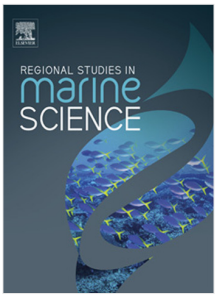
Accepted Manuscript



New ecological risk indices for evaluating heavy metals contamination in aquatic sediment: A case study of the Gulf of Guinea

Nsikak U. Benson, Adebusayo E. Adedapo, Omowunmi H. Fred-Ahmadu, Akan B. Williams, Essien D. Udosen, Olusegun O. Ayejuyo, Abass A. Olajire

PII: S2352-4855(16)30205-5
DOI: https://doi.org/10.1016/j.rsma.2018.01.004
Reference: RSMA 349

To appear in: *Regional Studies in Marine Science*

Received date : 29 September 2016
Revised date : 5 January 2018
Accepted date : 6 January 2018

Please cite this article as: Benson N.U., Adedapo A.E., Fred-Ahmadu O.H., Williams A.B., Udosen E.D., Ayejuyo O.O., Olajire A.A., New ecological risk indices for evaluating heavy metals contamination in aquatic sediment: A case study of the Gulf of Guinea. *Regional Studies in Marine Science* (2018), https://doi.org/10.1016/j.rsma.2018.01.004

New Ecological Risk Indices for Evaluating Heavy Metals Contamination in Aquatic Sediment: A Case Study of the Gulf of Guinea

[a*]Nsikak U. Benson, [a]Adebusayo E. Adedapo, [a]Omowunmi H. Fred-Ahmadu, [a]Akan B. Williams, [b]Essien D. Udosen, [a,c]Olusegun O. Ayejuyo, [d]Abass A. Olajire

[a]Analytical and Environmental Chemistry Unit, Department of Chemistry, Covenant University, Ota, Nigeria.
[b]Department of Chemistry, University of Uyo, Akwa Ibom State, Nigeria.
[c]Department of Chemistry, University of Lagos, Lagos, Nigeria.
[d]Industrial and Environmental Chemistry Unit, Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria.

*Corresponding Author: Email address:- nsikak.benson@covenantuniversity.edu.ng; Tel.:- +234-8077620692

Abstract

New indices - modified hazard quotient (*m*HQ) and ecological contamination index (ECI) - were developed for the evaluation of heavy metals contamination of sediment. Sequential extraction method was employed to determine the levels of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) in subtidal sediment samples from tropical ecosystems off the Gulf of Guinea. The results were used to assess the degree of contamination and estimate the extent of anthropogenic inputs from industrial activities. Results indicated that the concentrations of Cd, Cr, Cu, Ni and Pb ranged from 4.33 – 5.67, 11.12 – 28.52, 30.26 – 43.72, 2.02 – 2.60 and 162.0 – 190.37 mg/kg dw, respectively. The mean metal levels did not show significant variations among study sites during the wet and dry seasons. Spatial distribution and severity of sediment-associated contamination by heavy metals based on the newly developed indices (*m*HQ and ECI) were in good agreement with existing pollution indices and followed the descending sequence: Cd>Pb>Cu>Cr>Ni. Contamination severity index, mean hazard quotient and modified risk assessment code were also used to evaluate the sediment-heavy metal contamination, which generally indicated medium risk contamination of the investigated ecosystems. Aquatic pollution indicators (potential contamination index, ECI, hazard quotients, *m*HQ) revealed significant anthropogenic contamination by Cd and Pb, while Cr, Cu and Ni showed relatively low degree of contamination. Potential contamination index (PCI) generally followed the sequence Cd>Pb>Cu>Cr>Ni. A comparison of newly proposed indices with existing pollution indices revealed very good agreement. The contamination trends derived from the new indices were consistent and took into consideration site specificity, toxicity and a three-tier effect levels (threshold, mid-range and extreme effects guideline values) that support their reliability in evaluating contaminated aquatic ecosystems.

Key words: Sediment pollution indices; Heavy metals; Sediment quality; Ecological risks; New pollution indices; Contamination assessment.

1. Introduction

Sediments are important repositories of contaminants for trophic transfer and sources of pollution to the aquatic biota and environment with which they are associated. Recent investigations have indicated that contaminants such as heavy metals, organic chemicals, nutrients and pathogens in sediments are ubiquitous and pose substantial risks to humans and benthic communities (Ayejuyo et al., 2010; Benson et al., 2016a,b; Lin et al., 2013; Liu et al., 2014; Maanan et al., 2015; Morelli & Gasparon, 2014; Pan et al., 2014; Passos et al., 2010; Saleem et al., 2015; Tornero et al., 2014). Given the persistency, bio-accumulative and toxicity peculiarities of inorganic contaminants in the environment, the index-based contamination approach for classifying aquatic sediment becomes extremely imperative. Heavy metal pollution of sediments is of major concern because of their toxic effects, ability to accumulate in tissues of aquatic biota and considerable non-degradability (Díaz-de Alba et al., 2011; Saleem et al., 2015; Pejman et al., 2015; Wang et al., 2012; Zhang et al., 2012).

Sediments are known storehouses of heavy metals (Addo et al., 2012; Benson & Etesin, 2008; Benson et al., 2008a; Nilin et al., 2013) and the estimation of sedimentary heavy metal contamination and associated ecological risks can be evaluated using consensus- based indices (Atibu et al., 2016; Benson et al., 2017; Harikumar & Nasir, 2010; Håkanson, 1980; Kalender & Uçar, 2013; Malvandi, 2017; Perin et al., 1985; Goher et al., 2014). Sediment quality guidelines and background values are widely used in ecological risk assessments to determine heavy metal contamination in aquatic ecosystems (Burton, 2002). Several empirical and statistical approaches have also been developed in response to environmental concerns and as valuable contamination tools for monitoring aquatic ecosystems. Although these approaches have been in place since the early eighties and are widely accepted and employed in sediments studies, they have limitations and vary in reliability.

The Qua Iboe River, estuary and associated tidal wetlands are situated in the northeastern section of the Gulf of Guinea. This system is a complex network of eco-hydrological biotopes, characterized by fine sand-flats covering about 560 km^2 that are dominated by vast intertidal mangrove swamps, freshwater bodies and euryhaline creeks. The studied mangrove ecosystems, creeks and rivers are located in the Niger Delta region of Nigeria. The region experiences a relatively significant amount of precipitation and has a humid tropical climate with relatively invariable monthly temperatures. The hydrological conditions in the aquatic ecosystems are controlled by persistent strong winds and coastal upwelling from the equatorial Atlantic Ocean. Various coastal aquatic ecosystems in the study area serve as prime receivers of industrial effluents, oil spills and chemical contaminations produced by multi-national petroleum firms established on- and off-shore the Atlantic coastline (Asuquo, 1991; Essien & Antai, 2005; Onojake & Frank, 2013; Udosen & Benson, 2006; Benson et al., 2017). Increased concentrations of heavy metals, petroleum hydrocarbons, and high molecular weight organic contaminants in estuarine sediments, surface water, aquatic plants and organisms have been reported (Benson et al., 2007, 2008b, 2016a,b; Essien et al., 2008).

The objectives of the present study are: (a) to investigate the extent of heavy metal contamination in multiple tropical estuaries and creeks off the Gulf of Guinea using some contamination indices (PCI, RAC, *mRAC*, CSI), (b) to establish their contamination statuses using sediment quality guidelines, and (c) to develop two new indices using the derived data in an effort to establish a model system for evaluating heavy metal contamination in sediments.

2. Materials and Method

2.1 Study sites, sample collection and pretreatment

Five (5) mesotidal and intertidal coastal water systems were considered in the present study. The ecosystems include Douglas Creek (DOU), Okorotip Creek (OKT), Stubbs Creek (STB), Qua Iboe Estuary (QUE) and Qua Iboe River (QUR) (Fig. 1, Table 1). Three (3) sampling sites within the water bodies of each ecosystem were clearly designated for the collection of benthic sediments during the wet (June - August) and dry (November - January) seasons of the year. In every investigated aquatic ecosystem, triplicate samples of benthic sediment from each identified site were collected monthly using a van Veen Grab Sediment Sampler. The samples were pooled and the resultant composite samples were appropriately labeled. Fifteen (15) benthic sediment samples were collected every month from five (5) investigated locations between June and August, for the wet season, bringing about forty-five (45) benthic samples for the period. A comparative routine was carried out for the dry season months (November, December and January). Consequently, ninety (90) sediment samples were collected from the study areas in the course of the investigation. The collected samples were stored in ice-pressed coolers and transported to the laboratory. In order to maintain the integrity of the samples, they were additionally treated by refrigeration at 4°C to inactivate microorganisms. Standard quality control and quality assurance procedures were strictly observed during sample collection, transportation and storage. In the laboratory, the thawed sediment samples were dried in an oven maintained at 105±0.5°C, homogenized, ground using a hand mortar and sieved through a 2 mm mesh sieve before selective leaching. Subsamples were acquired from the individual composite samples by coning and quartering techniques (Benson et al., 2016a, 2017).

Table 1: Details of study area and sampling

Location	Type of ecosystem	Coordinates	Sampling Period	
			Wet season	Dry season
Douglas Creek	Freshwater	4.55°S, 8.00°N	June, July, August	November, December, January
Okorotip Creek	Freshwater	4.56°S, 7.93°N	June, July, August	November, December, January
Stubbs Creek	Freshwater	4.60°S, 7.99°N	June, July, August	November, December, January
Qua Iboe Estuary	Estuarine	4.53°S, 7.99°N	June, July, August	November, December, January
Qua Iboe River	Riverine	4.58°S, 7.93°N	June, July, August	November, December, January

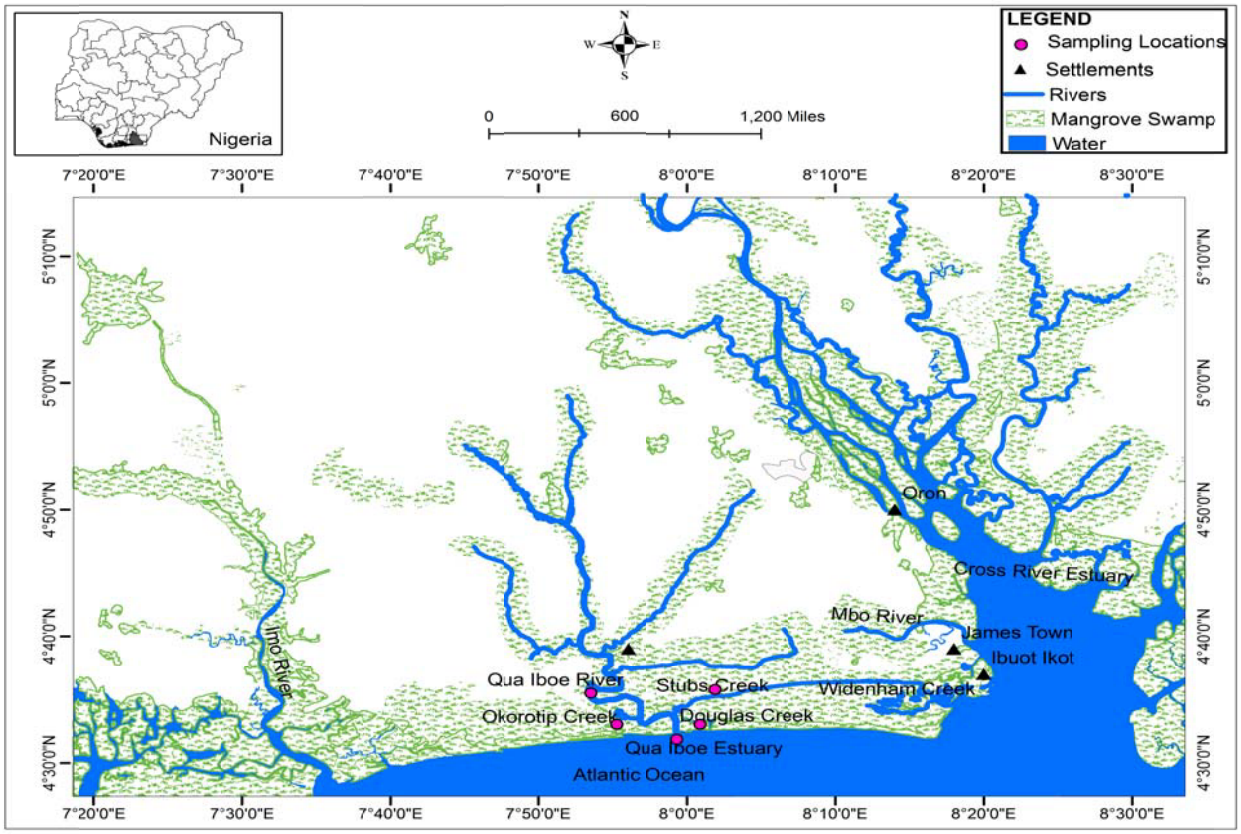


Figure 1: The investigated estuarine, creeks and freshwater ecosystems off the Gulf of Guinea

2.2 Fractionation procedure and chemical analysis of metals

The geochemical fractionation procedure of Tessier et al. (1979) was used in this study for the extraction of heavy metals. The selective speciation method is designed to separate heavy metals into five (5) operationally defined fractions: exchangeable (F1), carbonate bound (F2),

Fe-Mn oxide-bound (F3), organic bound (F4) and residual fractions (F5). A summary of the procedure is as follows:

Exchangeable (F1): 1.0 g of sieved sediment was extracted at room temperature for one hour with 8.0 mL of 1 M $MgCl_2$ solution at pH 7.0 with continuous agitation.

Carbonate-bound (F2): Sediment residue from fraction 1 was leached at room temperature with 8.0 mL of 1 M sodium acetate at a pH of 5.0 (adjusted using acetic acid) with continuous agitation.

Fe-Mn Oxide-bound (F3): The sediment residue obtained from fraction 2 was extracted with 20 mL of 0.04 M hydroxyl ammonium chloride in 25% (v/v) acetic acid for 6 hr at 96°C with occasional agitation of the solution.

Organic-bound (F4): The residue in fraction 3 was extracted with 3.0 mL of 0.02 M nitric acid and 5.0 mL of 30% hydrogen peroxide solution and heated for 2 hr at 85°C with intermittent agitation. 3.0 mL of 30% hydrogen peroxide was added and pH of mixture was adjusted to 2.0 using nitric acid, and then heated at 85°C for 3 hr with continuous agitation. On cooling, 5.0 mL of 3.2 M ammonium acetate in 20% (v/v) nitric was added and the mixture was subsequently diluted to 20.0 mL with continuous agitation for 30 min.

Residual (F5): The residue from F4 was digested in a Teflon vessel with a mixture of 50 mL of 40% hydrofluoric acid and 75 mL of 60% perchloric acid. The mixture was evaporated to dryness and 2.0 mL of 60% perchloric acid was then added and evaporated until white fumes were produced. The resultant residue was digested in 50 mL of 3 M hydrochloric acid.

Following each successive extraction, the mixtures were centrifuged at 14400 × g for 30 min. The supernatants were carefully removed with pipette, filtered with 0.2 μm pore polycarbonate membrane filters, and analyzed for metals. In between the extraction steps, samples were shaken for 30 min, with 8 cm^3 of de-ionized distilled water, centrifuged and the wash solutions

discarded. All extractions were done in triplicate to determine the precision of the method and spiked samples were carried out for the recoveries of the metals under investigation. Inductively coupled plasma atomic emission spectrometry (Optima 2000 DV Perkin Elmer was used for the determination of heavy metals in the sample extracts. Replicate samples, calibration standards, and method blanks were used to monitor the performance of the instrument and the quality of the data. The precision and the reproducibility of the extraction method were ascertained by carrying out triplicate analyses of the samples. For each of the extraction steps, appropriate blank preparations and determinations were carried out and the results subtracted from the concentrations found in the respective fractions of the extracts. The concentrations of the blanks for each fraction were deducted from the concentrations of respective fractionation extracts. The calibration standards were prepared by appropriate dilutions of commercially available stock solutions (1000 µg/mL BDH Grade) of the heavy metals determined. The limits of detection (LOD) for Cd, Cr, Cu, Pb and Ni were 0.02, 0.01, 0.02, 0.02 and 0.01 mg/kg, respectively.

2.3 Statistical analysis and GIS Mapping of Spatial Variability of Hazard Quotient

The XLSTAT-Pro Software (AddinSoft, USA) was used for data analysis. The Principal Component Analysis (PCA) was used to investigate the correlation among the identified metals in the subtidal sediment samples, while the Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were applied to evaluate fitness of data for PCA. A KMO difference of $p < 0.05$ was estimated to be significant and data were considered adequate for PCA. The ArcGIS10.2 software developed by Environmental Systems Research Institute, USA was employed for mapping the spatial variability of the modified hazard quotient. Moreover, a linear pre-aggregate of the observed data with weighted average results was employed to predict the concentrations of heavy metals at un-sampled locations within the studied ecosystems. This approach usually

incorporates distance and the direction of changes as a reflection of the spatial correlation between sample points into the interpolation to produce more sophisticated predictions. In this research, the geospatial data analysis, prediction and map generation were achieved using Ordinary Kriging. The underlying assumption for this statistical model is the non-existence of constant mean for the observed data over the aggregate average (i.e., no trend) (Wang et al., 2014).

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i) \qquad (i)$$

where, $Z^*(x_0)$ is the predicted value of Z at point x_0, $Z(x_i)$ is the observed value at point x_i and λ_i is the weight placed on $Z(x_i)$.

2.4 Potential contamination index (PCI)

Trace metals in aquatic sediments usually occur as complex mixtures with significant spatial and temporal variability; therefore, the potential contamination index of metal *i* (*PCIi*) was calculated using the following equation proposed by Davaulter & Rognerud (2001):

$$PCI_i = \frac{C^i_{\max}}{C_{bkg}} \qquad (ii)$$

where, PCI_i is the potential contamination index of metal *i*, $C^i_{\max}$ is the maximum concentration of metal *i* in the sediment, and C_{bkg} indicates the background concentration {geochemical background value of metal in the reference average shale (Turekian & Wedepohl, 1961)} of the same trace metal. Three grades are considered for the classification of sediment: PCI<1 indicates low contamination, 1< PCI <3 as moderate contamination, and PCI > 3 being considered as severe or very severe contamination (Davaulter & Rognerud, 2001).

2.5 Modified Risk Assessment Code (*mRAC*)

The evaluation of metal contamination in sediment samples in terms of their toxicity and bioavailability is an important aspect of pollution characterization that establishes risk information related to sediment-associated metals as well as their binding strength (Benson et al., 2013; Gao & Chen, 2012; Zhuang & Gao, 2014). The modified risk assessment code (*m*RAC) is an aggregative-based contamination index proposed for the evaluation of sediment-associated heavy metal pollution (Saeedi & Jamshidi-Zanjani, 2015). It incorporates the toxicity and bioavailability of heavy metals in marine and freshwater ecosystems in assessing the degree of metal pollution. In heavy metal pollution chemistry, it is widely believed that chemical fractionation provides more information on the bioavailability and biotoxicity (Duan et al., 2010; Gao & Chen, 2012; Yu et al., 2013), which are key components of this formulation. In the present study, *m*RAC was calculated using the following relationship:

$$mRAC = \frac{\sum_{i=1}^{n} T_{r_i} RAC_i}{\sum_{i=1}^{n} T_{r_i}} \qquad (iii)$$

where, T_{r_i} = the toxic-response factor for single metal *i*, RAC_i = risk assessment code of i^{th} metal derived from summation of percentage concentration of metal from the exchangeable and bound to carbonates fraction (Perin et al., 1985), and n = the total number of heavy metals. The ranking of modified risk assessment code as proposed by Saeedi & Jamshidi-Zanjani (2015) was adopted. However, the presentation of *m*RAC as a unit-less index was found inappropriate. In this report, a modification to the original classification was introduced to include the unit percentage of metals in the bioavailable fractions such that *m*RAC < 1% indicates no potential adverse effect, *m*RAC = 1 – 9% shows low potential adverse effect, *m*RAC = 10 – 29% reflects medium potential adverse effect, *m*RAC = 30 – 49% indicates high potential adverse effect, and

*m*RAC = 50% shows that aquatic sediments may pose very high adverse effect with associated possibility of heavy metals being readily bioavailable.

2.6 Ecotoxicological assessment of heavy metal concentrations in sediments

In the last two decades, numerous scientifically established sediment quality guidelines (SQGs) have evolved. The SQGs are important tools for determining the magnitude of sediment pollution associated with a particular heavy metal through comparison of the detected metal concentration in sediment with the correlative reference criteria (MacDonald et al., 2000). Such empirical approaches are widely used for sediment characterization and they typically present two threshold levels, one below which adverse biological effects rarely occur such as effects range low (ERL), minimal effect threshold (MET), lowest effect level (LEL), and threshold effect level (TEL), and one above which adverse biological effects frequently or likely occur. This gradation includes the effect range median (ERM), probable effects level (PEL), severe effect level (SEL), and toxic effect threshold (TET) (Burton, 2002; MacDonald et al., 1996; USEPA, 2005; Zhuang & Gao, 2014) (Table 2). In the present work, comparisons of trace metal (Zn, Pb, Cd, Ni, and Cr) concentrations (mg/kg) in benthic sediments from the studied ecosystems with threshold, midrange and extreme effects guideline values were carried out. Selected guideline values were employed for the calculation of mean probable effects level quotient, mean effect range median quotient, hazard quotient, contamination severity index, potential severity index and ecological contamination risk index.

Table 2: Threshold, midrange and extreme effects sediment guidelines for selected metals (mg/kg)

Sediment Quality Guidelines		Cu	Pb	Cd	Ni	Cr	Reference
ERL		70	35	5	30	80	MacDonald et al. (2000)
TEL		35.7	35	0.6	18	37.3	" " " " "
MET		28	42	0.9	35	55	" " " " "
ERM		390	110	9	50	145	" " " " "
PEL		197	91.3	3.53	36	90	" " " " "
SEL		110	250	10	75	110	" " " " "
TET		100	170	3	61	100	MacDonald et al. (2000)
GBG	Shale standard	95	20	0.3	68	90	Turekian & Wedepohl (1961)
	Earth Crust	70	12.5	0.15	75	100	Taylor (1964)

ERL = Effects range low ERM = Effects range median PEL = Probable effect level
TEL = Threshold effect level SEL = Severe effect level MET = Minimal effect threshold
TET = Toxic effect threshold GBG = Geochemical background

In this study, the characterization of sediment quality of the five investigated ecosystems as a function of trace metal concentrations was based on ERL, TEL, MET, PEL and TET. The mean concentrations of Cd, Cu and Pb exceeded the Minimal Effect Threshold (MET) and Threshold Effect Level (TEL) values in majority of the samples studied, indicating that there may be ecotoxicological risks to organisms living in these aquatic ecosystems.

In order to determine the possible biological effect of multiple sedimentary heavy metals, the mean Probable Effects Level quotient ($mPEL_Q$) was calculated using the formula:

$$mPEL_Q = \frac{\sum_{i=1}^{n}\left(C_i / PEL_i\right)}{n} \qquad (iv)$$

where, C_i is the concentration of metal *i*, PEL_i is the probable effect level value for metal i, and n is the sum of the metals considered. Moreover, the $mPEL_Q$ is classified into four grades: low degree of contamination (≤0.1), medium-low degree of contamination (0.11–1.5), high-medium degree of contamination (1.51–2.3), and high degree of contamination (>2.3), respectively having a 8%, 21%, 49% and 73% probability of being toxic (Carr et al., 1996; Long et al., 2006).

Similarly, the mean Effect Range Median quotient ($mERM_Q$) was calculated according to the equation:

$$mERM_Q = \frac{\sum_{i=1}^{n}\left(C_i / ERM_i\right)}{n} \qquad (v)$$

where, ERM_i is the *ERM* for metal *i*. The four levels classification of $mERM_Q$ is: low priority site (≤0.1), medium-low priority site (0.1–0.5), high-medium priority site (0.5–1.5), and high priority site (>1.5) with a 9%, 21%, 49% and 76% probability of being toxic, respectively (Long et al., 2000).

2.7 Contamination Severity Index (*CSI*) *and Hazard Quotients* (*HQ*)

CSI is a recently proposed index developed by Pejman et al. (2015) for ecological risk assessment of heavy metal pollution in sediments. It incorporates two-tier threshold levels of sediment quality guideline values, one below which adverse effects rarely occur (ERL – effects range low) and another above which adverse effects are likely to exist (ERM – effects range median) (Burton, 2002; MacDonald et al., 2000). The ERLs and ERMs are set at distribution percentiles of 10 and 50, respectively. According to this methodology, CSI is defined by the following equation:

$$W_t = \frac{\left(L_{f_i} \times E_v\right)}{\sum_{i=1}^{n}\left(L_{f_i} \times E_v\right)} \qquad (vi)$$

$$CSI = \sum_{i=1}^{n} W_t \left[\left(\frac{C_i}{ERL_i}\right)^{1/2} + \left(\frac{C_i}{ERM_i}\right)^{2}\right] \qquad (vii)$$

where, W_t is the weighted value for n number of heavy metals, L_{f_i} is the factor loading associated with individual metal, E_v is the eigenvalue, C_i is the measured concentration of metal in sediment, ERL_i is the effects range low and ERM_i is the effects range median. The following tiers

are used for CSI values: CSI <0.5 uncontaminated; 0.5≤CSI<1 very low severity of contamination; 1≤CSI<1.5 low severity of contamination; 1.5≤CSI<2 low to moderate severity of contamination; 2≤CSI<2.5 moderate severity of contamination; 2.5≤CSI<3 moderate to high severity of contamination; 3≤CSI<4 high severity of contamination; 4≤CSI<5 very high severity of contamination; and CSI ≤5 ultra high severity of contamination.

In aquatic ecosystems, the relative toxicities posed by trace metals to the environment and organisms can be evaluated by computing the hazard quotients (HQ) using the equation:

$$HQ = \frac{C_{metal}}{SQG} \qquad (viii)$$

where, C_{metal} is the observed concentration of a metal in sediment and SQG is the sediment quality guideline (Urban & Cook, 1986). The SQG adopted for calculating the HQ in this study was the threshold effects level (TEL) (MacDonald et al., 2000). According to Feng et al. (2011), HQ< 0.1 indicates no adverse effects; 0.1< HQ <1 indicates potential hazards; 1< HQ <10 shows moderate hazards; and HQ >10 indicates high hazards.

2.8 Newly developed contamination indices

2.8.1 Modified hazard quotient (mHQ)

In the present study, a new index for evaluating sediment pollution based on the degree of contamination by individual heavy metal is formulated and proposed. This new approach enables the assessment of contamination by comparing metal concentration in sediment with the synoptic adverse ecological effect distributions for slightly differing threshold levels (TEL, PEL and SEL) reported by MacDonald et al. (2000). The determination of modified hazard quotient (*m*HQ) of metals is an important assessment tool that elucidates the degree of risk of each heavy metal to aquatic environment and the biota, and is computed using the following mathematical formula:

$$mHQ = \left[C_i \left(\frac{1}{TEL_i} + \frac{1}{PEL_i} + \frac{1}{SEL_i} \right) \right]^{1/2} \qquad (ix)$$

where, C_i is the measured concentration of heavy metal in the sediment samples, TEL_i, PEL_i and SEL_i are acronyms for the threshold effect level, probable effect level and severe effect level for i^{th} metal, respectively. In the equation, the square root is introduced as a drawdown function for mathematical and ranking considerations. The proposed classification of contamination by a single metal is presented in Table 3.

Table 3: Classification of modified hazard quotient (*m*HQ)

*m*HQ	Degree of risk
*m*HQ > 3.5	Extreme severity of contamination
3.0 ≤ *m*HQ < 3.5	Very high severity of contamination
2.5 ≤ *m*HQ < 3.0	High severity of contamination
2.0 ≤ *m*HQ < 2.5	Considerable severity of contamination
1.5 ≤ *m*HQ < 2.0	Moderate severity of contamination
1.0 ≤ *m*HQ < 1.5	Low severity of contamination
0.5 ≤ *m*HQ < 1.0	Very low severity of contamination
*m*HQ < 0.5	Nil to very low severity of contamination

2.8.2 Ecological Contamination Index (*ECI*)

In this study, we proposed a reliable index known as ecological contamination index (ECI) for an aggregate ecological risk evaluation of sediment contamination by heavy metals. The ECI is an aggregative empirical approach that estimates the risks associated with an ecosystem using a source-specific factor derived primarily from principal component analysis/factor analysis. The proposed formula for ECI is mathematically expressed as:

$$ECI = B_n \sum_{i=1}^{n} mHQ_i \qquad (x)$$

where, B_n = the reciprocal of derived eigenvalue of heavy metal concentrations only. The proposed ranking of risks posed by heavy metals to ecological systems computed based on the proposed formulation is presented in Table 4.

Table 4: Classification of Ecological Contamination Index (ECI)

ECI	Degree of contamination
ECI > 7	Extremely contaminated
6 ≤ ECI < 7	Highly contaminated
5 ≤ ECI < 6	Considerably to highly contaminated
4 ≤ ECI < 5	Moderately to considerably contaminated
3 ≤ ECI < 4	Slightly to moderately contaminated
2 ≤ ECI < 3	Uncontaminated to slightly contaminated
ECI < 2	Uncontaminated

3. Results and discussion

3.1 Heavy metal distribution

The total concentrations (F1+F2+F3+F4+F5) of heavy metals (Cd, Cr, Cu, Ni, and Pb) in benthic sediments from the investigated aquatic ecosystems are presented in Table 5. From all metals studied, Pb showed the highest mean concentration in the sediment at both seasons, followed by Cu. The observed maximum mean concentration values of 5.67±1.78, 28.52±7.21, 43.72±8.95, 2.60±0.59 and 231.52±6.82 mg kg^{-1} were recorded for Cd, Cr, Cu, Ni and Pb, respectively. There was no significant variation in the mean metal levels (mg kg-1, dw) during the wet and dry seasons in all the sites. Effluents and sewage drainages from industrial activities are usually the potential sources for the enrichment of these metals into the aquatic ecosystems.

Table 5: Monthly concentration (mean±s.d, mg/kg) of trace metals in studied aquatic ecosystems

		Qua Iboe Estuary	Douglas Creek	Stubbs Creek	Okorotip Creek	Qua Iboe River
Cadmium	June	4.38±1.19	4.88±1.31	5.02±1.35	4.47±1.13	5.01±1.35
	July	4.96±1.41	4.63±1.22	5.08±1.34	5.67±1.78	5.63±1.67
	August	4.71±1.27	4.52±1.25	4.99±1.36	4.86±1.27	4.59±1.23
	November	4.84±1.33	5.21±1.44	4.47±1.16	4.41±1.55	4.89±1.38
	December	4.71±1.25	4.80±1.27	4.41±1.17	4.71±1.26	4.69±1.26
	January	4.64±1.26	4.78±1.23	4.33±1.12	4.67±1.26	4.64±1.24
Chromium	June	20.37±4.09	19.02±3.63	20.34±3.98	21.51±4.29	11.12±1.81
	July	20.08±4.04	20.63±3.92	19.86±3.70	20.84±4.19	18.11±3.55
	August	18.93±3.69	17.50±3.22	20.37±4.02	20.93±4.21	15.16±2.59
	November	20.60±4.17	18.95±3.55	19.05±3.62	19.54±3.83	17.09±3.39
	December	18.61±3.63	19.90±3.88	20.73±4.07	18.44±3.34	28.52±7.21
	January	20.52±3.99	20.11±3.88	18.78±3.58	20.06±3.73	18.37±3.46
Copper	June	31.74±4.80	40.70±7.35	43.01±8.08	30.86±4.53	43.73±8.95
	July	36.43±5.84	38.61±6.62	39.86±6.94	40.69±7.33	35.07±5.65
	August	38.73±6.69	36.39±6.16	43.08±7.93	30.26±4.97	38.56±6.67
	November	31.05±4.58	39.31±6.86	40.54±6.99	39.57±7.39	41.01±7.44
	December	35.75±5.68	37.25±6.41	38.00±6.54	42.02±7.61	39.87±7.43
	January	38.29±6.25	36.55±6.09	37.43±6.31	41.49±7.48	39.26±6.68
Lead	June	177.63±4.95	166.42±9.94	181.48±7.24	183.48±8.79	162.00±8.54
	July	180.03±4.23	172.50±2.91	187.06±8.08	167.61±0.87	182.37±6.05
	August	231.52±6.82	177.80±3.59	175.37±6.90	190.37±7.83	173.49±3.95
	November	185.81±8.10	185.11±6.68	176.86±5.30	169.25±3.78	178.42±4.12
	December	186.48±8.00	181.59±6.36	180.21±7.12	171.71±8.64	175.72±5.13
	January	185.07±6.59	186.58±8.71	183.34±5.51	185.38±6.06	183.13±6.51
Nickel	June	2.06±0.35	2.24±0.39	2.23±0.39	2.05±0.36	2.17±0.39
	July	2.60±0.59	2.12±0.34	2.25±0.40	2.17±0.39	2.23±0.41
	August	2.17±0.38	2.13±0.34	2.19±0.36	2.20±0.39	2.03±0.41
	November	2.25±0.40	2.17±0.37	2.23±0.41	2.26±0.39	2.28±0.40
	December	2.27±0.43	2.25±0.39	2.13±0.33	2.09±0.40	2.16±0.41
	January	2.26±0.41	2.27±0.40	2.18±0.36	2.22±0.38	2.26±0.40

3.2 Potential contamination index (PCI)

In the present study, the potential contamination index (PCI) was calculated for Cd, Cr, Cu, Ni and Pb at each studied site. Results of PCI are presented in Figure 2. According to the classification proposed by Davaulter & Rognerud (2001), Cd and Pb potential contamination index values were significantly high, indicating severe or very severe contaminations. The PCI values for Cr, Cu and Ni were low in all the sites, indicating low contamination. Lead and cadmium showed the highest degree of anthropogenic impact based on the PCI of the

investigated benthic sediment samples. The potential contamination index generally followed the sequence Cd>Pb>Cu>Cr>Ni.

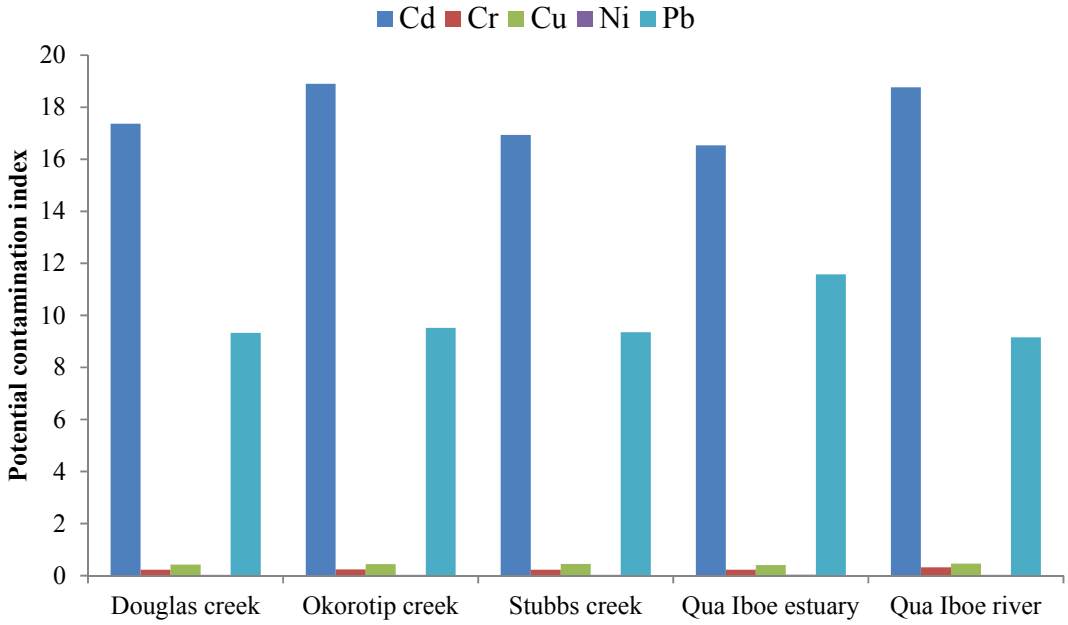


Figure 2: Estimated anthropogenic impact based on potential contamination index

3.3 Modified Risk Assessment Code (*mRAC*)

As shown in Fig. 3, the *m*RAC values for heavy metals within the five studied ecosystems revealed that the subtidal sediments were largely characterized by medium potential adverse effect. The application of this index could likely underestimate or exaggerate the degree of pollution considering the correlative differences between the chemical forms of metals, which might probably negate the combined bioavailability suggested by this approach. However, a medium or high risk value of *m*RAC for metals showed that heavy metals may be easily released from sediments into the overlying water body by alterations in physicochemical conditions of the

ecosystem, with the possibility of entering the food chain (Jain & Ran, 2004; Nemati et al., 2011).

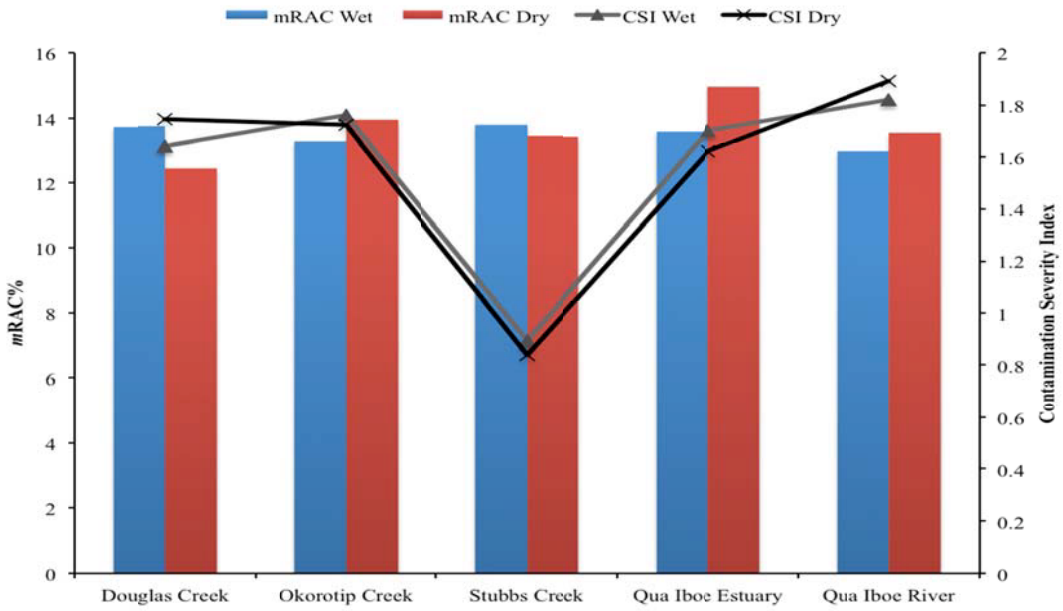


Figure 3: Description of modified risk assessment code (*m*RAC) and contamination severity index (CSI) of subtidal sediments from studied ecosystems.

3.4 Ecotoxicological assessment of heavy metal concentrations in sediments

Comparative results indicated that Cd was higher than TEL, PEL, MET, and TET in 100% and ERL in 20% of the samples. Cu was higher than TEL, MET in 80 and 100% of the samples, respectively. Lead (Pb) was higher than ERL, TEL, PEL, MET, ERM and TET in 100, 100, 3.33, 100, 100 and 86.67% of sediment samples. These results showed that the levels of Cd, Cu and Pb primarily characterized the sediment quality of the studied ecosystems, and could pose deleterious effects on benthic dwelling biota. Cadmium, copper and lead exceeded the threshold effect level and minimal effect threshold concentrations indicating anthropogenic contamination of sediments of aquatic ecosystems in this region; there may be some ecotoxicological risk to organisms living in these sediments.

Our results indicated that the monthly $mPEL_Q$ varied within the range of 0.73 – 0.79 (DOU), 0.71 – 0.78 (OKT), 0.73 – 0.79 (STB), 0.72 – 0.87 (QUE), and 0.72 – 0.80 (QUR) (Fig. 4). These values indicated that all the investigated sites recorded medium-low degree of contamination with all trace metals in these ecosystems having about 21% probability of being toxic during the wet and dry seasons. On the other hand, the $mERM_Q$ varied within the range of 0.46 – 0.50 (DOU and OKT), 0.47 – 0.58 (STB and QUE), and 0.45 – 0.50 (QUR) (Fig. 4). The $mERM_Q$ values indicated that the studied sites were medium–low priority sites with trace metals having a combined 21% probability of being toxic.

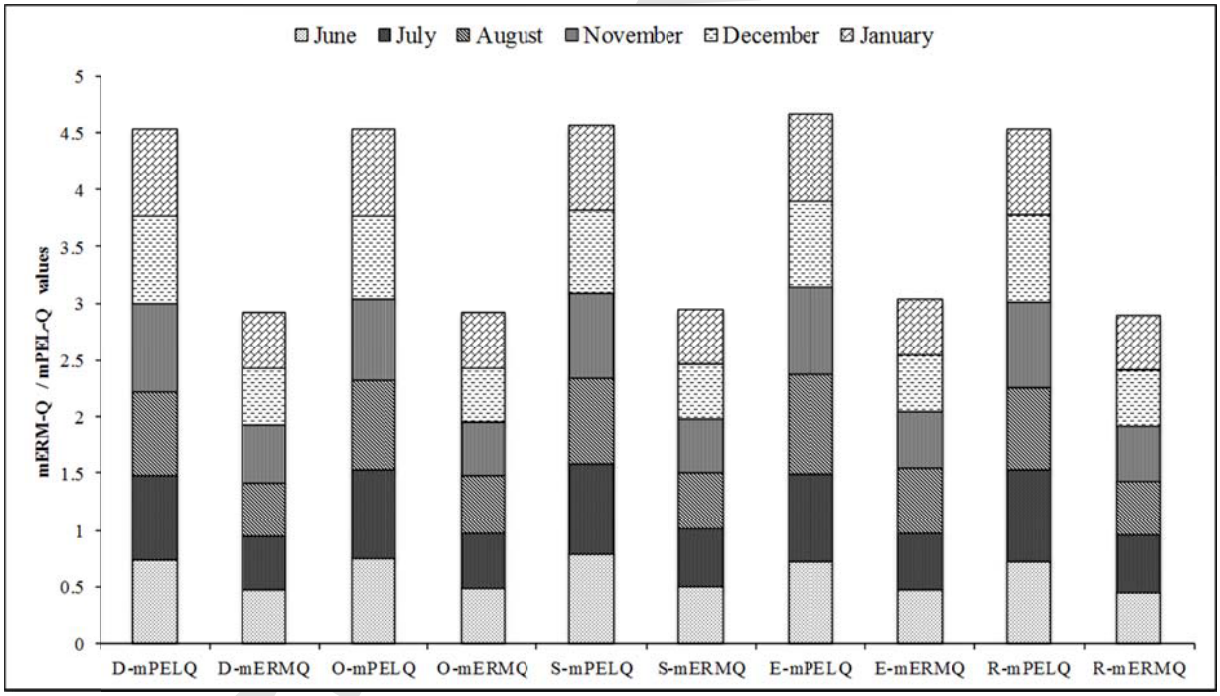


Figure 4: Monthly distributions of calculated $mPEL_Q$ and $mERM_Q$ in benthic sediments (*First letter before the calculated quotients signifies the name of the aquatic ecosystem:* D=Douglas Creek; O=Okorotip Creek; S=Stubbs Creek; E=Qua Iboe Estuary; R=Qua Iboe River)

3.5 Contamination Severity Index (CSI)

Results of the calculated CSI values for both wet and dry seasons are presented in Fig. 3. Based on the CSI, the severity of sediment-associated heavy metal pollution in ecosystems were generally characterized by low to moderate severity of contamination except at the Stubbs Creek where the index was within the very low severity tier. However, no significant differences in terms of severity ranking were observed between the wet and dry seasons.

3.6 Hazard Quotients (*HQ*)

Results of the calculated hazard quotients for trace metals (Cd, Cr, Cu, Ni and Pb) in the investigated ecosystems are presented in Table 6. The HQ values of Cr and Ni were in the range of $0.1 < HQ < 1$, indicating that these trace metals could pose potential hazards to the aquatic organisms and the ecosystems under study. However, the HQ values of Cd, Cu and Pb were between 1 and 10 ($1 < HQ < 10$) at all investigated sites during the wet and the dry seasons. These values indicated the possibility of Cd, Cu and Pb triggering moderate hazards in these ecosystems. Cadmium and lead are notable environmental toxicants, and their considerable HQ values indicated that they might be associated with adverse biological and ecosystem risks. This observation would point to the fact that the consumption of seafoods from the studied aquatic systems might result in possible health risks especially from Cd and Pb poisoning.

Table 6: Comparison of hazard quotients of trace metals at all sites

	Douglas Creek	Okorotip Creek	Stubbs Creek	Qua Iboe Estuary	Qua Iboe River
Cd	7.8 (8.2)	8.3 (7.7)	8.4 (7.3)	7.8 (7.9)	8.5 (7.9)
Cr	0.5 (0.5)	0.6 (0.5)	0.5 (0.5)	0.5 (0.5)	0.4 (0.6)
Cu	1.1 (1.0)	1.0 (1.1)	1.2 (1.1)	1.0 (0.9)	1.1 (1.1)
Ni	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)	0.1 (0.1)
Pb	4.9 (5.3)	5.2 (5.0)	5.2 (5.1)	5.6 (5.3)	4.9 (5.1)

(dry season values in parentheses).

3.7 Principal component analysis

Multivariate statistical procedures such as principal component analysis/factor analysis are usually employed to elucidate interrelationships that exist among parameters (principal components) investigated in an observational dataset. Similar data exploratory approach is widely used in chemical fractionation research studies, and has been reported by several authors (Benson et al., 2016a; Ianni et al., 2009; Passos et al., 2010; Pejman et al., 2015). In this study, principal component analysis was used to evaluate similarities in the occurrence and concentrations of trace metals (Cd, Cr, Cu, Ni, Pb) obtained in each fraction. The compatibility and adequacy of observed data was further examined using KMO and Bartlett's sphericity test. The calculated KMO coefficients obtained were 0.31, 0.51, 0.50, 0.60 and 0.32, and were less than 1 for DOU, OKT, STB, QUE and QUR sites, respectively. The concomitant probability of Bartlett's sphericity test was not significant at $\alpha = 0.05$ level. These generally highlighted the statistical suitability of the observed data obtained from the mangrove ecosystems for deriving the principal components (PC). In the PCA, a principal component with eigenvalue >1 is regarded as significant. Thus, the observations at OKT, STB and QUE were averagely adequate for a factor model.

The factor loadings of trace metals in sediment at DOU, OKT, STB, QUE and QUR sampling sites were grouped into two principal component models for principal components >1 (Table 7). The eigenvalues of PC1 and PC2 associated with sediments from Douglas Creek were greater than 1 and in general accounted for 66% of the variability in concentrations of trace metals. PC1 indicated that 34% of the total variance was positively related to Cd and Cu. However, PC2, which explained 32% of the total variance, indicated strong negative interrelationships for Ni and Pb. The eigenvalues of components 1 and 2 associated with sediment samples from Qua Iboe estuary were also greater than 1 and accounted for 80% of the

total variance in metal concentrations. PC1 showed that 43% variability was attributed to Cu and Pb showing relatively high positive factor loadings, while Cr indicated a strong negative relationship. Moreover, PC2 accounted for 37% of the total variance and was associated with strong negative interrelationships between Cd and Ni.

From Table 7, the factor loading of heavy metals in Qua Iboe River indicated that eigenvalues of PC1 and PC2 derived for sediment samples were greater than 1 and, accounted for 72% of the variability in trace metal levels. PC1 was the most significant principal component and was dominated by Cu, Ni and Pb, which accounted for 45% of the total variance. A very high loading of Ni (0.522) and Pb (0.913) indicated a significantly positive interrelationship. Additionally, the high loading of Cu (-0.832) showed strong negative correlation. However, the variability in interrelationships by heavy metals possibly suggests that metal contamination of sediment from these ecosystems might have originated from multiple anthropogenic pollution sources (Zhang et al., 2007, 2009).

Table 7: Loadings of two principal components for benthic sediment variables

	Douglas Creek		Okorotip Creek		Stubbs Creek		Qua Iboe River		Qua Iboe Estuary	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Load of Cd	**0.634**	-0.571	0.234	**-0.936**	**0.953**	0.114	0.484	**-0.758**	0.576	**-0.734**
Load of Cr	0.208	-0.437	**-0.786**	-0.508	0.439	**-0.635**	0.485	**0.708**	**-0.682**	-0.459
Load of Cu	**0.980**	0.183	**0.943**	-0.002	**0.907**	-0.252	**-0.832**	-0.068	**0.821**	0.149
Load of Ni	0.163	**-0.707**	**0.368**	-0.095	0.623	**0.716**	**0.522**	-0.431	0.467	**-0.865**
Load of Pb	-0.524	**-0.742**	**-0.817**	-0.265	-0.060	**0.783**	**0.913**	0.210	**0.662**	0.590
Eigenvalue	1.705	1.601	2.366	1.214	2.317	1.605	2.268	1.311	2.128	1.868
Variability (%)	34.108	32.022	47.314	24.275	46.337	32.110	45.365	26.226	42.565	37.360
Cumulative %	34.108	66.130	47.314	71.589	46.337	78.447	45.365	71.591	42.565	79.925

3.8 Review of results for new indices

The new indices for evaluating ecological risk assessment for sediment-associated contaminants in this study take into consideration the individual contribution as well as net chemical concentrations of heavy metals in reference to the standard sediment quality guidelines (threshold effect level, probable effect level and severe effect level) to evaluate the potential impacts of contamination. The formulation approach also incorporated the eigenvalue results derived from the principal component analysis. However, the significance of the principal components in PCA is known to be a function of the respective calculated eigenvalues. Table 7 presents the calculated results of PCA including the metal loading factors, eigenvalues and variance (variability and cumulative) for the two principal components (PC1 & PC2). The eigenvalues of PC1 are considered to be very significant variables that could be associated with potential human-induced sources of the investigated heavy metals. The eigenvalues, therefore, were used in calculating the net ecological contamination index.

3.8.1 Modified hazard quotient (mHQ)

As indicated in the formula for the calculation of *m*HQ (Eq. 9) for assessing the impacts of sediment-associated contamination by individual heavy metals in an ecosystem, the fundamental assumption considered in formulating this new index is that if the degree of contamination by metal is significant and its concentration is appreciably found above the TEL, PEL and SEL, then, the reciprocal of metal specific threshold, midrange and severe guideline values will definitely determine the outcome of the calculated quotient. In other words, this approach compares the concentration of individual metals with sediment quality advisory levels in order to compute and grade the magnitude of exceedance of each individual heavy metal. The estimated *m*HQ values for benthic sediments of all the investigated sites during the wet and the

dry seasons period are presented in Table 8, while the spatial distributions of derived modified hazard quotient values are shown in Figs. 5 and 6. The *m*HQs calculated according to the proposed formulation indicated that the severity of sediment-associated pollution of the five heavy metals were in the descending sequence: Cd>Pb>Cu>Cr>Ni. This trend is in good agreement with other contamination sequence obtained for pollution assessment indices earlier reported for these ecosystems and other reports (Manaan et al., 2015; Ruiz et al., 2006). Results indicated that Cd gave very high degree of contamination, while Pb severity ranking was characterized by high degree of contamination. However, Cu, Cr and Ni generally showed low to very low degree of contamination during the wet and dry seasons at all the sites investigated.

Table 8: Modified hazard quotient (*m*HQ) for heavy metals at all sites

Metals	Sampling sites				
	Douglas creek	Okorotip creek	Stubbs creek	Qua Iboe Estuary	Qua Iboe River
Cd	VH (VH)	VH (VH)	VH (VH)	VH (VH)	VH (VH)
Cr	VL (VL)	VL (VL)	VL (VL)	VL (VL)	VL (VL)
Cu	L (L)	L (L)	L (L)	L (L)	L (L)
Ni	VL (VL)	VL (VL)	VL (VL)	VL (VL)	VL (VL)
Pb	H (H)	H (H)	H (H)	H (H)	H (H)

VH = very high degree of contamination; VL = very low degree of contamination; L = low degree of contamination
H = high degree of contamination; Notation in parenthesis = dry season; notation not in parenthesis = wet season.

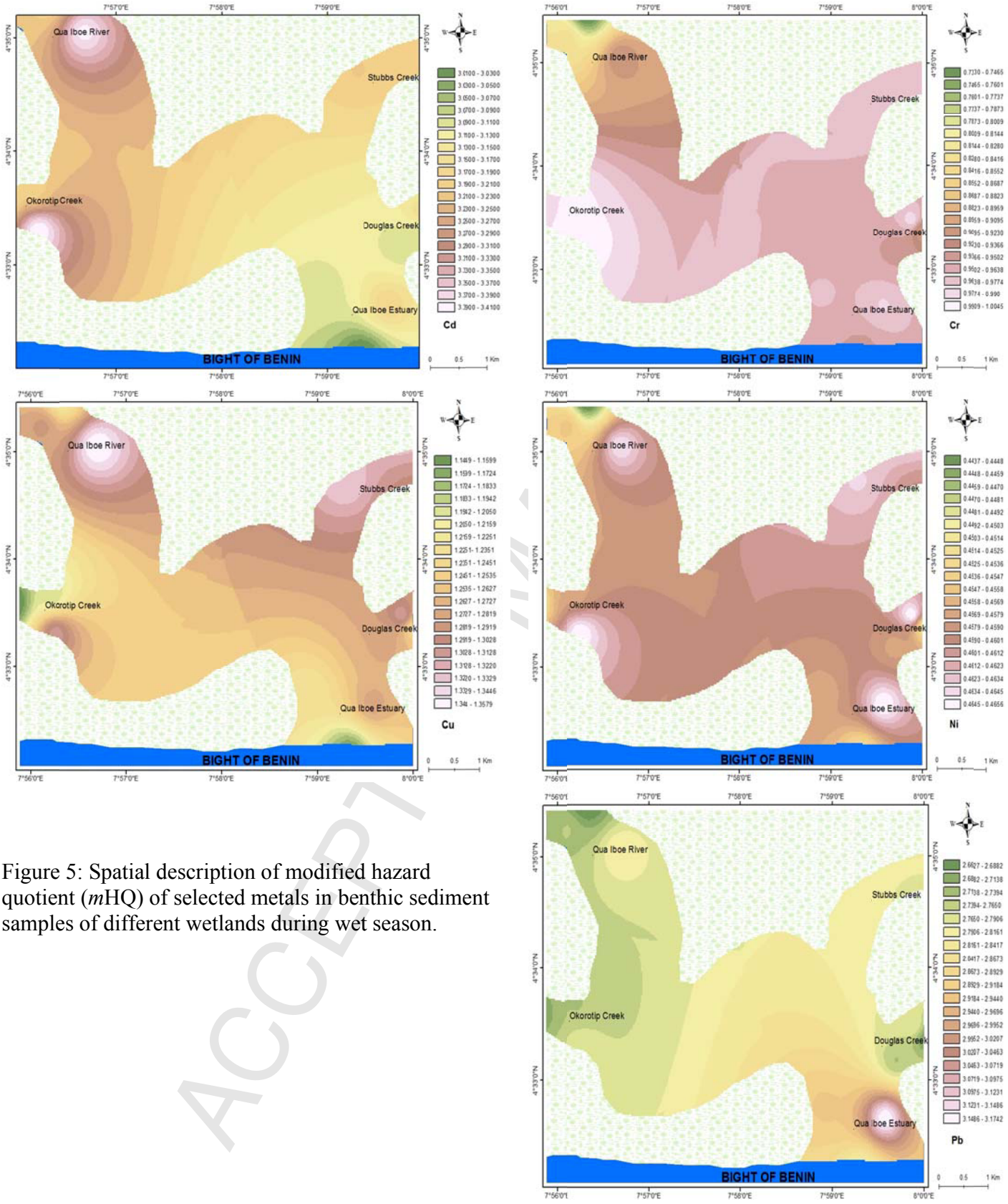


Figure 5: Spatial description of modified hazard quotient (*m*HQ) of selected metals in benthic sediment samples of different wetlands during wet season.

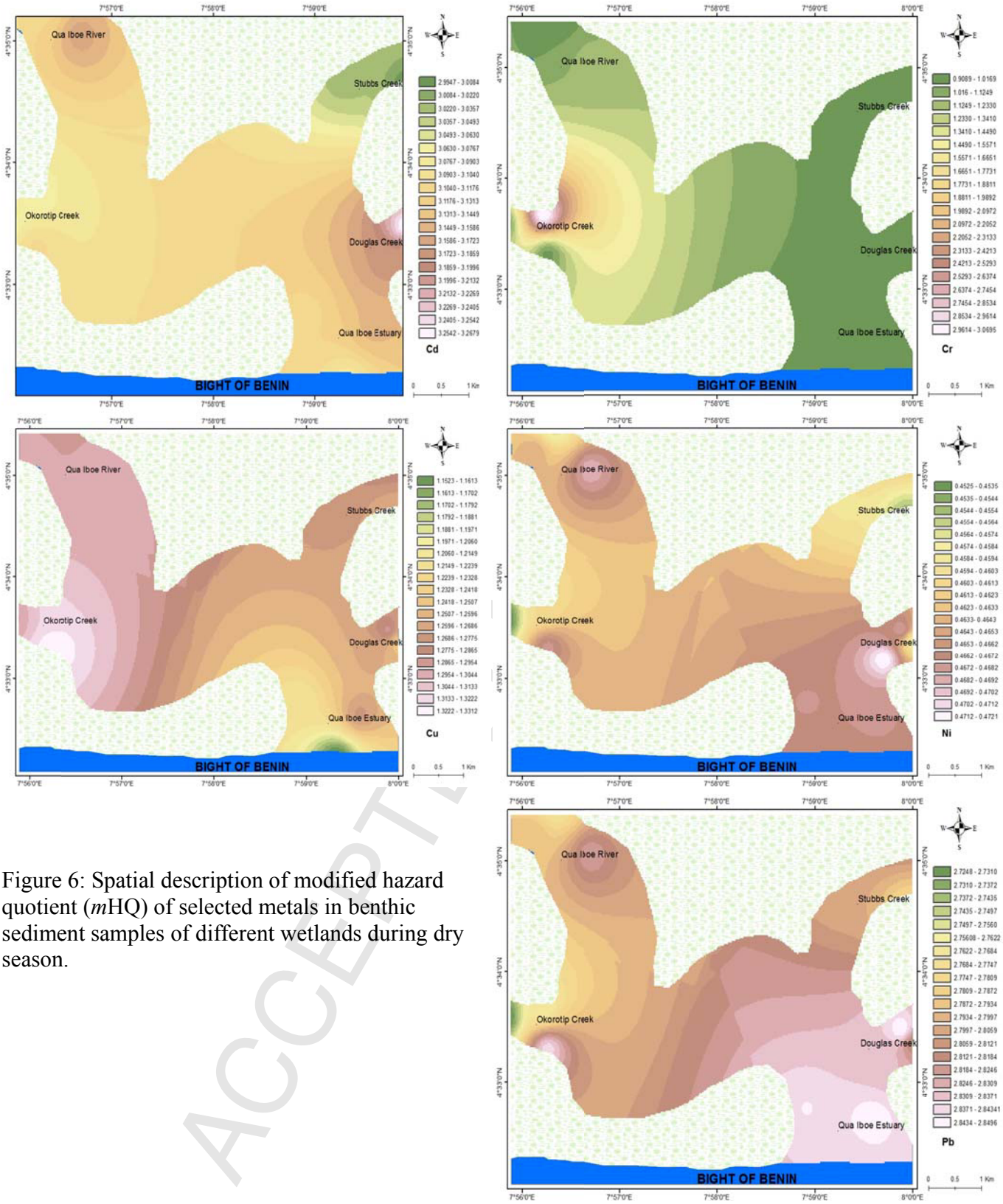


Figure 6: Spatial description of modified hazard quotient (*m*HQ) of selected metals in benthic sediment samples of different wetlands during dry season.

3.8.2 Ecological Contamination Index (*ECI*)

The multi-elemental potential ecological contamination indices (*ECIs*) for all the sites are presented in Fig. 7. The results for all the metals (Cd, Cr, Cu, Ni and Pb) in benthic sediments were between 3.79 and 5.06 at Qua Iboe River and Douglas Creek, respectively. The calculated *ECIs* indicated a slightly contaminated to highly contaminated ecosystems. The ecological risk ranking based on percentage contribution to *ECI* followed the sequence Cd>Pb>Cu>Cr>Ni, while the severity of ecosystem pollution based on the five heavy metals decreased in the following sequence: DOU>QUE>QUR>STB>OKT. In general, cadmium contributed considerably to the ecological contamination risk index of the investigated aquatic ecosystems compared to Ni, Cr, and Cu.

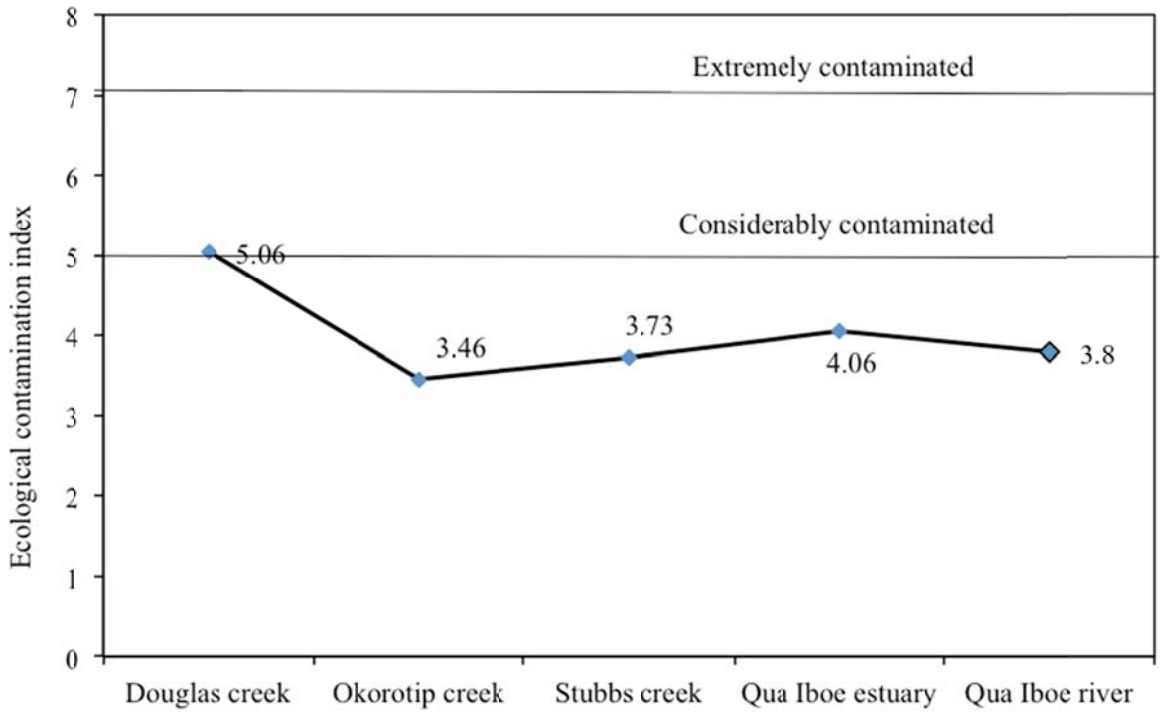


Figure 7: Description of ecological contamination index (ECI) of sedimentary metals.

The reliability and accuracy of the newly proposed formulae for assessment of sediment-associated heavy metals in aquatic ecosystems were ascertained by comparing the calculations with other existing pollution indices. The trends of sediment metal contamination using existing and newly proposed indices are as presented in Table 9. Results indicated that the *m*HQ and ECI are reliable and useful pollution tools that can be used to estimate the extent of pollution state, site-specific status and aggregative contamination effects by heavy metals in aquatic ecosystems.

Table 9: Comparison of contamination trends using existing and newly proposed pollution contamination indices

Type of index		**Pollution sequence and status of heavy metals**				**Reference**
	Douglas creek	Okorotip creek	Stubbs creek	Qua Iboe Estuary	Qua Iboe River	
Contamination factor	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Benson et al. 2017
Pollution load index	Unpolluted	Unpolluted	Polluted	Unpolluted	Unpolluted	
% contribution of single metal to degree of contamination	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	
Modified degree of contamination	High degree of contamination	High degree of contamination	High degree of contamination	High degree of contamination	High degree of contamination	
Potential ecological risk index	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	
% contribution to risk index	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	
Potential contamination index	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	This study
Individual contamination factor	Cu>Cr>Ni>Cd>Pb	Cu>Cr>Ni>Cd>Pb	Cu>Cr>Ni>Cd>Pb	Cu>Cr>Ni>Cd>Pb	Cu>Cr>Ni>Cd>Pb	Benson et al. 2016a
Contamination severity index	Cd>Cr>Cu>Ni>Pb	Cd>Cr>Cu>Ni>Pb	Cd>Cr>Cu>Ni>Pb	Cd>Cr>Cu>Ni>Pb	Cd>Cr>Cu>Ni>Pb	Pejman et al. (2015)
Modified risk assessment code	Ni>Cd>Cr>Cu>Pb	Ni>Cd>Cr>Cu>Pb	Ni>Cd>Cr>Cu>Pb	Ni>Cd>Cr>Cu>Pb	Ni>Cd>Cr>Cu>Pb	Pejman et al. (2015)
Hazard quotient	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	This study
Modified hazard quotient	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	New proposed formula
Ecological contamination index	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	Cd>Pb>Cu>Cr>Ni	New proposed formula

4. Conclusion

Heavy metal levels and contamination status in sediment samples of five equatorial estuarine, riverine and lacustrine wetlands were evaluated using existing pollution indices and newly proposed indices. The later indices were employed to evaluate the potential adverse effect of individual heavy metal and also estimate the overall ecological severity risk of sediment-associated heavy metals. Modified hazard quotient (*m*HQ) provides valuable information on the severity of contamination posed by individual heavy metal to the biological communities and the environment. The ecological contamination index (*ECI*) is an aggregate index that represents overall contamination and associated ecological risks based on the contribution of all hazardous heavy metals in an aquatic ecosystem. The spatial distribution and severity of sediment contamination by heavy metals based on the proposed indices (modified hazard quotient, *m*HQ and ecological contamination index, ECI) are in the descending sequence: Cd>Pb>Cu>Cr>Ni. The risk assessment indices employed in the present study has revealed significant contamination risk by Cd and Pb. PCA has shown that both anthropogenic and lithogenic sources are responsible for the possible contamination of the investigated ecosystem by Cd, Cr, Cu, Ni and Pb. The calculated $mPEL_Q$ and $mERM_Q$ indices indicated that benthic sediments at all the sites have 21% probability of being toxic. Sediment quality guideline based comparative results indicated that Cd was higher than TEL, PEL, MET, and TET in 100% and ERL in 20% of the samples, which implies that Cd could pose potential adverse biological effects to benthic communities of these aquatic ecosystems. However, the newly proposed index (modified hazard quotient, *m*HQ) has shown that the severity of sediment contamination by heavy metals followed the sequence: Cd>Pb>Cu>Cr>Ni. Estimation of potential risks by metals using the proposed ecological contamination index revealed possible pollution hotspot sites. A comparison of newly proposed indices with existing pollution indices revealed very good agreement. The

contamination trends derived from new indices were consistent and took into consideration site specificity, toxicity and the three-tier effect levels (threshold, midrange and extreme effects guideline values) that support their reliability and significant usage in evaluating contaminated aquatic ecosystems.

Acknowledgement
We are grateful to three anonymous reviewers who offered constructive comments and suggestions in an earlier draft of this paper.

References

Addo, M., Affum, H., Botwe, B. O., Gbadago, J. K., Acquah, S., Senu, J. K., Mumuni, I.I., 2012. Assessment of Water Quality and Heavy Metal Levels in Water and Bottom Sediment Samples from Mokwé Lagoon, Accra, Ghana. Res. J. Environ. Earth Sci., 4(2), 119–130.

Atibu, E.K., Devarajan, N., Laffite, A., Giuliani, G., Salumu, J.A., Muteb, R.C., Mulaji, C.K., Otamonga, J.P., Elongo, V., Mpiana, P.T., Poté, J., 2016. Assessment of trace metal and rare earth elements contamination in rivers around abandoned and active mine areas. The case of Lubumbashi River and Tshamilemba Canal, Katanga, Democratic Republic of the Congo, In Chem. Erde, 76, 353-362.

Asuquo, F.E., 1991. Tarballs in Ibeno-Okposo beach of South Eastern Nigeria. Mar. Pollut. Bull., 22: 150–151.

Ayejuyo, O. O., Omojole, M. O., Ojoniyi J. O., 2010. Sediment load and bioconcentration of heavy metals by shrimp (Peaneus notalis) from Epe Lagoon, Nigeria. Environ. Monit Assess., 163, 295 – 30. doi.10. 1007/s10661-009-083-8

Benson, N.U., Udosen, E.D., Essien, J.P., Anake, W.U., Adedapo, A.E., Akintokun, O.A., Fred-Ahmadu, O.H., Olajire, A.A., 2017. Geochemical fractionation and ecological risks assessment of benthic sediment-bound heavy metals from coastal ecosystems off the Equatorial Atlantic Ocean, Int. J. Sediment Res., 32(3), 410 – 420, http://dx.doi.org/10.1016/j.ijsrc.2017.07.007

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 sediments from equatorial ecosystems using multivariate statistical techniques. PLoS ONE, 11(6), 1-19. doi:10.1371/journal.pone.0156485

Benson, N. U., Anake, W. U., Essien, J. P., Enyong, P. A., Olajire, A. A., 2016b. Distribution and risk assessment of trace metals in *Leptodius exarata*, surface water and sediments from Douglas Creek, Qua Iboe estuary. J. Taibah University for Science, 11 (3), 434 – 449, http://dx.doi.org/10.1016/j.jtusci.2016.08.004

Benson, N. U., Udosen, E. D., Akpabio, O., 2008a. Interseasonal distribution and partitioning of heavy metals in subtidal sediment of Qua Iboe Estuary and associated Creeks, Niger Delta (Nigeria). Environ. Monit. Assess., 146(1-3), 253–265.

Benson, N.U., Essien, J.P., Ebong, G.A., Williams, A.B., 2008b. Petroleum hydrocarbons and limiting nutrients in *Macura reptantia, Procambarus clarkii* and benthic sediment from Qua Iboe Estuary, Nigeria. The Environmentalist, 28(3): 275-282.

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., Essien, J.P., Williams, A.B., Bassey, D.E., 2007. Mercury accumulation in fishes from tropical aquatic ecosystems in the Niger Delta of Nigeria. Curr. Sci., 96 (2): 781-785.

Benson, N.U., Anake, W.U., Olanrewaju, I.O., 2013. Analytical relevance of trace metal speciation in environmental and bio-physicochemical systems. American J. Anal. Chem., 4, 633-641.

Burton, G. A. Jr., 2002. Sediment quality criteria in use around the world. Limnol., 3, 65–75

Carr, R.S., Long, E.R., Windom, H.L., Chapman, D.C., Thursby, G., et al., 1996. Sediment quality assessment studies of Tampa Bay, Florida. Environ. Toxicol. Chem., 15, 1218–1231

Davaulter, V., Rognerud, S., 2001. Heavy metal pollution in sediments of the Pasvik River drainage. Chemosphere, 42, 9–18.

Díaz-de Alba, M., Galindo-Riano, M.D., Casanueva-Marenco, M.J., García-Vargas, M., Kosore, C.M., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. J. Hazard. Mater., 190, 177–187.

Duan, L.Q., Song, J.M., Xu, Y.Y., Li, X.G., Zhang, Y., 2010. The distribution, enrichment and source of potential harmful elements in surface sediments of Bohai Bay, North China. J. Hazard. Mater., 183, 155–164.

Essien J.P, Antai S.P., 2005. Negative direct effects of oil spill on beach microalgae in Nigeria. World J. Microbiol. Biotechnol., 21(4), 567–573.

Essien J.P., Benson, N.U., Antai S.P., 2008. Seasonal dynamics of physicochemical properties and heavy metal burdens in Mangrove sediments and surface water of the brackish Qua Iboe Estuary, Nigeria. Toxicol. Environ. Chem., 90(2), 259 – 273. doi: 10.1080/02772240701550497

Feng, H., Jiang, H.Y., Gao, W.S., Weinstein, M.P., Zhang, Q.F., Zhang, W.G., Yu, L.Z., Yuan, D.K., Tao, J.H., 2011. Metal contamination in sediments of the western Bohai Bay and adjacent estuaries, China. J. Environ. Manage., 92, 1185–1197.

Gao, X.L., Chen, C.T.A., 2012. Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water Res. 46, 1901–1911.

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 J. Aquat. Res., 40, 213–224.

Harikumar, P. S., Nasir, U. P., 2010. Ecotoxicological impact assessment of heavy metals in core sediments of a tropical estuary. Ecotoxicol. Environ. Saf., 73(7), 1742–1747.

Håkanson, L., 1980. Ecological risk index for aquatic pollution control, a sedimentological approach. Water Res., 14, 975–1001.

Ianni, C., Magi, E., Soggia, F., Rivaro, P., Frache, R., 2009. Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antarctica). Microchem. J., 96(2), 203-212. doi: 10.1016/j.microc.2009.07.016.

Jain, C.K., Ran, D., 2004. Metal fractionation study on bed sediments of river Yamuna, India. Water Res. 38, 569–578.

Kalender, L., Uçar, Ç.S., 2013. Assessment of metal contamination in sediments in the tributaries of the Euphrates River, using pollution indices and the determination of the pollution source, Turkey. J. Geochem. Explor., 134, 73–84.

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. Mar. Pollut. Bull., 76(1-2), 266–275.

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

Long, E.R., Ingersoll, C.G., MacDonald, D.D., 2006. Calculation and uses of mean sediment quality guideline quotients: a critical review. Environ. Sci. Technol. 40, 1726–1736.

Long, E.R., MacDonald, D.D., Severn, C.G., Hong, C.B., 2000. Classifying probabilitiesof acute toxicity in marine sediments with empirically derived sedimentquality guideline. Environ. Toxicol. Chem. 19, 2598–2601.

Maanan, M., Saddik, M., Maanan, M., Chaibi, M., Assobhei, O., Zourarah, B., 2015. Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco. Ecol. Indic., 48, 616–626.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for fresh- water ecosystems. Arch. Environ. Contam. Toxicol., 39, 20–31.

MacDonald, D.D., Scottcarr, R., Calder, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicol., 5, 253–278

Malvandi, H., 2017. Preliminary evaluation of heavy metal contamination in the Zarrin-Gol River sediments, Iran. Mar. Pollut. Bull., 117, 547-553.

Morelli, G., Gasparon, M., 2014. Metal contamination of estuarine intertidal sediments of Moreton Bay, Australia. Mar. Pollut. Bull., 89 (1-2), 435–443.

Nemati, K., Abu 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. J. Hazard. Mater. 192,402–410.

Nilin, J., Moreira, L.B., Aguiar, J.E., Marins, R., Souza, D.M., Abessa, T., Cruz Lotufo, M.,Costa-Lotufo, L.V., 2013. Sediment quality assessment in a tropical estuary: The case of Ceará River, Northeastern Brazil. Mar. Environ. Res. 90, 1–8.

Onojake, M.C., Frank, O., 2013. Assessment of heavy metals in a soil contaminated by oil spill: a case study in Nigeria. Chem. Ecol. 29: 246–254.

Pan, S., An, W., Li, H., Su, M., Zhang, J., Yang, M., 2014. Cancer risk assessment on trihalomethanes and haloacetic acids in drinking water of China using disability-adjusted life years. J. Hazard. Mater., 280, 288–294.

Passos, E. D. A., Alves, J. C., dos Santos, I. S., Alves, J. D. P. H., Garcia, C. A. B., Spinola Costa, A. C., 2010. Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. Microchem. J., 96(1), 50–57.

Pejman, A., Bidhendi, N.G., Ardestani, M., Saeedi, M., Baghvand, A., 2015. A new index for assessing heavy metals contamination in sediments: A case study, Ecol. Indic., 58, 365–373.

Perin, G., Craboledda, L., Cirillo, M., 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: Lekkas TD, editor. Heavy Metal in the Environment. CEP Consultant, Edinburgh 2. pp. 454–456.

Radojevic, M. and Bashkin, V.N., 1999. Practical Environmental Analysis. Royal Society of Chemistry, 465pp.

Ruiz, F., Abad, M., Olias, M., Galan, E., Gonzalez, I., Aguila, E., Hamoumi, N., Pulido, I., Cantano, M., 2006. The present environmental scenario of the Nador Lagoon (Morocco). Environ. Res. 102, 215–229.

Saeedi, M., Jamshidi-Zanjani, A., 2015. Development of a new aggregative index to assess potential effect of metals pollution in aquatic sediments. Ecol. Indic., 58, 235–243

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. Environ. Nanotechnol. Monit. Manage., 4, 27-36. http://doi.org/10.1016/j.enmm.2015.02.002

Taylor, S.R., 1964. Abundances of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28 (8), 1273 – 1285.

Tessier, A., Campbell, P. and Bison, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., 51 (7), 844-850.

Tornero, V., Arias, A. M., Blasco, J., 2014. Trace element contamination in the Guadalquivir River Estuary ten years after the Aznalcóllar mine spill. Mar. Pollut. Bull., 86(1-2), 349–360.

Turekian, K.K., Wedepohl, K. H., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72, 175–192.

Udosen, E.D., Benson, N.U., 2006. Spatio-temporal distributions of heavy metals in sediments and surface water in Stubbs Creek, Nigeria. Trends Appl. Sci. Res., 1(3), 292-300.

Urban, D.L., Cook, N.J., 1986. Hazard Evaluation Division standard evaluation procedure: ecological risk assessment. U.S. Environmental Protection Agency, Washington, D.C. EPA-540/9-85-001.

USEPA., 2005. Predicting toxicity to amphipods from sediment chemistry. EPA/600/R-04/030, Washington, DC.

Wang, C., Liu, S., Zhao, Q., Deng, L., Dong, S., 2012. Spatial variation and contamination assessment of heavy metals in sediments in the Manwan Reservoir, Lancang River. Ecotoxicol. Environ. Saf. 82, 32–39.

Wang, J., Liu, R., Zhang, P., Yu, W., Shen, Z., Feng, C., 2014. Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary. Mar. Pollut. Bull., 87, 364–373

Yu. Y., Song, J.M., Li, X.G., Yuan, H.M., Li, N., et al., 2013. Fractionation, sources and budgets of potential harmful elements in surface sediments of the East China Sea. Mar. Pollut. Bull., 68, 157–167.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., Liang, R., Chen, W., 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. Mar. Pollut. Bull., 54, 974–982.

Zhang, W., Feng, H., Chang, J., Qu, J., Xie, H., Yu, L., 2009. Heavy metal contamination in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. Environ. Pollut., 157, 1533-1543.

Zhang, W., Liu, X., Cheng, H., Zeng, E.Y., Hu, Y., 2012. Heavy metal pollution in sediments of a typical mariculture zone in South China. Mar. Pollut. Bull. 64,712–720.

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(4): e94145. doi:10.1371/journal.pone.0094145.

Highlights

1. New indices were developed for predicting sediment-associated risk adverse effects;
2. Newly proposed indices agree closely with the existing pollution indices;
3. Pollution indices reveal significant anthropogenic contamination by Cd and Pb;
4. Ecotoxicological indices reveal sediments of having 21% probability of being toxic;
5. Factor analysis reveals anthropogenic and lithogenic as sources of metal contamination.