International Journal of Engineering Inventions
e-ISSN: 2278-7461, p-ISSN: 2319-6491
Volume 10, Issue 4 [April. 2021] PP: 12-22

Ecological Risk Indices Developed For Evaluating Heavy Metals In Asa River Sediments, Ilorin, Kwara State, Nigeria.

Oluwadurotimi O. Akintade[1], Rotimi A. Oderinde[2], Abiodun B. Ogbesejana[3]
Department of Chemical Sciences, KolaDaisi University, Ibadan-Oyo Expressway, Oyo State.
Department of Chemistry, University of Ibadan, Ibadan, Oyo State.
Department of Applied Chemistry, Federal University Dutsin-ma, Katsina State.

ABSTRACT
Sequence extraction method was employed to analyse the levels of Lead (Pb), Copper (Cu), Cobalt (Co), Chromium (Cr), Nickel (Ni), Zinc (Zn), Aluminum (Al), Iron (Fe) and Manganese (Mn) in sediment samples from tropical ecosystems of Asa River in Ilorin, Kwara State, Nigeria. Heavy metals assessed in Asa River sediments are Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn and their concentrations ranged from 0.74-0.76, 47.68-47.71, 33.20-36.55, 53.05-55.64, 24.15-25.97, 32.29-37.11, 28.15-32.90, 15.33-18.14, 10.32-13.36 mg/kg respectively. The mean metal levels did not show significant variations among study sites during the wet and dry seasons. Contamination Ecological Index (CEI) and Hazard Quotient modified (HQm) were indices developed for the assessment of heavy metals pollution in sediments. The results were used to assess the degree of pollution and estimate the extent of human-made inputs from industrial activities. HQm and CEI were in good agreement with existing pollution indices and followed the ascending sequence Co>Cu>Cr>Ni>Zn>Al>Pb>Mn>Fe. Indicators of water pollution which are contamination potential index, contamination ecological index [CEI], hazard quotient and Hazard Quotient modified revealed significant human-made pollution by Cu and Co while Pb, Ni, Zn, Al, Fe and Mn showed relatively low degree of contamination. The developed ecological risks assessment when compared with existing pollution indices revealed very good agreement. The contamination trends derived from the recently developed indices were consistent and reliable in evaluating polluted abyssal ecosystem.
KEYWORDS: *sediment pollution indices, heavy metals, ecological risks, Asa River;*

Date of Submission: 30-04-2021 Date of Acceptance: 15-05-2021

I. INTRODUCTION

Sediment is a naturally occurring material that is broken down by processes of weathering and erosion, and is subsequently transported by the action of wind, water, or ice and by the force of gravity acting on the particles [1-2]. Pollutants release to surface water from industrial and municipal discharges, atmospheric deposition and polluted runoff from agricultural, urban mining areas can accumulates to environmentally harmful level in sediment. Heavy metals are intrinsic constituents of our environment. They are generally present in small amounts in natural aquatic environments. Apart from the natural sources, several anthropogenic ones also contribute to metal concentrations in the environment. In recent times, industrial activities have raised natural concentration causing environmental problems [3].

Sediments are known as store houses of heavy metals [4-5], while the estimation of sedimentary heavy metal contamination and associated ecological risks can be evaluated using consensus-based indices [6-7]. Sediment quality guidelines and background values are widely used in ecological risk assessments to determine heavy metal contamination in aquatic ecosystems [8]. Several empirical and statistical approaches have also been developed in response to environments 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 sediment studies, they have limitations and vary in reliability.

Asa River is situated in Ilorin, Kwara State, Nigeria. Its catchment basin is about 1040 km in area and lies at latitudes (8^{o}24' and 8^{o}36'N) and longitudes (4^{o}10' and 4^{o}36'E), **Figure 1**. The city experiences a tropical wet and dry climate each lasting for about six months with mean annual rainfall of 1200 mm. Its temperature varies between 25-30^{o}C in March which marks the hottest month [9].

Variations observed in the metals distribution from Asa River sediment could be attributed to environmental contents of the different areas in the vicinity of the river such as activities around the studied area, population density, domestic and municipal disposal, atmospheric fallout, sewage effluents, traffic volume, substantial contribution from industrial premises and natural origin.

The objectives of the present study are: (a) to investigate the extent of contamination in Asa River sediments using some contamination indices (CPI, HQm, CEI) (b) to establish their contamination status using sediment quality guidelines and (c) to use two recently developed indices using the derived data in an effort to establish a model system for evaluating heavy metal contamination in sediments.

II. MATERIALS AND METHOD

2.1 Study sites, sample collection and pretreatment

Twenty-six sediment samples were collected along the course of Asa River, **Figure 1, Table 1,** seasonally for two years [February 2013-April, 2015]. In every investigated aquatic ecosystem, triplicate samples of benthic sediment from each identified site were collected every six months using a grab sediment sampler. The samples were pooled and the resultant composite samples were appropriately labeled. One hundred and four (104) samples were collected from twenty-six sampling locations for both seasons. 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^{o}C to in activate 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 107±0.5^{o}C, homogenized, grinded using a hand mortar and sieved through a 2 mm mesh sieve before selective leaching [10, 7].

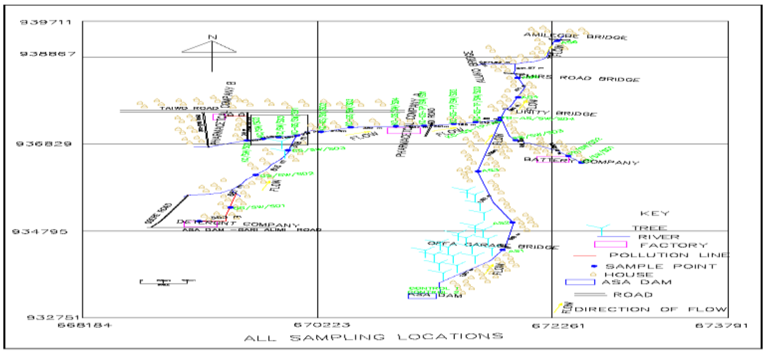

Figure 1: The investigated freshwater and riverine ecosystem map of Asa River

Table 1. Sampling locations and study areas of Asa River

S/No.	Locations/Code site	Type of ecosystem	Name of site	Latitude – N	Longitude – E
1	GS1/SD	Freshwater	Detergent company point one	8 °27' 27.84"N	4°32' 20.57" E
2	GS2/SD	Freshwater	Detergent company point two	8°27'58.83'' N	4 °32'28.96''E
3	GS3/SD	Freshwater	Detergent company point three	8°28'17.54'' N	4°32'38.32'' E
4	KC1/SD	Freshwater	Pharmaceutical company B point one	8°28'25.14''N	4°32'26.62'' E
5	KC2/SD	Freshwater	Pharmaceutical company B point two	8°28'26.42''N	4°32'31.33''E
6	KC3/SD	Freshwater	Pharmaceutical company B point three	8°28'27.51'' N	4°32'35.68'' E
7	KC-GS1/SD	Freshwater	Pharmaceutical company B-Detergent company point one	8°28'29.15''N	4°32'40.95'' E
8	KC-GS2/SD	Freshwater	Pharmaceutical company B-Detergent company point two	8°28'31.76''N	4°32'47.86''E
9	KC-GS3/SD	Freshwater	Pharmaceutical company B-Detergent company point three	8°28'35.12''N	4°32'56.31''E
10	KC-GS4/SD	Freshwater	Pharmaceutical company B-Detergent company point four	8°28'35.59'' N	4°33'9.61''E
11	KC-GS-TP1/SD	Freshwater	Pharmaceutical company B-Detergent company point-Pharmaceutical company A meeting point one	8°28'36.21'' N	4°33'16.91'' E
12	KC-GS-TP2/SD	Freshwater	Pharmaceutical company B-Detergent company point-Pharmaceutical company A meeting point two	8°28'37.41''N	4°33'25.55''E
13	KC-GS-	Freshwater	Pharmaceutical company B-	8°28'38.72''N	4°33'31.67''E

	TP3/SD		Detergent company point-Pharmaceutical company A meeting point three		
14	KC-GS-TP-AS/SD	Riverine	Pharmaceutical company B-Detergent company point-Pharmaceutical company A as it enters Asa River	8°28'39.93''N	4°33'38.44''E
15	FB1/SD	Freshwater	Battery company point one	8°28'7.97''N	4°34'1.36''E
16	FB2/SD	Freshwater	Battery company point two	8°28'12.73''N	4°33'57.46''E
17	FB3/SD	Freshwater	Battery company three	8°28'25.23''N	4°33'42.89''E
18	FB-AS/SD	Riverine	Battery company as it enters Asa River	8°28'41.98''N	4°33'38.81''E
19	AS1/SD	Riverine	Asa River after the dam	8°27'1.29''N	4°33'39.25''E
20	AS2/SD	Riverine	Asa River Dangote Area	8°27'22.63''N	4°33'41.86''E
21	AS3/SD	Riverine	Asa River 7UP Bridge	8°28'1.28''N	4°33'32.30''E
22	AS4/SD	Riverine	Asa River Unity Bridge	8°28'57.88''N	4°33'43.58''E
23	AS5/SD	Riverine	Asa River Emir Bridge	8°29'12.56''N	4°33'43.80''E
24	AS6/SD	Riverine	Asa River Amilegbe Bridge	8°29'40.90''N	4°33'55.07''E
25	CTRL1/SD	Riverine	Asa Dam water corporation	8°26'30.76''N	4°33'21.02''E
26	CTRL2/SD	Riverine	Egbejila before Asa Dam site	8°26'16.08''N	4°33'20.05''E

Note: For results and discussion sections: GS1, 2,3 becomes (GS1-GS3/SD); KC1,2,3 (KC1-KC3/SD); KC-GS1,2,3,4 (KC-GS1-KC-GS4/SD); KC-GS-TP1,2,3 and KC-GS-TP-AS becomes(KC-GS-TP1-KC-GS-TP-AS); FB1,2,3 and FB-AS (FB1-FB-AS/SD); AS1,2,3 (AS1-AS3/SD); AS4,5,6 (AS4-AS6/SD); CTRL1,2 (CTRL1-2/SD)

2.2 Sediment analysis for heavy metals

Air-dried sediment (0.15-0.20 mm) was weighed at 0.5-1.0 g into a clean 100 mL Teflon beaker and wet with 5 mL distilled water. Conc. $HClO_4$ acid of 2 mL was added with 12 mL conc. HF acid and heated to near dryness, 8 mL conc. HF acid was added and heated to near dryness followed by 2 mL conc. $HClO_4$ acid added and 5 mL of distilled water and heated to near dryness. The remaining residue was dissolved in 8 mL conc. HCl acid and 20 mL distilled water was added, also make up to 100 mL volume and store in polyethylene bottles [11]. Flame Atomic Absorption Spectrophotometer was used for the determination of heavy metals in the sample. Replicate samples, calibration standards and method blanks were used to monitor the performance of the instrument and the quality of the data.

2.3 Statistical analysis of hazard quotient

The SPSS 23.0 was used for data analysis. The principal component analysis (PCA) was used to estimate the correlation among the identified metals in the sediment samples. $P<0.05$ was calculated to be significant and data were considered adequate for PCA. 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. Distance and the direction of changes as a reflection of the spatial correlation were incorporated between sample points into the interpolation to produce more advanced predictions.

Table 2. Sediment quality guidelines parameters for selected metals (mg/kg) [12-13]

Sediment Quality Guidelines		Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
ERL		35	70	ND	80	30	150	ND	ND	ND
ELT		35	35.7	ND	37.3	18	46.9	2.55	18.84	630
EMT		42	28	ND	55	35	410	1.80	22.0	260
ERM		110	390	ND	145	50	88.1	ND	ND	ND
ELP		91.3	197	ND	90	36	270	1.80	22.0	260
ELS		250	110	ND	110	75	520	15.6	4.00	1110
TET		170	100	ND	100	61	ND	ND	ND	ND
GBG	shale standard	20	95	29	90	68	95	15.53	46700	850
	Earth crust	12.5	70	13	100	75	20	15.6	35900	750

Note: For Cobalt calculations geochemical background value was used
ND = Not detected
ERL = Effects range low
ERM = Effects range median
PEL = Effect level probable
TEL = Effect level threshold
SEL = Effect level severe
EMT = Effect minimal threshold
TET = Toxic effect threshold

GBG = Geochemical background

2.4 Contamination Potential Index (CPI)

Aquatic sediments trace metals were calculated using potential contamination index of metal I (CPIi) with this equation by [14].

$CPIi = \frac{Cimax}{Cbkg}$ ------- (I)

Where CPIi is the potential contamination index of metal i, Cimax is the maximum concentration of metal i in the sediment, and Cbkg indicates the background concentration [geochemical background value of metal in the reference average shale] [15] of the same trace metal. Three grades are considered for the classification of sediment. CPI <1 indicates low contamination, 1<CPI<3 as moderate contamination and CPI>3 being considered as severe or very severe contamination [14].

2.5 Heavy metal concentrations ecotoxicological assessment in sediments

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 correlation reference criteria [12, 16-17]. **Table 2**. In the present research, comparisons of trace metal (Pb, Cu, Co, Cr, Ni, Zn, Al, Fe, Mn) concentrations (mg/kg) in 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 and ecological contamination risk index.

In this study, the characterization of sediment quality of the twenty-six ecosystems as a function of trace metal concentration was based on ERL, TEL, MET, PEL and TET. The mean concentrations of Cu, Cr, Ni and Al 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 Effects level probable quotient ($mELP_Q$) was calculated using the formula:

$mELP_Q = \sum_{i=1}^{n} (\frac{Ci}{ELPi}) \div n$ (II)

where, Ci is the concentration of metal i, ELP_i is the probable effect level for metal, i and n is the sum of the metals considered. Moreover, the $mELP_Q$ 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 an 8%, 21%, 49% and 73% probability of being toxic [18-19].

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

$mERM_Q = \sum_{i=1}^{n} \left(\frac{Ci}{ERMi}\right) \div n$ (III)

where, ERMi 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.

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:

$HQ = \frac{Cmetal}{SQG}$ (IV)

Where, Cmetal is the observed concentration of a metal in sediment and SQG is the sediment quality guideline [20]. The SQG adopted for calculating the HQ in this study was the effects level threshold (ELT) [12]. According to [21], 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.

2.6 Contamination indices developed

2.6.1 Hazard quotient modified (HQm)

An index for estimating sediment pollution based on the level of contamination by each heavy metal is formulated and proposed [13] in this present study. This approach enables the assessment of contamination by comparing metal concentration in sediment with the laconic unfavourable environmental effect distributions for slightly differing threshold levels (ELT, ELP and ELS) reported by [12]. The calculation of hazard quotient modified (HQm) for metals is the main evaluation tool that explains the degree of risk of each heavy metal to water habitats and the biota which is expressed mathematically using the below formula [13].

$HQm = [Ci (\frac{1}{ELTi} + \frac{1}{ELPi} + \frac{1}{ELSi})]^{½}$ (V)

Where, Ci is the measured concentration of heavy metal in the sediment samples, ELTi, ELPi and ELSi are acronyms for the effect level threshold, effect level probable and effect level severe for ith metal, respectively.

The square root is introduced as a draw down function for mathematical and ranking considerations in the equation. Classification of pollution proposed by a single metal is presented in Table 3.

Table 3. Classification of Hazard Quotient modified (HQm) [13]

HQm	Degree of risk
HQm > 3.5	Extremely severity of contamination
3.0 < HQm < 3.5	Very high severity of contamination
2.5 < HQm <3.0	High severity of contamination
2.0 < HQm <2.5	Considerable severity of contamination
1.5 < HQm < 2.0	Moderate severity of contamination
1.0 < HQm <1.5	Low severity of contamination
0.5 < HQm < 1.0	Very low severity of contamination
HQm < 0.5	Nil to very low severity of contamination

2.6.2 Contamination Ecological Index (CEI)

In this study, a proposed index known as ecological contamination index is used for an aggregate ecological risk evaluation of sediment contamination by heavy metals [13]. The CEI is an aggregative empirical approach that estimates the risks associated with an ecosystem using a source-specific factor derived primarily from principal component analysis and factor analysis. The proposed formula for CEI is mathematically expressed as:

$$CEI = Bn\sum_{i=1}^{n} mHQi \qquad (VI)$$

Where Bn = the reciprocal of derived eigen value of heavy metal concentrations only. The proposed ranking of risks posed by heavy metals to ecological systems computed based on the formulation is presented in **Table 4.**

Table 4. Classification of Contamination Ecological Index (CEI) [13]

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

III. RESULTS AND DISCUSSION

3.1 Heavy metal distribution

Concentrations (G1+G2+G3+G4+G5+G6+G7+G8+G9) of heavy metals (Pb, Cu, Co, Cr, Ni, Zn, Al, Fe, Mn) in sediments from the investigated abyssal ecosystems are presented in **Table 5.** Chromium showed the highest mean concentration in the sediment at both seasons, followed by copper. The observed maximum mean concentration values of 0.75±0.01, 47.70±0.02, 34.88±2.37, 54.35±1.83, 25.06±1.29, 34.70±3.41, 30.58±3.36, 16.74±1.99 and 11.84±2.15 were recorded for Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn respectively (mg/kg) during the dry and wet seasons in all the sites. Discharges of sewage and effluents from industrial activities are mostly the major origins for the enhancement of these metals into the abyssal ecosystems.

Table 5. Seasonal concentration (Mean± S.D, mg/kg) of heavy metals in studied aquatic ecosystems

PARAMETERS		GS1 – GS3/SD	KC1 – KC3/SD	KC-GS1 – KC-GS4/SD	KC-GS-TP1 – KC-GS-TP-AS/SD
Pb	FEB. 2013 –APR. 2015 (DS & WS)	0.36±0.12	0.49±0.05	0.10±0.06	0.41±0.14
Cu	FEB. 2013 –APR. 2015 (DS &WS)	56.50±3.68	54.87±6.12	31.23±7.88	37.33±10.71
Co	FEB. 2013 –APR. 2015 (DS &WS)	38.02±2.83	39.18±2.92	47.18±4.70	35.63±10.63
Cr	FEB. 2013 –APR. 2015 (DS &WS)	72.35±3.66	57.78±8.53	54.50±13.38	53.40±6.76
Ni	FEB. 2013 –APR. 2015 (DS &WS)	25.90±3.79	24.07±7.87	30.32±2.08	25.21±3.74
Zn	FEB. 2013 –APR. 2015 (DS &WS)	32.19±2.93	33.54±1.51	31.41±2.96	30.10±3.23
Al	FEB. 2013 –APR. 2015 (DS &WS)	21.34±1.61	26.21±5.12	31.41±3.28	36.75±2.39
Fe	FEB. 2013 –APR. 2015 (DS &WS)	14.67±2.82	12.09±0.71	13.91±2.58	18.78±3.50
Mn	FEB. 2013 –APR. 2015 (DS &WS)	8.00±1.53	10.17±0.85	13.07±1.59	10.94±2.77

DS = Dry season; WS = Wet season

Table 5 (cont'd). Seasonal concentration (Mean± S.D, mg/kg) of heavy metals in studied aquatic ecosystems

PARAMETERS		FB1– FB-AS/SD	AS1 – AS3/SD	AS4 – AS6/SD	CTRL1 – CTRL2/SD
Pb	FEB. 2013 –APR. 2015 (DS & WS)	1.31±1.18	0.36±0.01	0.29±0.01	0.36±0.28
Cu	FEB. 2013 –APR. 2015 (DS &WS)	51.60±20.52	37.57±9.82	38.83±9.71	36.74±8.68
Co	FEB. 2013 –APR. 2015 (DS &WS)	36.21±5.11	39.50±8.66	29.53±2.78	36.74±12.53
Cr	FEB. 2013 –APR. 2015 (DS &WS)	53.40±2.58	57.77±9.00	51.43±5.57	43.95±12.09
Ni	FEB. 2013 –APR. 2015 (DS &WS)	26.43±6.14	19.15±3.34	28.67±2.47	16.08±1.13
Zn	FEB. 2013 –APR. 2015 (DS &WS)	36.63±3.45	32.08±1.81	50.09±5.06	27.88±1.94
Al	FEB. 2013 –APR. 2015 (DS &WS)	28.10±1.71	26.96±2.27	43.75±7.21	21.25±1.06
Fe	FEB. 2013 –APR. 2015 (DS &WS)	17.53±1.31	19.42±1.42	23.17±3.19	12.69±1.68
Mn	FEB. 2013 –APR. 2015 (DS &WS)	12.91±2.96	11.46±1.61	18.13±4.22	8.44±0.79

DS = Dry season; WS = Wet season

3.2 Principal component analysis

Principal component analysis and factor analysis which are examples of multivariate statistical methods are mostly utilized to illuminate interdependence that exist among parameters (principal components) investigated in an observational dataset [22-24]. In this study, principal component analysis was used to evaluate similarities in the occurrence and concentrations of trace metals (Pb, Cu, Co, Cr, Ni, Zn, Al, Fe, Mn) obtained in each fraction. The agreeable and acceptability of observed data was further examined using Bartlett's sphericity test and KMO. The computed KMO coefficients achieved were 0.63, 0.57, 0.98, 0.87, 0.97, 0.24, 0.29, -1.00, and were less than one for GS1-3/SD, KC1-3/SD, KC-GS1-4/SD, KC-GS-TP1-3,AS/SD, FB1-3,AS/SD, AS1-3/SD, AS4-6.SD and CTRL1-2/SD sites respectively. The associated probability of Bartlett's sphericity test was not significant at ά=0.05 level. In the PCA, a principal component with eigen value > 1 is regarded as significant. Thus, the observations at most sites were averagely adequate for a factor model.

The factor loadings of trace metals in sediment at all the sampling sites were grouped into two principal component models for principal components >1 **Table 6**. The eigen values of PC1 and PC2 associated with sediments from GS1-3/SD were greater than 1 and in general accounted for 80% of the variability in concentrations of trace metals. PC1 indicated that 34% of the total variance was positively related to Pb, Co, Cr, Zn and Fe. However, PC2 which explained 46% of the total variance, indicated strong negative interrelationships for Cu, Co and Cr. The eigen values of components 1 and 2 associated with sediment samples from KC1-3/SD were also greater than 1 and accounted for 85% of the total variance in metal concentrations. PC1 showed that 39% variability was attributed to Pb, Cr, Zn, Fe and Mn showing relatively high positive factor loadings, while Co indicated a strong negative relationship. Moreover, PC2 accounted for 46% of the total variance and was associated with strong negative interrelationships between Cu and Al. From **Table 6**, the factor loading of heavy metals in Asa River downstream (AS4-6/SD) indicated that eigen values of PC1 and PC2 derived for sediment samples were greater than 1 and, accounted for 92% of the variability in trace metal levels. PC1 was the most significant principal component and was dominated by Pb, Co, Zn, Al, Fe and Mn, which accounted for 79% of the total variance. A very high loading of Pb (0.970), Zn (0.996) and Al (1.000) indicated a significantly positive association. Moreover, Cu (-0.980) 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 [13, 25-26].

Table 6. Principal components loadings for sediment variables

	GS 1 – GS3/SD		KC1 - KC3/SD		KC-GS1 – KC-GS4/SD		KC-GS-TP1-KC-GS-TP-AS/SD	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Load of Pb	**0.960**	0.279	**0.980**	-0.172	0.680	0.206	-0.073	0.953
Load of Cu	0.097	**-0.995**	0.413	-0.911	0.678	0.149	**0.975**	0.202
Load of Co	**0.929**	-0.371	-0.955	0.297	**0.941**	-0.355	0.147	-0.247
Load of Cr	**0.992**	-0.128	0.641	0.768	-0.930	-0.133	**0.925**	-0.110
Load of Ni	-0.573	0.805	-0.007	1.000	0.893	0.447	-0.955	-0.015
Load of Zn	**0.832**	0.555	**0.990**	0.143	-0.103	0.095	-0.836	0.548
Load of Al	-0.969	-0.247	-0.196	-0.981	0.009	0.811	-0.141	-0.095
Load of Fe	**0.553**	0.833	0.814	0.581	0.044	0.970	0.270	0.960
Load of Mn	-0.905	0.425	0.839	0.544	-0.062	0.997	-0.269	0.956
Eigen value	5.885	3.115	5.482	3.518	4.549	3.034	4.249	2.906

Variability	34.612	46.325	39.089	46.139	50.542	38.829	40.144	35.187
Cumulative	34.612	53.325	39.089	53.861	50.542	72.131	40.144	75.332

Table 6 (cont'd). Principal components loadings for sediment variables

	FB 1 – FB-AS/SD		AS1 - AS3/SD		AS4 – AS6/SD		CTRL1 – CTRL 2/SD	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Load of Pb	**0.944**	-0.273	-0.990	0.141	**0.970**	0.243	-1.000	-1.000
Load of Cu	0.966	-0.260	0.251	0.968	**-0.980**	-0.197	-1.000	-1.000
Load of Co	**0.990**	0.006	-0.787	0.617	0.928	0.372	**1.000**	1.000
Load of Cr	0.084	-0.634	-0.150	1.000	-0.737	-0.676	-1.000	-1.000
Load of Ni	0.926	0.321	-0.87	-0.491	0.037	0.999	-1.000	-1.000
Load of Zn	-0.306	0.943	0.743	-0.670	**0.996**	0.089	1.000	1.000
Load of Al	-0.695	0.666	0.991	0.133	1.000	0.003	1.000	1.000
Load of Fe	0.562	0.823	0.993	0.115	0.948	0.319	1.000	1.000
Load of Mn	-0.971	0.239	-0.015	1.000	0.993	0.177	1.000	1.000
Eigen value	5.707	2.512	5.001	3.999	7.743	1.257	9.000	9.000
Variability (%)	61.147	30.176	55.571	44.429	79.827	13.963	100	100
Cumulative (%)	61.147	91.322	55.571	54.917	79.827	86.037	100	100

3.3 Contamination Potential index (CPI)

In this study, the CPI was calculated for Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn at each studied site. Results of CPI are presented in **figure 2.** According to the classification proposed by [12], Co, Al, Zn potential contamination index values were moderate contamination. The CPI values for Pb, Co, Cr, Ni, Fe and Mn were low in all the sites, indicating low contamination. Co, Al and Zn showed high degree of anthropogenic impact based on the CPI of the investigated benthic sediment samples. The CPI generally followed the sequence Co>Al>Zn>Cu>Cr>Ni>Pb>Mn>Fe.

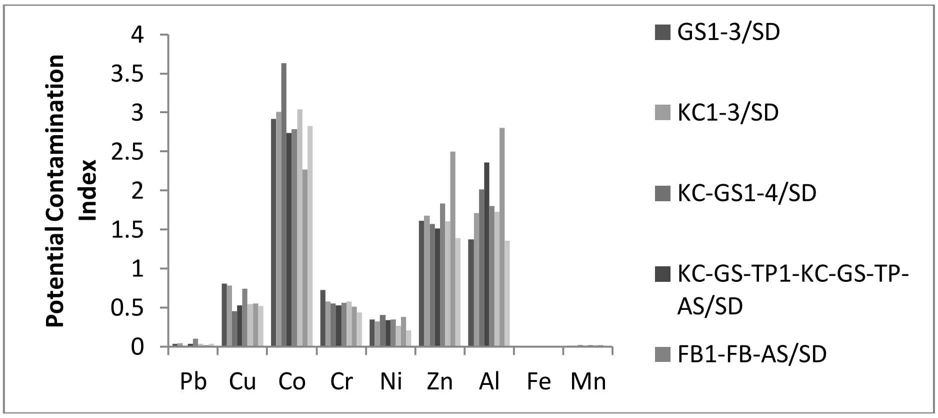

Figure 2. Contamination Potential Index of approximated human-made impact

3.4 Heavy metal concentrations ecotoxicological evaluation in sediments

Relative results indicated that Cu, Ni, Cr, Al were higher in 65.3%, 88.4%, 88.4% and 100% of the samples than the effect level threshold (ELT), Cu and Al were higher in 88.4% and 100% for effect minimal threshold (EMT) while, Cobalt was higher than mean shale and earth crust geochemical background in 88.4% and 100%. These results showed that the levels of Ni, Cu, Cr, Al, and Fe primarily characterized the sediment quality of the studied ecosystems, and could pose deleterious effects on benthic effects on benthic dwelling biota. Cu and Al exceeded the TEL and EMT concentrations indicating human-caused contamination of sediments of aquatic ecosystems in this region, there may be some ecotoxicological risk to organisms living in these sediments.

Our results showed that the seasonal $mELP_Q$ varied within the range of 0.33-0.35 (GS 1 – GS3/SD); 0.32-0.34 (KC1 – KC3/SD); 0.30-0.33 (KC-GS1 – KC-GS4/SD); 0.29-0.33 (KC-GS-TP1-KC-GS-TP-AS/SD); 0.31-0.38 (FB1 – FB-AS/SD); 0.28-0.33 (AS1-AS3/SD); 0.35-0.37 (AS4 –AS6/SD); 0.25-0.26 (CTRL1-2/SD) **Figure 3**. 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 0.18-0.20 (GS1 – GS3/SD and KC1 - KC3/SD); 0.16-0.20 (KC-GS1 – KC-GS4/SD and KC-GS-TP1 – KC-GS-TP3/SD); 0.16-0.21 (AS1 – AS6/SD); 0.14-0.15 (CTRL1-2/SD) **Figure 3**. The $mERM_Q$ values showed that the studied sites were medium-low priority sites with trace metals having a combined 21% probability of being toxic.

Results of the calculated hazard quotients (HQ) for trace metals (Pb, Cu, Co, Cr, Ni, Zn, Al, Fe, Mn) in the investigated ecosystems are presented in **Table 7.** The HQ values of Pb, Fe and Mn was 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 Cu, Co, Cr, Ni, Zn, Al were between 1 and 10 (1<HQ<10) at all investigated sites. These values indicated the possibility of Cu, Co, Cr, Ni, Zn and Al triggering moderate hazards in these ecosystems. Cu, Co and Al are notable environmental toxicants, and their considerable HQ values indicated that they might be associated with adverse biological and ecosystem risks.

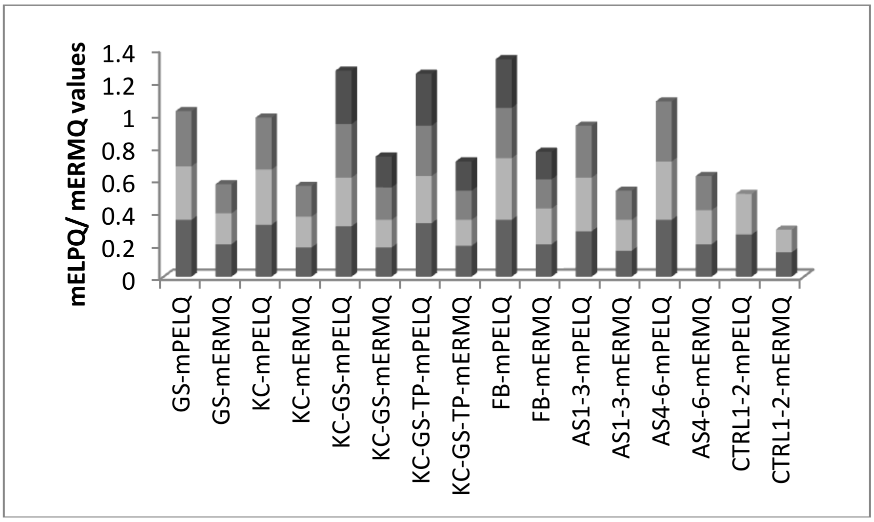

Figure3. Seasonal distributions of calculated $mELP_Q$ and $mERM_Q$ in benthic sediments (Beginning letters before the calculated quotients signifies the name of the aquatic ecosystem: GS = GS1-3/SD; KC = KC1-3/SD; KC-GS = KC-GS1-4/SD; KC-GS-TP = KC-GS-TP1-KC-GS-TP-AS/SD; FB = FB1-FB-AS/SD; AS1-3 = AS1-AS3/SD; AS4-6 = AS4-AS6/SD; CTRL1-2/SD = CTRL1-CTRL2/SD)

Table 7. Hazard Quotients of trace metals at all sites

Metals	GS1 –GS3/SD	KC1 –KC3/SD	KC-GS1 - KC-GS4/SD	KC-GS-TP1–KC-GS-TP-AS/SD
Pb	0.02	0.02	0.01	0.02
Cu	5.04	4.90	2.79	3.33
Co	2.00	1.35	1.63	1.23
Cr	0.80	0.64	0.61	0.59
Ni	0.38	0.35	0.45	0.37
Zn	0.34	0.35	0.33	0.32
Al	1.37	1.69	2.02	2.37
Fe	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.02	0.01

Table 7(cont'd). Hazard Quotients of trace metals at all sites

Metals	FB1–FB-AS/SD	AS1 –AS3/SD	AS4 – AS6/SD	CTRL1 – CTRL2/SD
Pb	0.07	0.02	0.01	0.02
Cu	4.61	3.35	3.47	3.28
Co	1.25	1.36	1.02	1.27
Cr	0.59	0.64	0.57	0.49
Ni	0.39	0.28	0.41	0.24
Zn	0.39	0.34	0.53	0.29
Al	1.81	1.74	2.82	1.37
Fe	0.00	0.00	0.00	0.00
Mn	0.02	0.01	0.02	0.01

3.5 Review of results for developed contamination indices

The developed indices for evaluating ecological risk assessment for sediment-associated contaminants used by 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 (effect level threshold, effect level probable and effect level severe) to evaluate the potential impacts of contamination. The formulation approach also incorporated the eigen value results from principal component analysis. However, the significance of the PCA is known to be a function of the respective calculated eigen values. **Table 6** presents the calculated results of PCA including the metal loading factors, eigen values and variance (variability and cumulative) for two principal components (PC1 and PC2). The eigen values of PC1 are considered to be very significant variables that could be associated with potential human-induced sources of the investigated heavy metals. The eigen values, therefore were used in calculating the net ecological contamination index.

3.5.1 Hazard Quotient modified (HQm)

mHQ in equation V is used for calculation in 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 above the ELT, ELP and ELS, 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 HQm values for benthic sediments of all the investigated sites during the wet and dry season's period are presented in **Table 8.** The HQms calculated according to the formulation indicated that the severity of sediment-associated pollution of the nine heavy metals were in the descending sequence: Co>Cr>Ni>Al>Cu>Zn>Pb>Mn>Fe. This trend is in good agreement with other contamination sequence obtained for pollution assessment indices earlier reported for these ecosystem and other reports [27-28, 13]. Results indicated that Co gave moderate degree of contamination, followed by Cr, Ni, Al and Cu. However, Fe, Mn, Zn and Pb showed low to very low degree of contamination during both seasons at all sites investigated.

Table 8. Hazard Quotient modified (HQm) for heavy metals at all sites

Metals	GS1 –GS3/SD	KC1 –KC3/SD	KC-GS1 - KC-GS4/SD	KC-GS-TP1–KC-GS-TP-AS/SD
Pb	0.12	0.15	0.07	0.27
Cu	1.54	1.52	1.14	1.24
Co	1.71	1.74	1.91	1.64
Cr	1.88	1.68	1.62	1.62
Ni	1.61	1.55	1.76	1.59
Zn	0.51	0.51	0.50	0.50
Al	1.17	1.29	1.41	1.53
Fe	0.02	0.02	0.02	0.02
Mn	0.01	0.11	0.13	0.12

Table 8 (cont'd). Hazard Quotient modified (HQm) for heavy metals at all sites

Metals	FB1–FB-AS/SD	AS1 –AS3/SD	AS4 – AS6/SD	CTRL1 – CTRL2/SD
Pb	0.21	0.13	0.11	0.12
Cu	1.45	1.25	1.27	1.33
Co	1.67	1.74	1.51	1.67
Cr	1.62	1.68	1.58	1.46
Ni	1.63	1.38	1.68	1.28
Zn	0.54	0.50	0.63	0.47
Al	1.34	1.32	1.67	1.17
Fe	0.02	0.02	0.03	0.02
Mn	0.13	0.12	0.15	0.11

3.5.2 Contamination Ecological index (CEI)

The multi-elemental potential (ECIs) for all the sites are presented in **Figure 4.** The results for all the metals (Pb, Cu, Co, Cr, Ni, Zn, Al, Fe, Mn) in sediments were between 0.07 and 6.38 at GS1/SD site to CTRL2/SD site, respectively. The calculated CEIs indicated a slightly contaminated to highly contaminated ecosystems. The CEI ranking based on percentage contribution to CEI followed the sequence Co>Cu>Cr>Ni>Zn>Al>Pb>Mn>Fe while the severity of ecosystem pollution based on the nine heavy metals decreased in the following sequence FB1-FB-AS/SD > AS4-AS6/SD > GS1-3/SD > KC1-3/SD > KC- GS1-4/SD > KC-GS-TP1-KC-GS-TP-AS/SD > AS1-AS3/SD > CTRL1-2/SD. In general, Cobalt contributed considerably to the ecological contamination risk index of the investigated aquatic ecosystem compared to Pb, Mn, Fe.

The reliability and accuracy of the developed formulas 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 developed indices are presented in **Table 9.** Results indicated that the mHQ and CEI 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 ecosystem.

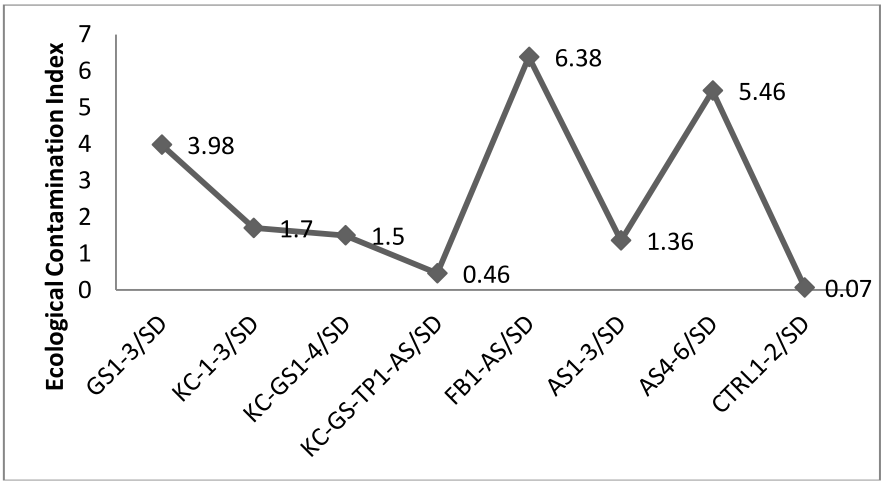

Figure 4. Description of ecological contamination index (ECI) of sedimentary metals

Table 9. Contamination trends comparisons using existing and developed pollution indices

Type of index	GS/SD KC/SD KC-GS/SD KC-GS-TP/SD FB/SD AS/SD CTRL/SD Pollution sequence and status of heavy metals	Reference
Contamination Factor	Co>Al>Zn>Cu>Cr>Ni>Pb>Mn>Fe	PhD Thesis (2019) [29]
Pollution Load Index	Co>Al>Zn>Cu>Cr>Ni>Pb>Mn>Fe	PhD Thesis (2019) [29]
Potential Contamination Index	Co>Al>Zn>Cu>Cr>Ni>Pb>Mn>Fe	This study
Modified hazard quotient	Co>Cr>Ni>Al>Cu>Zn>Pb>Mn>Fe.	This study
Contamination Ecological index	Co>Cu>Cr>Ni>Zn>Al>Pb>Mn>Fe	This study

IV. CONCLUSIONS

Twenty-six sites on Asa River zones in Ilorin, Kwara State, Nigeria were evaluated using existing contamination and developed indices. The latter indices were employed to evaluate the adverse effect potential of each heavy metal and also measure the ecological risk of sediment-associated heavy metals. Hazard Quotient modified (HQm) provides useful information on the gravity of contamination posed by single heavy metal to the biological groups and the environment. The CEI is a cluster index that represents overall pollution and associated ecological risks based on the contribution of all hazardous heavy metals in an abyssal ecosystem. PCA has shown that both human-caused and lithogenic sources are responsible for the possible contamination of the investigated ecosystems by the heavy metals. The calculated $mELP_Q$ and $mERM_Q$ indices indicated that benthic sediments at all sites have 21% probability of being toxic.

Sediment quality guideline based comparative results indicated that Cobalt was higher than mean shale and earth crust geochemical background in 88.4% and 100% respectively of the samples, while Cu and Al are higher than ELT and EMT in 88.4% and 100% load, which implies that Co, Cu and Al could pose adverse potential biological effects benthic contaminants of these aquatic ecosystems. However, the developed index (HQm) has shown that the severity of sediment contamination by heavy metals followed the sequence: Co>Cr>Ni>Al>Cu>Zn>Pb>Mn>Fe. Assessment of potential risks by metals using the developed CEI revealed possible pollution hotspot sites. The indices developed were compared with existing contamination indices and it revealed very good agreement. The contamination trends derived from developed indices were consistent and took into consideration geochemical background toxicity, site specificity and the effect levels guideline values that support their dependability and significant usage in assessing contaminated abyssal ecosystems.

ACKNOWLEDGMENTS

We are grateful to Prof. A. A. Olajire who gave good contributions and his paper for this type of results to come forth. My special thanks to Prof. R. A. Oderinde, Prof. E. O. Odebunmi, Prof. G. O. Adewuyi, Prof. I. A. Oladosu and Dr O.A.A. Eletta for their useful corrections and contributions to the success of this work. I appreciate my parents (Late Rev'd Canon and Mrs M. O. Akiwumi) for their moral and financial support. Finally, I appreciate my husband Oladipupo Akintade and my children for their support. Thank you all.

REFERENCES

[1]. C. Fernandez, J. O. Wu, D. K McCool, and C. O. Stockle, "Estimating water erosion and sediment yield with GIS, RUSLE and SEDD", *Journal of soil and water conservation*, **58(3)**, 128-136 (2003).

[2]. R. Van, J. J. Anton, G. Verstraeten, K. Van Oost, G. Govers, and J. Poesen, "Modelling mean annual sediment yield using a distributed approach," *Earth surface processes and landforms.* 26(11)**,** 1221-1236 (2001). doi:10/1002/esp.275

[3]. P. Borelli, K. Van Oost, K. Meusburger, C. Aleivell, E. Lugato, and P. Panagos, "A step towards a holistic assessment of soil degradation in Europe: Coupling on-site erosion with sediment transfer and carbon fluxes". *Environmental Research.* **161,** 291-298 (2018). doi:10.1016/j.envres.2017.11.009

[4]. M. Addo, H. Affum, B. O. Botwe, J. K. Gbadago, S. Acquash, J. K. Senu and I. J. Mumuni, "Assessment of water quality and heavy metal levels in water and bottom sediment samples from Mokwe Lagoon, Accra, Ghana," *Resource Journal of Environmental Earth Science.* **4(2),** 119-130 (2012).

[5]. N. U. Benson, J. P. Essien, G. A. Ebong and A. B. Williams, "Petroleum hydrocarbons and limiting nutrients in Macura reptantia, Procambarus clarkia and benthic sediment from Qua Iboe Estuary, Nigeria". *Environmentalist.* **28(3),** 275-282 (2008a).

[6]. E. K. Atibu, N. Devarajan, A. Laffite, G. Giuliani, J. A. Salumu, R. C. Mureb, C. K. Mulaji, J. P. Otamonga, V. Elongo, P. T. Mpiana, and J. Pote, "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". *Chem. Erde.* **76,** 353-362 (2016).

[7]. N. U. Benson, E. D. Udosen, J. P. Essien, W. U. Anake, A. E. Adedapo, O. A. Akintokun, O. H. Fred-Ahmadu, and A. A Olajire, "Geochemical fractionation and ecological risks assessment of benthic sediment-bound heavy metals from coastal ecosystems off the Equatorial Atlantic Ocean". *International Journal of sediment Resource.* **32(3),** **4**10-420 (2017). http://dx.doi.org/10.1016/j.ijrsc2017.07.007

[8]. G. Burton Jr, "Sediment quality criteria in use around the world", *Limnology* **3,** 65-75 (2002)

[9]. P. G. Oguntunde, B. J. Abiodun, and G. Lischeid, "Rainfall trends in Nigeria, 1901-2000". *Journal of Hydrology.* **411(3),** 207-218 (2011). doi:10.1016/jyhydrol.2011.09.037.

[10]. N. U. Benson, W. U. Anake, J. P. Essien, P. A. Enyong, and A. A. Olajire, "Distribution and risk assessment of trace metals in Leptodius exarata, surface water and ediments from Douglas Creek, Qua Iboe estuary". *Journal of Taibah Universal Science.* **11(3),** 434-449 (2016a). http://dx.doi.org/10.1016/j.jtusci.2016.08.004.

[11]. A. Tessier, P. Campbell and M. Bison, "Sequential extraction procedure for the speciation of particulate trace metals". *Analytical Chemistry.* **51(7),** 844-850 (1979).

[12]. D. D. MacDonald, C. G. Ingersoll and T. A. Berger, "Development and evaluation of consensus-based sediment quality guidelines fresh-water ecosystems". *Arch. Environ. Contam. Toxicol.* **39,** 20-31 (2000).

[13]. N. U. Benson, A. E. Adedapo, O. H. Fred-Ahmadu, A. B. Williams, J. P. Essien, O. O. Ayejuyo and A. A. Olajire, "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. Elsevier.* **18,** 44-56 (2018) http://doi.org/10.1016/j.rsma.2018.01.004

[14]. V. Davaulter and S. Rognerud, "Heavy metal pollution in sediments of the Pasvik River drainage". *Chemosphere* **42,** 9-18 (2001)

[15]. K. K. Turekian and K. H. Wedepohl, "Distribution of the elements in some major units of the earth's crust'. *Geol. Soc. Am. Bull.* **72,** 175-192 (1961).

[16]. USEPA, "Predicting toxicity to amphipods from sediment chemistry". EPA/600/R-04/030. Washington, DC. (2005)

[17]. W. Zhang, and X. Gao, "Integrated assessment of heavy metal pollution in the surface sediments of the Laizhou Bay and the coastal waters of the Zhangzi Island, China: Comparison among typical marine sediment quality indices". *PloS ONE* **9(4),** e94145 (2014) http://dx.doi.org/10.1371/journal.pone.0094145.

[18]. R. S. Carr, E. R. Long, H. L. Windon, D. C. Chapman, and G. Thursby, "Sediment quality assessment studies of Tampa Bay, Florida". *Environmental Toxicology Chemistry.* **15,** 1218-1231 (1996)

[19]. E. R. Long, C. G. Ingersoll and D. D MacDonald, "Calculation and uses of mean sediment quality guideline quotients: a critical review". *Environmental Science Technology.* **40,** 1726-1736 (2006)

[20]. D. L. Urban and N. J. Cook, "Hazard evaluation division standard evaluation procedure: Ecological Risk Assessment". US Environmental Protection Agency, Washington, DC. Pp. 9.85. EPA-540/-001. (1986).

[21]. H. Feng, X. Han, W. G. Zhang, and L. Z. Yu, 'Preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization". *Marine Pollution Bulletin.* **49(11-12),** 910-915 (2004). doi:10.1016/j.marpolbul.2004.06.014.

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

[23]. C. Lanni, E. Magi, F. Soggia, P. Rivaro and R. Frache, R "Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antartica)". *Microchemistry Journal.* **96(2),** 203-212 (2009). http://dx.doi.org/10.1016/j.microc.2009.07.016.

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

[25]. L. Zhang, X. Ye, H. Feng, Y. Jing, T. Ouyang, X. Yu, R. Liang, and Y. Chen, "Heavy metal contamination in Western Xiamen Bay sediments and its vicinity. China". *Marine Pollution Bulletin.* **54,** 974-982 (2007).

[26]. W. Zhang, H. Feng, J. Chang, J. Qu, H. Xie, and L.Yu, "Heavy metal contamination in surface sediments of Yangtze River intertidal zone. An assessment from different indexes". *Environmental Pollution.* **157,** 1533-1543 (2009).

[27]. M. Maanan, M. Saddik, M. Chaibi, O. Assobhei, and B. Zourarah, "Environmental and ecological risk assessment of heavy metals in sediments of Nador Lagoon, Morocco". *Ecology Indicators* **48,** 616-626 (2015).

[28]. F. Ruiz, M. Abad, M. Olias, E. Galan, I. Gonzalez, E. Aguila, N. Hamoumi, L. Pulido, and M. Cantano, "The present environmental scenario of the Nador Lagoon (Morocco)". *Environmental Resource.* **102,** 215-229 (2006).

[29]. O. O. Akiwumi, " Pollution status of water and sediments of Asa River exposed to industrial effluents in Ilorin, Kwara State, Nigeria". PhD thesis, University of Ibadan, Ibadan, Nigeria. (2019)