1371/journal.pone.0156485.

Benson, N. U., Enyong, P. A., & Fred-Ahmadu, O. H. (2016b). Trace metal contamination characteristics and health risks assessment of Commelina africana L. and psammitic sandflats in the Niger Delta, Nigeria (*Article ID 8178901*). *Applied and Environmental Soil Science* (pp. 1–14), 1–14. http://dx.doi.org/10.1155/2016/8178901.

Benson, N. U., & Etesin, U. M. (2008). 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*, *28*(3), 195–202.

Benson, N. U., Udosen, E. D., & Akpabio, O. (2009). Interseasonal distribution and partitioning of heavy metals in subtidal sediment of Qua Iboe Estuary and associated creeks, Niger Delta (Nigeria). *Environmental Monitoring and Assessment*, *146*(1-3), 253–265.

Buccolieri, A., Buccolieri, G., Cardellicchio, N., Dell'Atti, A., Di Leo, A., & Maci, A. (2006). Heavy metals in marine sediments of Taranto Gulf, Ionian sea, Southern Italy. *Marine Chemistry*, *99*, 227–235.

Gao, X., & Chen, C. T. A. (2012). Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Research*, *46*, 1901–1911.

Gao, X., Chen, C. T. A., Wang, G., Xue, Q., Tang, C., & Chen, S. (2010). Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique. *Estuarine, Coastal and Shelf Science*, *86*, 369–378.

Goher, M. E., Farhat, H. I., Abdo, M. H., & Salem, S. G. (2014). Metal pollution assessment in the surface sediment of Lake Nasser, Egypt. *Egyptian Journal of Aquatic Research*, *40*, 213–224.

Gong, Q., Deng, J., Xiang, Y., Wang, Q., & Yang, L. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences*, *19*(3), 230–241.

Håkanson, L. (1980). Ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, *14*, 975–1001.

Hill, N. A., Simpson, S. L., & Johnston, E. L. (2013). Beyond the bed: Effects of metal contamination on recruitment to bedded sediments and overlying substrata. *Environmental Pollution*, *173*, 182–191.

Horst, M. F. (1997). Heavy metal distribution in sediments and ecological risk assessment: The role of diagenetic processes in reducing metal toxicity in bottom sediments. *Environmental Pollution*, *97*, 317–325.

Hou, D., He, J., Lü, C., Ren, L., Fan, Q., Wang, J., & Xie, Z. (2013). *Distribution characteristics and potential ecological risk assessment of heavy metals (Cu, Pb, Zn, Cd) in water and sediments from Lake Dalinouer, China*. *Ecotoxicology and Environmental Safety*, 93.

Huang, L., Pu, X., Pan, J. F., & Wang, B. (2013). Heavy metal pollution status in surface sediments of Swan Lake lagoon and Rongcheng Bay in the northern Yellow Sea. *Chemosphere*, *93*(9), 1957–1964. http://dx.doi.org/10.1016/j.chemosphere.2013.06.080.

Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, *38*, 569–578.

Kalloul, S., Hamid, W., Maanan, M., Robin, M., Sayouty, E. H., & Zourarah, B. (2012). Source contributions to heavy metal fluxes into the Loukous Estuary (Moroccan Atlantic Coast). *Journal of Coastal Research*, *28*(1), 174–183.

Leung, H. M., Leung, A. O. W., Wang, H. S., Ma, K. K., Liang, Y., Ho, K. C., & Yung, K. K. L. (2014). Assessment of heavy metals/metalloid (As, Pb, Cd, Ni, Zn, Cr, Cu, Mn) concentrations in edible fish species tissue in the Pearl River Delta (PRD), China. *Marine Pollution Bulletin*, *78*(1–2), 235–245.

Li, F., Zeng, X. Y., Wu, C. H., Duan, Z. P., Wen, Y. M., Huang, G. R., & Xu, J. Y. (2013). Ecological risks assessment and pollution source identification of trace elements in contaminated sediments from the Pearl River Delta, China. *Biological Trace Element Research*, *155*, 301–313.

Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., & He, X. (2012). Integrated assessment of heavy metal contamination in sediments from a Coastal Industrial Basin, NE China. *PLoS One*, *7*(6), 039690. http://dx.doi.org/10.1371/journal.pone.0039690.

Lin, Y. C., Chang-Chien, G. P., Chiang, P. C., Chen, W. H., & Lin, Y. C. (2013). Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan. *Marine Pollution Bulletin*, *76* (1-2), 266–275.

Maanan, M., Landesman, C., Maanan, M., Zourarah, B., Fattal, P., & Sahabi, M. (2013). Evaluation of the anthropogenic influx of metal and metalloid contaminants into the Moulay Bousselham lagoon Morocco, using chemometric methods coupled to geographical information systems. *Environmental Science and Pollution Research*, *20*, 4729–4741.

MacDonald, D. D., Carr, R. S., Calder, F. D., Long, E. R., & Ingersoll, C. G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, *5*, 253–278.

MacDonald, D. D., Ingerosoll, C. G., & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, *39*, 20–31.

Matagi, S. V., Swai, D., & Mugabe, R. (1998). Heavy metal remove/mechanisms in wetlands. *African Journal of Tropical Hydrobiology and Fisheries*, *8*, 23–35.

Morelli, G., & Massimo, G. (2014). Metal contamination of estuarine intertidal sediments of Moreton Bay, Australia. *Marine Pollution Bulletin*, *89*(1-2), 435–443.

Müller, G. (1979). Heavy metals in the sediment of the Rhine-changes seity. 1971. *Umschau Wissenschaff und Technik*, *79*, 778–783.

Nemati, K. A., Bakar, N. K., Abas, M. R., & Sobhanzadeh, E. (2011). Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *Journal of Hazardous Materials*, *192*, 402–410.

Passos, E. D. A., Alves, J. C., dos Santos, I. S., Alves, J. D. P. H., Garcia, C. A. B., & Spinola, C. A. C. (2010). Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal*, *96*, 50–57.

Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanette, M. L., & Orio, A. A. (1985). Heavy metal speciation in the sediments of Northern Adriatic Sea: A new approach for environmental toxicity determination In: T. D. Lekkas (Ed.), *Heavy metals in the environment*, 2 (pp. 454–456). Edinburgh CEP Consultants.

Radojevic, M., & Bashkin, V. N. (1999). *Practical environmental analysis*. Cambridge: Royal Society of Chemistry.

Rahman, M. A., & Ishiga, H. (2012). Trace metal concentrations in tidal flat coastal sediments, Yamaguchi Prefecture, Southwest Japan. *Environmental Monitoring and Assessment*, *184*, 5755–5771.

Ruiz, F., Abad, M., Olias, M., Galan, E., Gonzalez, I., Aguila, E., & Cantano, M. (2006). The present environmental scenario of the Nador Lagoon (Morocco). *Environmental Research*, *102*, 215–229.

Saleem, M., Iqbal, J., & Shah, M. H. (2015). Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—A case study from Mangla Lake, Pakistan. *Environmental Nanotechnology, Monitoring Management*, *4*, 27–36. http://dx.doi.org/10.1016/j.enmm.2015.02.002.

Soon, Y. K., & Bates, T. E. (1982). Chemical pools of cadmium, nickel and zinc in polluted soil and some preliminary indications of their availability to plants. *Journal of Soil Science*, *33*, 477–488.

Sundaray, S. K., Nayak, B. B., Lin, S., & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments – A case study: Mahanadi basin, India. *Journal of Hazardous Materials*, *186*, 1837–1846.

Suresh, G., Ramasamy, V., Meenakshisundaram, V., Venkatachalapathy, R., & Ponnusamy, V. (2011). Influence of mineralogical and heavy metal composition on natural radionuclide contents in the river sediments. *Applied Radiation and Isotopes*, *69*, 1466–1474.

Tessier, A., Campell, P., & Bison, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, *51*(7), 844–850.

Tessier, E., Garnier, C., Mullot, J. U., Lenoble, V., Arnaud, M., Raynaud, M., & Mounier, S. (2011). Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). *Marine Pollution Bulletin*, *62*, 2075–2086.

Tomlinson, D. C., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy metals levels in estuaries and the formation of pollution index. *Helgolander Wissenschaff Meeresuntersuchungen*, *33*, 566–569.

Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the Earth's crust. *Geological Society of American Bulletin*, *72*, 175–192.

Usman, A. R. A., Alkredaa, R. S., & Al-Wabel, M. I. (2013). Heavy metal contamination in sediments and mangroves from the coast of Red Sea: Avicennia marina as potential metal bioaccumulator. *Ecotoxicology Environmental Safety*, *97*, 263–270.

Uzairu, A., Harrison, G. F. S., Balarabe, M. L., & Nnaji, J. C. (2009). Concentration levels of trace metals in fish and sediment from Kubanni River, Northern Nigeria. *Bulletin Chemical Society Ethiopia*, *23*, 9–17.

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials*, *195*, 355–364.

Wang, Y., Yang, L., Kong, L., Liu, L., Wang, L., & Zhu, J. (2015). Spatial distribution, ecological risk assessment and source identification for heavy metals in surface sediments from Dongping Lake, Shandong, East China. *CATENA*, *125*, 200–205.

Williams, A. B., & Benson, N. U. (2010). Interseasonal hydrological characteristics and variabilities in surface water of tropical estuarine ecosystems within Niger Delta, Nigeria. *Environmental Monitoring and Assessment*, *165*, 399–406. http://dx.doi.org/10.1007/s10661-009-0955-0.

Yu, G. B., Liu, Y., Yu, S., Wu, S. C., Leung, A. O. W., Luo, X. S., & Wong, M. H. (2011). Inconsistency and comprehensiveness of risk assessments for heavy metals in urban surface sediments. *Chemosphere*, *85*, 1080–1087.

Yuan, G. L., Liu, C., Chen, L., & Yang, Z. (2011). Inputting history of heavy metals into the inland lake recorded in sediment profiles: Poyang Lake in China. *Journal of Hazardous Materials*, *185*, 336–345.

Zahra, A., Hashmi, M. Z., Malik, R. N., & Ahmed, Z. (2014). Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-Feeding tributary of the Rawal Lake Reservoir, Pakistan. *Science of the Total Environment*, *470*, 925–933.

Zhuang, W., & Gao, X. (2014). 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*, *9*, e94145. http://dx.doi.org/10.1371/journal.pone.0094145.