Assessment of Sediment-Associated Contamination Risks Using New Multivariate Statistical Indexes

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Abstract

This paper presents the assimilation of heavy metal concentration data from sequential extraction method (SEM) with metal toxicity factors to develop and propose a new sediment quality index called ecological contamination index (ECI), to predict the potential ecological risk associated with sediment contamination. Chemical speciation sediment data of five heavy metals: cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) from five coastal aquatic ecosystems of the Equatorial Atlantic Ocean were used in assessment of the degree of heavy metal contamination. Other contamination indicators (degree of contamination, modified degree of contamination) used in characterization and identification of pollution hotspots, indicate considerably contaminated ecological ecosystems. Evaluation based on ECI indicates that sediments of most aquatic ecosystems were considerably to highly contaminated. The results illustrate that the proposed index is reliable, precise, and in good agreement with similar existing indexes for evaluating the severity of sediment-associated contamination by heavy metals. The principal component analysis (PCA) and factor analysis indicate that heavy metals in the benthic sediments originate mostly from anthropogenic sources.

Keywords: Fractionation, heavy metals, sediment, sediment pollution, contamination index.

1. Introduction

Sediments are integrated components of aquatic ecosystems, and have been recognised as sinks of heavy metals (Addo *et al*., 2012; Benson *et al*., 2008, 2016a; Benson & Etesin, 2008; Nilin *et al*., 2013; Pejman *et al*., 2015). Heavy metal concentration data are commonly applied in monitoring and assessing the degree of contamination of aquatic environments using sediment quality indices (Ajibola & Ladipo, 2011; Goher *et al*., 2014; Harikumar & Nasir, 2010; Håkanson, 1980; Kazemi *et al*., 2012; Lin *et al*., 2013; Liu *et al*., 2014; Maanan *et al*., 2015). Reports indicate that heavy metals in sediments could pose considerable adverse effects on aquatic animals, plants and the environment due to their bioaccumulation potential, non-biodegradability, and toxicity (Abreu *et al*., 2016; Benson *et al*., 2013, 2016b; Bu-Olayan & Thomas, 2013; Chen *et al*., 2016; Ma *et al*., 2016; Morelli & Gasparon, 2014; Tornero *et al*., 2014; Zhan *et al*., 2016). Several empirical and statistical indexes have also been developed as contamination assessment tools for monitoring sediments in aquatic ecosystems. Sediment quality indexes developed and widely applied in assessment of heavy metal contamination in aquatic ecosystems include risk assessment code (Håkanson, 1980), ecological risk index (Perin *et al*., 1985), pollution load index (Tomlinson *et al*., 1980), modified degree of contamination (Abrahim & Parker, 2008), modified risk assessment code (Saeedi & Jamshidi-Zanjani, 2015), and contamination severity index (Pejman *et al*., 2015). Although these approaches of characterizing sedimentary contamination hazards have existed since the early 80’s and are widely accepted and employed in sediments associated studies, each of these indices and reference values has its peculiar reliability advantages and limitations.

In this study, a new composite index, ecological contamination index, ECI, has been developed and proposed as sediment quality assessment approach, based on the assimilation of heavy metal concentration data from SEM in sediments from multiple tropical estuaries and freshwater ecosystems off the Equatorial Atlantic Ocean. This report provides a better understanding of the metal pollution status in aquatic ecosystems.

2. Materials and Method

2.1 Study Area and Sampling

In this study, five mesotidal and intertidal coastal water systems were considered. The aquatic ecosystems include Douglas Creek (DOU), Okorotip Creek (OKT), Stubbs Creek (STB), Qua Iboe Estuary (QUE) and Qua Iboe River (QUR). Sampling sites within the water bodies of these ecosystems were clearly mapped and designated for the collection of benthic sediments during the dry (June-August) and wet (November-January) seasons of the year. Benthic sediment samples from each ecosystem were collected using a modified van Veen (0.1 m^2) grab sampler and were preserved in clean, well-labelled glass bottles. After collection, the samples were all stored in ice-packed coolers and transported to the laboratory. These samples were further refrigerated in the laboratory at 4^oC to inactivate microbes and to preserve the integrity of the samples prior to analysis. A total of 90 benthic sediment samples were collected. In the laboratory, the sediment samples were dried in an oven maintained at 105±0.5°C, homogenized, comminuted using a hand mortar and sieved using a 2 mm mesh sieve prior to leaching (Radojevic & Baskin, 1999). Coning and quartering method was used to obtain subsamples from the respective composite samples.

2.2 Sample Extraction, Instrumentation and Data Analysis

The Tessier's procedure (Table 1) designed to separate heavy metals into five operationally defined fractions: exchangeable (F1), carbonate bound (F2), Fe-Mn oxides bound (F3), organic bound (F4) and residual fractions (F5) was used for this study (Tessier *et al*., 1979). The determinations of cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb) and nickel (Ni) were performed using inductively coupled plasma spectrophotometer (ICP-AES). The detection limits were 0.02, 0.01, 0.02, 0.02 and 0.01 ppm for Cd, Cr, Cu, Pb and Ni, respectively. Data analyses were carried out with XLSTAT-Pro software (AddinSoft Inc. USA).

2.3 Degree of Contamination and Modified Degree of Contamination

The degree of contamination, DC, was calculated with the sole aim of elucidating information on the potential risks posed by the presence of multiple heavy metals in sediments (Cheng *et al*., 2013; Hou *et al*., 2013). In this study, the DC was calculated according to the formula developed by Håkanson (1980):

$$DC = \sum_{i=1}^{i=n} CF_i \qquad where \quad CF_i = \left(\frac{C^i_{mc}}{C^i_{bkg}}\right) \qquad (2)$$

where CF_i = the contamination factor of metal i, C^i_{mc} = the mean concentration derived from investigated heavy metals from the five sampling sites, C^i_{bkg} = the background value of individual metal. The DC is classified into: low contamination (DC ≤ 6), moderate contamination (6 < DC ≤ 12), considerable contamination (12 < DC ≤ 24), and very high contamination (24 > DC). The modified degree of contamination commonly denoted as *mCd* is an empirical and generalized form of the Håkanson's formulae (equation 3) (Håkanson, 1980), used by Abrahim (2008) to determine the net contamination magnitude associated with heavy metals at any specific study location. *mCd* is expressed as follows:

$$mCd = \frac{\sum_{i=1}^{i=n} CF_i}{n} \qquad (3)$$

where CF_i = contamination factor, n = the number of analysed metals, and i = ith metal. The following classifications and descriptions of *mCd* are adopted for the present study: *mCd* < 1.5 refers to nil to very low contamination; 1.5 ≤ *mCd* < 2 indicates low contamination; 2 ≤ *mCd* < 4 implies moderate contamination; 4 ≤ *mCd* < 8 indicates high contamination; 8 ≤ *mCd* < 16 means very high contamination; 16 ≤ *mCd* < 32 implies extremely high contamination and *mCd* ≥ 32 refers to ultra high degree of contamination (Maanan *et al*., 2015).

3. Results and discussion

3.1 Heavy Metal Concentration

The fractionation metal concentrations indicate that Pb shows the highest mean concentration in the sediment during both seasons, followed by Cu. The maximum mean concentration values for Cd (5.67 mg kg^{-1}), Cr (28.52 mg kg^{-1}), Cu (43.72 mg kg^{-1}), Ni (2.60 mg kg^{-1}), and Pb (190.37 mg kg^{-1}) are obtained in the benthic sediments for both seasons. Mean metal levels (mg kg^{-1}) during wet and dry seasons did not show significant variability at all sites. Intensive fishing activities, sewage drainage from the mainland and other industrial activities are possible potential sources for the enrichment of these elements during the two seasons.

3.2 Degree of contamination and modified degree of contamination

The degree of contamination (DC) for Qua Iboe estuary, river and associated creeks were generally greater than 24, thus indicating very high degree of contamination. However, the severity of the heavy metals contamination followed the trend QUR > QUE > DOU > OKT > STB.

Table 1. Tessier's procedure for chemical fractionation

Extraction step	Fractionation phase	Nominal target phase	Reagents
Step 1	Fraction A	Exchangeable metals	$MgCl_2$ (1.0 mol/dm^3)
Step 2	Fraction B	Carbonate bound	NaOAc (1.0 mol/dm^3) at pH = 5.0
Step 3	Fraction C	Oxides Fe/Mn	$NH_2OH.HCl$ (0.04 mol/dm^3) / CH_3COOH (4.4 mol/dm^3)
Step 4	Fraction D	Organic matter and sulphides	HNO_3 (0.02 mol/dm^3) / H_2O_2 (12.8 mol/dm^3); then NH_4OAc (3.2 mol/dm^3) at pH = 2.0
Step 5	Fraction E	Residual bound to silicates	HF/$HClO_4$; then HCl (3.0 mol/dm^3)

Table 2. Modified degree of contamination by analysed trace metals

	June	July	August	November	December	January
DOU	H	H	H	H	H	H
OKT	H	H	H	H	H	H
STB	H	H	H	H	H	H
QUE	H	H	H	H	H	H
QUR	H	H	H	H	H	H

H: High degree of contamination

Additionally, the monthly DC values for all metals ranged between 25.63 and 27.31 with the wet season recording higher values than the dry season. The tidal influence within these aquatic ecosystems is usually remarkable during the wet season. The contamination ranking of heavy metals based on percent contribution to DC was Cd>Pb>Cu>Cr>Ni. Also, the *mCd* values obtained for all investigated heavy metals in benthic sediments ranged between 4.86 and 5.55, further indicating that the ecosystems are characterized by high degree of contamination during both seasons (Table 2).

3.3 Principal Component Analysis

3.4 The rotated factor loadings of principal component analysis (PCA) conducted to evaluate the interrelationships of trace metals in benthic sediments from the five studied aquatic ecosystems are presented in Table 3. The different trace metals contamination behaviours are observed in all five studied ecosystems. As shown in Table 3, there are two principal components (PC1 and PC2) for sedimentary heavy metals at the DOU, OKT, STB, QUE and QUR sites. Multivariate statistical analyses using PCA show that heavy metals pollution in these ecosystems originate from two principal sources – anthropogenic and lithogenic sources. The 1st principal component (PC1) indicates heavy metal contamination from anthropogenic sources, while the second principal component (PC2) represents natural sources of contamination. Cd, Pb and Cu may have common human-induced sources such as industrial and vehicular related activities. More so, Cr and Ni indicate a mixed origin from natural rock weathering processes and anthropogenic on- and off-shore-based industrial related activities. *Newly developed contamination index*

3.4.1 Ecological Contamination Index (ECI)

In this study, we proposed a reliable index known as ECI for an overall ecological risk assessment 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:

$$ECI = B_n \sum_{i=1}^{n} mHQ_i \quad (5)$$

$$mHQ = \left[C_i \left(\frac{1}{SQG_i} \right) \right]^{1/2} \quad (6)$$

where B_n = the reciprocal of derived eigenvalue of heavy metal concentrations only. mHQ = the modified hazard index, and SQG = the metal toxicity threshold, probable, and severe effect factors (MacDonald *et al*., 2000). The proposed ranking of risks posed by heavy metals to ecological systems computed based on the proposed formulation is presented in Table 4. The multi-elemental potential ECIs for all sites are 4.06, 3.80, 3.46, 5.06, and 3.73 for sites QUE, QUR, OKT, DOU, and STB, respectively. The calculated ECIs indicate that the ecosystems are characterized by slightly contaminated to a highly contaminated degree of pollution. 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 six heavy metals decreases in the following sequence: DOU> QUE>QUR>STB>OKT.

Table 3. Loadings of two principal components for benthic sediment variables

	DOU		OKT		STB		QUR		QUE	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Load of Cd	0.634	0.452	0.234	0.936	0.953	0.114	0.576	0.734	0.484	-0.758
Load of Cr	0.160	0.345	-0.786	0.508	0.439	-0.635	-0.682	0.459	0.485	0.708
Load of Cu	0.750	-0.144	0.943	-0.002	0.907	-0.252	0.821	-0.149	-0.832	-0.068
Load of Ni	0.125	0.558	0.368	-0.095	0.623	0.716	0.467	0.865	0.522	-0.431
Load of Pb	-0.401	0.587	-0.817	-0.265	-0.060	0.783	0.662	-0.590	0.913	0.210
Eigenvalue	1.705	1.601	2.366	1.214	2.317	1.605	2.128	1.868	2.268	1.311
Variability (%)	34.108	32.022	47.314	24.275	46.337	32.110	42.565	37.360	45.365	26.226
Cumulative %	34.108	66.130	47.314	71.589	46.337	78.447	42.565	79.925	45.365	71.591

Table 4. Ecological contamination index categorizations

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

Again, Cd contributes significantly to the ecological contamination risk index of these ecosystems than other heavy metals. The reliability and accuracy of the newly proposed formulae for assessment of sediment-associated heavy metals in aquatic ecosystems were ascertained by a thorough comparison of calculations using existing pollution indices. Results indicate that the ECI is a reliable and useful pollution tool that can be used to estimate the extent of pollution, site-specific status and aggregative contamination effects by heavy metals in aquatic ecosystems.

4. Conclusion

Heavy metals levels and contamination status in benthic sediments of five equatorial estuarine and riverine ecosystems are evaluated using existing pollution indices. Newly proposed index is used to evaluate the holistic ecological severity risk of sediment-associated heavy metals. The ECI is an aggregative index that represents the overall contamination pedigree and associated ecological risks based on the contribution of all hazardous heavy metals in an aquatic ecosystem. The risk assessment indices employed in the present study reveal significant contamination risk by Cd and Pb. The PCA reveals that both anthropogenic and lithogenic sources are responsible for the possible contamination of the investigated ecosystem by Cd, Cr, Cu, Ni and Pb. Estimation of potential risks by metals using the proposed ECI reveals possible pollution hotspot sites. A comparison of the newly proposed indices with existing pollution indices reveals very good agreement.

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