ZEAL SCIENTIFIC PUBLICATION

World Journal of Advanced Pharmaceutical and Medical Research

Journal homepage: https://zealjournals.com/wjapmr/

ISSN: 2799-0656 (Online)

(RESEARCH ARTICLE)

Check for updates

Spatial and seasonal variations, ecological and human risks of trace metals in major rivers within the oil producing zone of Nigeria

Helen Solomon Etuk [1], Godwin Asukwo Ebong [1, *], Aniefiokmkpong Okokon Okon [2], Idongesit Bassey Anweting [1] and Anietie Ekong Ekot [3]

[1] *Department of Chemistry, University of Uyo, P.M.B. 1017, Uyo, Akwa Ibom State, Nigeria.*
[2] *Department of Animal and Environmental Biology, University of Uyo, P. M. B 1017, Uyo, Nigeria.*
[3] *Department of Geology, Akwa Ibom State University, Mkpat Enin, P. M. B.1167 Uyo, Nigeria.*

World Journal of Advanced Pharmaceutical and Medical Research, 2023, 05(02), 001–017

Publication history: Received on 29 September 2023; revised on 13 November 2023; accepted on 16 November 2023

Article DOI: https://doi.org/10.53346/wjapmr.2023.5.2.0037

Abstract

The concentrations of Mn, Fe, Cu, Zn, Pb, and Cd in sediments from Great Kwa, Calabar, Cross River, Imo, and Qua Iboe Rivers were investigated during the dry and wet seasons using standard techniques. Results indicated that the mean concentrations of all the metals were within their acceptable limits although; higher concentrations were obtained during the wet season. Cd was the major contaminant in the studied sediments; the ecological risks of all the metals except Cd were in the low class. The potential ecological risks of the metals were in the low and moderate categories during the dry and wet seasons, respectively. Sediments from Qua Iboe River exhibited very high human health risks for both seasons. Factor analysis revealed anthropogenic and natural factors as the major sources of these metals in sediments from the rivers investigated for both seasons. The estimated daily intake (EDI) rates of these metals via exposure to the studied sediments were within their recommended oral reference doses however; higher wet season values were recorded. The hazard index (HI) values of the trace metals were less than one (1) but, higher during the wet season. Pb and Cd were the major contributors to the total HI during the dry and wet seasons. The relative risk analysis for both seasons also confirmed Cd as the major human risk in the studied sediments. This research has exposed the levels of trace metals and their associated human risks in sediments from the rivers investigated.

Keywords: Sediments; Water pollution; Human health risks; Aquatic ecosystem; South-south; Nigeria

1. Introduction

Human population explosion, urbanization, and industrialization in both developed and developing nations of the world have increased the level of trace metals contamination of the aquatic ecosystems globally, [1, 2]. Consequently, there is global concern on the levels of trace metals in the aquatic environments and the associated human health problems. The aquatic environment receives wastes from both the natural and anthropogenic sources hence; there is a high tendency to be highly contaminated, [3, 4]. The problem of water contamination is more serious in the developing countries such as Nigeria where there is no strict enforcement of regulations on proper waste management methods, [5-7]. The aquatic ecosystems in the oil producing Region of Nigeria have been highly degraded by the activities of Oil Companies and this can be noticed by their turbid status due to their high levels of contaminants, [8, 9]. Majority of trace metals in water channels are deposited in the sediment, [10]. Subsequently, these trace metals accumulated in the sediments are released into the water channel, [11]. These metals also accumulate in aquatic organisms, which are sources of food for man hence; pose adverse human health problems on the consumers, [12]. Prolonged exposure to polluted water body can destroy more human lives than the other causes of death, [13, 14].

*Corresponding author: Godwin Asukwo Ebong

A comprehensive assessment of trace metals in sediments should consider some indices such as factor and cluster analyses, sediment quality guidelines, contamination factor, ecological risk factor, and potential ecological index should be considered for effective evaluation and identification of pollution status, [15, 16].

The levels of trace metals in sediments from rivers in the northern and western Regions of Nigerian have been investigated, [17 - 21]. The evaluation of metals loads in sediments from rivers in the Niger Delta Area of Nigeria has also been undertaken, [9, 22 - 24]. These studies revealed high levels of trace metals in sediments however; most of the pollution indices and the health risks related to trace metals in sediments were not incorporated in these studies. Hence, this research was undertaken to assess comprehensively the trace metals loads and associated human health risks in sediments from major rivers in the Niger Delta Area of Nigeria. Related indices have also been employed to assess the pollution status of these sediments and to establish the human health risks associated with prolonged exposure to trace metals in these sediments. Results obtained will be useful to those exposed to aquatic ecosystems directly or indirectly in the Niger Delta Area and beyond. The outcome of this study will also expose the health risks related to prolonged exposure to contaminated sediments. This study will certainly close the gaps the previous studies on sediments from water channels within the study area had created.

2. Materials and methods

2.1. Study area

The study area varied from latitude 4°33' N - 5°10' N to longitudes 7°31' E - 8°23' E within the Oil producing Zone of Nigeria (Fig. 1). The Rivers investigated are Great Kwa, Calabar, Cross River, Imo, and Qua-Iboe as shown in Figure 1. The studied locations are within the tropical rainforest zone, [25, 26].These locations investigated have two (2) outstanding seasons namely dry and wet. According to Murtala *et al.* [27], the dry season commences from November and ends in March, while the wet season begins in April and stops in October[27]. Highest temperature of the studied locations is in February and the lowest is in July and August, [28]. The highest and lowest humidity of these locations vary between July and January, respectively, [29, 30]. The coordinates and symbols of the rivers investigated are shown in Table 1 below.

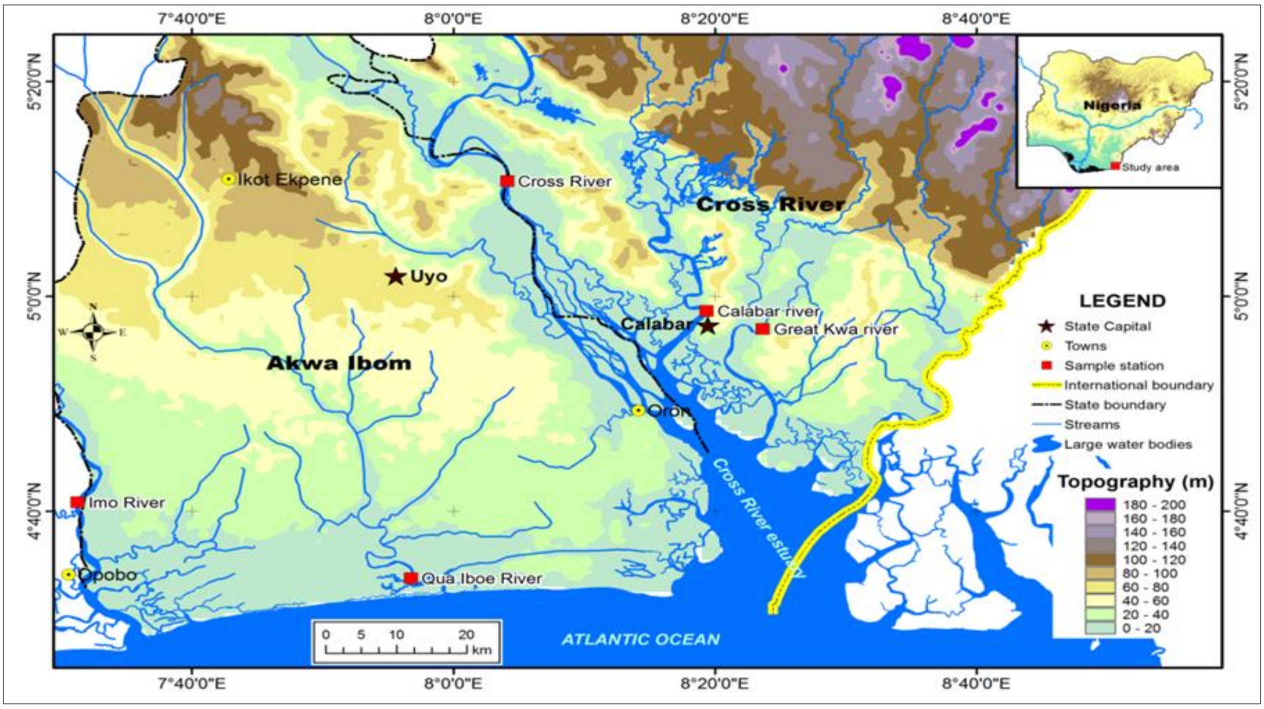


Figure 1 Map showing the studied rivers

Table 1 Site location and Coordinates

S/N	River System	Symbol	Longitude	Latitude
1	Great KwaRiver	GKR	8° 23' E	4° 56' N
2	Calabar River	CR	8° 19' E	4° 58' N
3	Cross River Estuary	CRE	8° 04' E	5° 10' N
4	Imo River Estuary	IRE	7° 31' E	4° 40' N
5	Qua Iboe River Estuary	QIRE	7° 56' E	4° 33' N

2.2. Sample collection and treatment

Surface sediments were obtained from Calabar River, Cross River Estuary, Great Kwa River, Imo River Estuary, and Qua Iboe River Estuary in the Oil producing Area of Nigeria using Grab Sampler, [31]. Sample collection was done during the wet (April and June 2011) and dry season (December to February 2012). Thirty (30) composite sediment samples were obtained from the studied rivers for the study. Surface sediments were preferred for this study because this portion controls the exchange of trace metals among sediments and the water channel, [32, 33]. Samples collected were put in polyethylene bags and transported to the laboratory inside a cooler. These samples were oven dried at 104 °C for two (2) days, ground and sieved using a 2-mm plastic sieve to eliminate debris, gravels and other unwanted materials, [34]. One gram (1 g) of the sieved sample was digested with 10ml of freshly prepared Aqua regia on a hot plate for 45 minutes according to the methods of Mendham *et al*. 35. The mixture was allowed to cool, filtered with Whatmann No. 1 filter paper into a 100 mL standard flask and made to mark with distilled water, [36].

2.2.1. Contamination factor (C_f)

Contamination factor was used as a mechanism for evaluating the extent to which trace metals contaminate the studied sediments and it was determined by Equation 1 below, [37, 38].

$$Cf = \frac{Cmetal}{Cbackground} \ldots\ldots\ldots\ldots\ldots..(1)$$

Where Cmetal indicates the determined metal concentration of the sediment samples, and Cbackground is the background concentrations of the different trace metals. In this study, the Turekian and Wedepohl, [39] concentrations of Mn, Fe, Cu, Zn, Pb, and Cd as adopted by Achi *et al*. [40] were used as the background concentrations of the metals in the calculation of C_f. The values for Mn, Fe, Cu, Zn, Pb, and Cd are 850.0, 47,000.0, 45.0, 95.0, 20.0, and 0.30 mgkg-1, respectively. The different categories of contamination factor according to Hakanson, [41] and Saha *et al*. [42] are in Table 2.

2.2.2. Ecological risk factor (ERF)

Ecological risk factor (ERF) evaluates the negative impacts of contaminants/pollutants on the host environment[43]. Ecological risk factor was computed based on Equation 2 as described by Hakanson, [41].

$$ERF = Tr\ x\ CF \ldots\ldots\ldots\ldots\ldots.(2)$$

Where Tr indicates the toxic-response factor of metals analyzed for and CF shows the contamination factor of the metals. Toxic response factors for the metals are Mn (1.00), Fe (0.00), Cu (5.00), Zn (1.00), Pb (5.00), and Cd (30.00), [41]. The different categories of ecological risk factor based on the classifications of Mahabadi *et al*. [44] and Rostami *et al*. [45].

2.2.3. Potential ecological risk index (PERI)

Potential ecological risk index (PERI) was used to assess the effect of trace metals on sediment from each of the studied rivers and was estimated using Equation 3 as reported by Cao *et al*. [46] and Ebong *et al*. [47]. The various classes of potential ecological risk index according to Hu *et al*. [48] and Kang *et al*. [49] are in Table 2.

$$PERI = \Sigma ERF \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where ΣERF is the summation of ecological risk factor for each location.

Table 2 Pollution indices, categories, and ecological implications of trace metals in sediments from rivers investigated

Pollution Index	Class	Implication	Source
Contamination factor (CF)	Cf < 1	Low contamination	Hakanson, [41] and Saha *et al*. [42].
	1 ≤ Cf < 2	Low to moderate contamination	
	2 ≤ Cf < 3	Moderate contamination	
	3 ≤ Cf < 4	Moderate to high contamination	
	4 ≤ Cf < 5	High contamination	
	5 ≤ Cf < 6	High to very high contamination	
	Cf ≥ 6	Extreme contamination	
Ecological risk factor (ERF)	Er < 40	Low risk	Mahabadi *et al*. [44] and Rostami *et al*. [45].
	40 ≤ Er < 80	Moderate risk	
	80 ≤ Er < 160	Considerable risk	
	160 ≤ Er < 320	High risk	
	Er ≥ 320	Very high risk	
Potential ecological risk index (PERI)	RI < 150	Low risk	Hu *et al*. 48 and Kang *et al*. [49].
	150 ≤ RI < 300	Moderate risk	
	RI ≥ 600	Considerable risk	
	RI ≥ 600	High risk	

2.2.4. Estimated daily intake

The estimated daily intake (EDI) of trace metals due to the exposure to sediments from the studied rivers during the dry and wet seasons was determined using Equation (4).

$$EDI = \frac{C \times DI}{BW} \dots\dots\dots\dots..(4)$$

Where C indicates the concentration of trace metals in sediments from the studied rivers, DI is the average daily intake rate, which is 114 mg/day, BW signifies body weight which is 70 kg for an adult, [50, 51].

2.2.5. Hazard quotients

Hazard index (HQ) of the trace metals through exposure to the studied sediments was estimated by Equation (5).

$$HQ = \frac{CDI}{RfD} \dots\dots\dots..(5)$$

Where EDI is the estimated daily intake rate calculated and RfD is the oral reference dose as recommended by USEPA, [52] are shown in Table 6.

2.2.6. Total hazard index

The total hazard index (THI) was calculated using Equation 6.

$$THI = \Sigma HQ = HQZn + HQFe + HQNi + HQCu + HQPb + HQCd + HQCr + HQMn - (6)$$

In equation 6 above, ΣHQ is the sum of all the hazard quotients (HQ) of the metals determined.

2.2.7. Relative risk (RR)

Trace element with the highest potentials to cause both cancer and non-cancer risks was identified by the calculation of relative risk (RR) using Equation (7) according to the methods of Adebiyi *et al*. [53].

$$RR\ (\%) = \frac{Cm}{Rfd}\ X\ 100 \ldots\ldots\ldots\ldots\ldots(7)$$

Where Cm represents the concentration of trace metals, Rfd indicates the oral reference dose.

2.3. Data Analysis

Analysis of data obtained during the study was performed with IBM SPSS Statistics 20 (IBM USA). Multivariate analyses (Principal component analysis and Hierarchical cluster analysis) were done using Duncan's multiple range tests at 90% confidence limit. Factor analysis was accomplished using Varimax Rotation procedures on six (6) parameters and values from 0.622 and higher were considered as significant. Cluster analysis was carried out by Dendrograms to separate the parameters based on their common sources and properties.

3. Results and discussion

Results of the distribution of trace metals in sediments from rivers investigated are shown below (Figures 2 and 3).

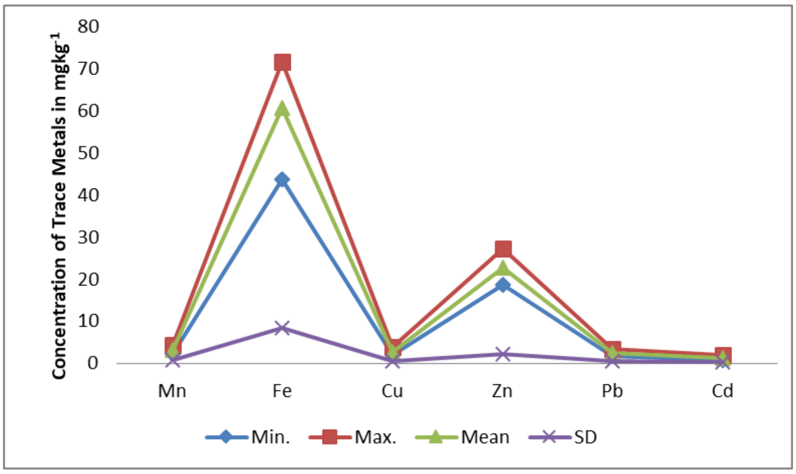


Figure 2 Statistical Data of Trace Metals in Sediments during the Dry Season

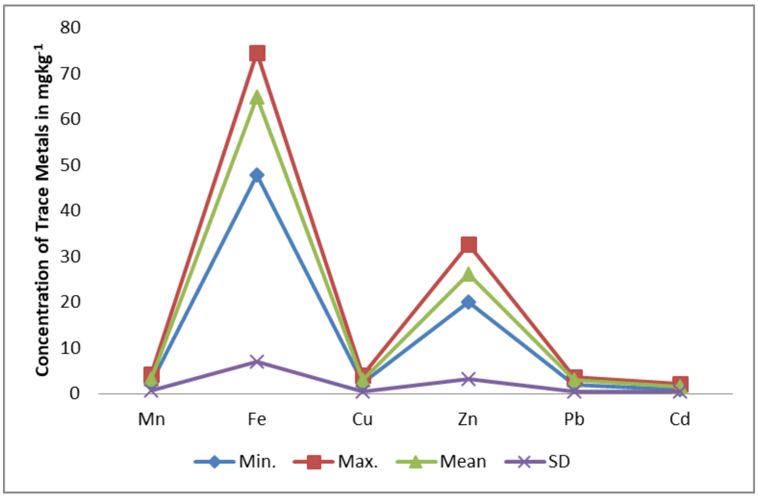


Figure 3 Statistical Data of Trace Metals in Sediments during the Wet Season

3.1. Distribution of trace metals in sediments from the studied rivers

Manganese (Mn) in sediments from the rivers examined during the dry and wet seasons varied from 2.15 – 4.42 $mgkg^{-1}$ and 2.32 – 4.22 $mgkg^{-1}$, respectively (Figure 2-3). The highest level of Mn was recorded in sediments from Qua Iboe River Estuary while the lowest was obtained at Cross River Estuary. The ranges obtained for both seasons are below 25.90 – 73.67 $mgkg^{-1}$ reported in sediments form Ogbere River in Ibadan, Nigeria by Achi *et al*. [40]. The general range reported in this study is also lower than 128.0 – 976.0 $mgkg^{-1}$reported in sediments from Al-Diwaniyah River, Iraq by SAl-Asadi and Al-Kafari, [54].

Iron (Fe) concentrations in sediments from the studied rivers ranged from 43.70 to 71.46 $mgkg^{-1}$ and 47.74 to 74.57 $mgkg^{-1}$ for the dry and wet seasons, respectively (Figure 2-3). The lowest concentration of Fe was reported in the samples from Imo River Estuary while the highest was recorded at Qua Iboe River Estuary. Generally, the obtained range is higher than 2.70 – 32.11 $mgkg^{-1}$reported in sediments from Eleyele Lake, Ibadan, Nigeria by Utete and Fregene, [55]. However, the range is lower than 9350.0 –18400.0 $mgkg^{-1}$ obtained by Iwegbue *et al*. [56] in sediments from Forcados River, Niger Delta Region of Nigeria.

Copper (Cu) in sediments ranged as follows: 2.04 - 3.87 $mgkg^{-1}$ and 2.39 – 3.93 $mgkg^{-1}$, respectively for the dry and wet seasons (Fig. 2-3). The highest level of Cu was obtained at Qua Iboe River Estuary while the lowest was recorded in sediments from Calabar River. The range reported in sediments from Poprad River in Poland by Sojka and Jaskuła, [57] (0.200 – 84.30 $mgkg^{-1}$) is higher than the ranges obtained for both seasons in this study. However, ranges obtained are higher than 0.02 – 0.33 mgg^{-1}recorded in sediments from Manyera River located between Nasarawa and Niger States, Nigeria by Omotugba *et al*. [58].

The ranges 18.76 – 27.34 $mgkg^{-1}$ and 20.13 – 32.71 $mgkg^{-1}$ were recorded for zinc (Zn) during the dry and wet seasons, respectively (Figure 2-3). Sediments from Calabar River had the lowest level of Zn while the highest concentration was obtained in samples from Qua Iboe River Estuary. These ranges are below 51.16 – 84.42 $mgkg^{-1}$obtained in sediments from rivers in Niger Delta Area, Nigeria by Ebong and Etuk, [9]. However, these ranges lower than 32.29 - 37.11 $mgkg^{-1}$ reported by Akintade *et al*. [18] in Asa River Sediments in Ilorin, Nigeria.

Lead (Pb) in the studied sediments varied from 1.72 to 3.41 $mgkg^{-1}$for the dry and 2.03 – 3.55 $mgkg^{-1}$ for the wet season (Figure 2-3). The highest level was reported in samples from Qua Iboe River Estuary and the lowest in Calabar River. Ranges obtained for both seasons are generally higher than 0.27— 0.72 $mgkg^{-1}$reported by Osakwe and Peretiemo-Clarke, [59] in Sediments of River Ethiope, Nigeria. Nevertheless, these values are lower than 0.60 – 86.40 $mgkg^{-1}$ obtained in sediments from the Eastern Niger Delta Basin, South-East Nigeria by Ekwere, [60].

Cadmium (Cd) in the sediments investigated in the dry and wet seasons ranged as follows: 0.75 – 1.98 $mgkg^{-1}$and 0.93 – 2.20 $mgkg^{-1}$, respectively (Figure 2-3). The lowest level of Cd in the studied sediments was obtained in Great Kwa River whereas; the highest was obtained at Qua Iboe River Estuary. Ranges reported are lower than 0.03–14.50 $mgkg^{-1}$ obtained in sediments from Warta River, Poland by Jaskuła *et al*. [61]. Nevertheless, is higher than 0.05–0.38 $mgkg^{-1}$ obtained in sediments from Euphrates River, Turkey by Varol, [62].

The results revealed that, the mean values of all the metals for both seasons except Fe were within their acceptable limits of 30.0, 25.0, 123.0, 40.0, and 6.0 $mgkg^{-1}$ for Mn, Cu, Zn, Pb, and Cd, respectively by WHO, [63] and USEPA, [64]. However, the mean values of Fe for the dry and wet seasons were higher than 30.0 $mgkg^{-1}$ stipulated for unpolluted sediment by WHO, [63]. Consequently, as an essential element for both aquatic and human lives the high level of Fe reported in the studied sediments may not pose serious threat to the food chain, [65, 66]. However, proper monitoring is encouraged to forestall bioaccumulation and the associated environmental problems. The results also revealed that, the highest levels of all the metals were obtained in sediments from Qua Iboe River Estuary. This may be due to the negative impact of oil activities in the area and the interaction of the Qua Iboe River Estuary with the Atlantic Ocean, [4, 67, 68].

Table 3 Comparison of mean levels (mgkg^{-1}) of metals in sediments with sediment quality guidelines (SQGs)

	Mean Level		**Sediment quality guidelines (SQGs)**					**Sediment quality assessment guideline**	
			Threshold effect levels						
	Dry	**Wet**	**[a]TEL**	**[b]PEL**	**[c]ERL**	**[d]LEL**	**[e]MET**	**[f]TEC**	**[g]PEC**
Mn	3.19	3.24	-	-	-	460.0	-	-	-
Fe	60.49	64.89	-	-	-	2 x 10^4	-	-	-
Cu	2.80	3.06	35.7	197	70	16	28	32	150
Zn	22.66	26.19	123	315	120	120	150	120	460
Pb	2.50	3.05	35	91.3	35	31	42	36	130
Cd	1.32	1.56	0.6	3.5	5	0.6	0.9	1	5

[a]Threshold effect level (TEL), [69]; [b]Probable effect level (PEL), [69]; [c]Effect range low (ERL), [69][d]Lowest effect level (LEL), [70; [e]Minimal effect threshold 70; [f]Threshold effect concentrations (TEC), [71]; [g]Probable effect concentrations (PEC), [71].

The sediment quality guidelines (SQGs) are useful for the assessment of sediment quality, [71]. The quality of sediments from the studied rivers was evaluated using threshold effect level (TEL), probable effect level (PEL), effect range low (ERL), lowest effect level (LEL), minimal effect threshold (MET), threshold effect concentrations (TEC), and probable effect concentrations. These parameters indicate the extent to which toxic substances in sediments can affect the aquatic organisms. A comparison between the metals in the studied sediments with SQGs is in Table 3. Results obtained revealed that all the elements were within the sediment quality guidelines except Cd. The mean levels of Cd obtained during the dry and wet seasons were higher than the TEL, LEL, MET, and TEC. This shows that the concentrations of Cd in sediments from the studied river can cause serious effects to the aquatic organisms and human exposed to sediments from the sources investigated, [72].

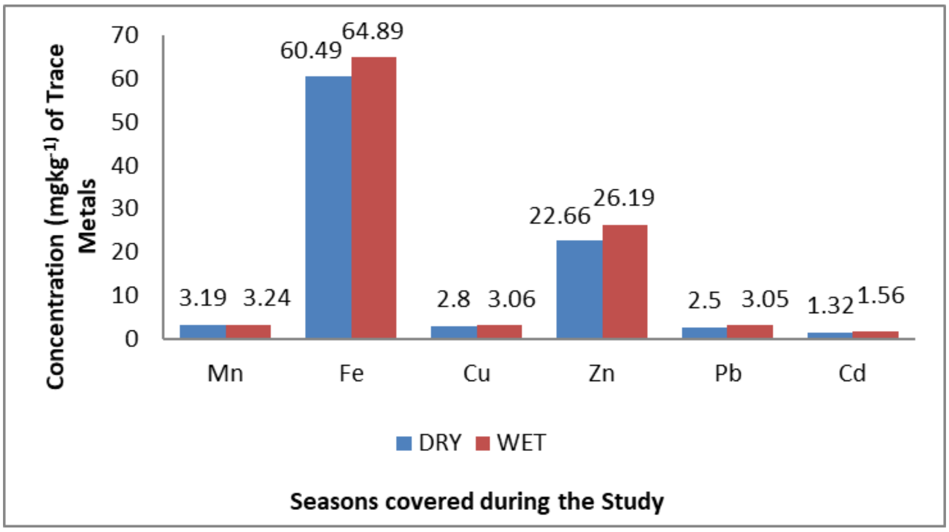


Figure 4 Mean concentrations (mgkg^{-1}) of Trace Metals in sediments during the dry and wet seasons

3.2. Seasonal Variations of Trace Metals in Sediments from the Studied Rivers

Results of trace metals in sediments during the dry and wet seasons are in Figure 4. Results obtained indicated that the mean concentrations of all the metals were higher during the wet season than in dry season though insignificantly at $p < 0.05$. This is consistent with the findings by Edokpayi *et al*. [73] and Hong *et al*. [74] during their studies in river sediments. This may be due to runoff from adjoining farmlands into the studied rivers during wet season, [75, 76].

Table 4 Contamination Factor (CF), Ecological Risk Factor (ERF), and Potential Ecological Risk Index (PERI) of Trace Metals in the Studied Sediments

	DRY SEASON							**WET SEASON**					
		Mn	**Fe**	**Cu**	**Zn**	**Pb**	**Cd**	**Mn**	**Fe**	**Cu**	**Zn**	**Pb**	**Cd**
CF	MIN	0.003	0.001	0.05	0.22	0.09	2.90	0.003	0.001	0.06	0.24	0.13	3.87
	MAX	0.005	0.002	0.08	0.28	0.16	6.40	0.005	0.002	0.09	0.32	0.17	6.87
	MEAN	0.004	0.001	0.06	0.24	0.12	4.41	0.004	0.001	0.07	0.28	0.15	5.21
ERF	MIN	0.003	0.00	0.25	0.22	0.45	87.00	0.003	0.00	0.30	0.32	0.65	116.10
	MAX	0.005	0.00	0.40	0.28	0.80	192.00	0.005	0.00	0.45	0.24	0.85	206.10
	MEAN	0.004	0.00	0.30	0.24	0.62	132.24	0.004	0.00	0.35	0.28	0.76	156.18
PERI	MIN	87.93						117.51					
	MAX	193.49						207.73					
	MEAN	133.40						157.57					

Results of Contamination factor (C_f) of trace metals are shown in Table 4. The mean $C_f$values obtained are 0.004, 0.001, 0.06, 0.24, 0.12, and 4.41 for Mn, Fe, Cu, Zn, Pb, and Cd, respectively during the dry season. The mean CF values for Mn, Fe, Cu, Zn, Pb, and Cd during the wet season are 0.004, 0.001, 0.07, 0.28, 0.15, and 5.21, respectively. The results obtained revealed that, Mn and Fe showed similar mean values during the dry and wet seasons. Higher mean CF values were recorded for Cu, Zn, Pb, and Cd during the wet than dry season. The obtained results indicated that the CF values of Mn, Fe, Cu, Zn, and Pb for both seasons were in the low class. The mean CF values of Cd during the dry (4.41) and wet season (5.21) were in the High contamination and high to very high contamination classes, respectively (Table 2). The evaluation of contamination factor indicated that Cd was the main contaminant in sediments from the studied rivers. The trend for Cf of Cd in the studied aquatic ecosystems for both seasons varied as follows: QIRE < IRE < CR < GKR < CRE. Consequently, for both seasons the highest CF value of Cd was recorded in sediments from Qua Iboe River Estuary and the lowest at Cross River Estuary.

Results of ecological risk factor (ERF) for trace metals determined in the studied sediments are in Table 4. Results in Table 4 indicate that, mean ERF values of the metals are 0.004, 0.30, 0.24, 0.62, and 132.24 for Mn, Cu, Zn, Pb, and Cd, respectively during the dry season. During the wet season, the mean ERF values were 0.004, 0.35, 0.28, 0.76, and 156.18 for Mn, Cu, Zn, Pb, and Cd, respectively. Iron (Fe) with no toxic-response factor was not assigned any ecological risk factor. The sequence for ERF values varied as Cd < Pb < Cu < Zn < Mn during the dry and wet seasons. Based on the classifications of ERF in Table 2 all the trace metals except Cd are in the low contamination class. The mean ERF values for Cd during the dry and wet seasons were in the considerable risk category[44, 45]. The high ERF values of Cd reported in this study is similar to that obtained by Wang *et al. [*77].

Results of potential ecological risk index (PERI) of trace metals in sediments from the rivers examined are in Table 4. The PERI value of trace metals varied from 87.93 to 193.49 between CRE and QIRE, respectively during the dry season. However, a higher range (117.51 – 207.73) for the trace metals was recorded during the wet season between CRE and QIRE, respectively. The mean PERI values of trace metals in sediments during the dry season (132.23) belong to the low risk class, [49, 78]. However, a higher mean PERI value of 156.18 recorded during the wet season belong to the moderate risk class (Table 2). The high PERI values at QIRE can result in adverse health problems on those expose to the aquatic ecosystem for a long time, [79]. This can be the negative impact of anthropogenic activities on the quality of the Qua Iboe River Estuary, [80].

Table 5 Results of Principal Component analysis (PCA) of Trace Metals determined in the studied sediments

	DRY SEASON		WET SEASON	
	PC1	**PC2**	**PC1**	**PC2**
Parameter				
Mn	0.827	0.136	0.769	0.354
Fe	0.532	0.782	0.525	0.698
Cu	0.868	0.404	0.848	0.393
Zn	0.884	-0.289	0.879	-0.208
Pb	0.897	-0.351	0.856	-0.385
Cd	0.906	-0.340	0.766	-0.601
% Total Variance	68.78	18.60	61.29	21.99
Cumulative %	68.78	87.38	61.29	83.28
Eigen value	4.13	1.12	3.68	1.32

The identification of the actual sources of trace metals in sediments from the studied aquatic ecosystem was done by the use of principal component analysis (PCA), [81, 82]. During the dry season, the PCA revealed two major sources of trace metals in the studied sediments with a total variance of 87.38%. The first source (PC1) with Eigen value 4.13 contributed 68.78% of the total variance with significant positive loadings on Mn, Cu, Zn, Pb, and Cd (Table 5). This represents the negative impact of human activities on the quality of the aquatic channels examined and their sediments, [75, 83]. The second source has Eigen value of 1.12 and added 18.60% to the total variance with strong positive loading on Fe only. This may be due to the impact of natural geological activities in the studied water channels, [29, 84].

The PCA results in the wet season also revealed two (2) fundamental sources of trace metals in the studied sediments with 83.28% total variance. The first source (PC1) with Eigen value 3.68 donated 61.29% to the total variance has strong positive loadings on Mn, Cu, Zn, Pb, and Cd (Table 5). This may be due to the impacts of human activities and runoff from farmlands into these rivers, [85, 86]. The second factor (PC2) with Eigen value 1.32 contributed 21.99% to the total variance had significant positive loading on Fe only. This may signify the influence of natural factor on the quality of the studied sediments, [87, 88].

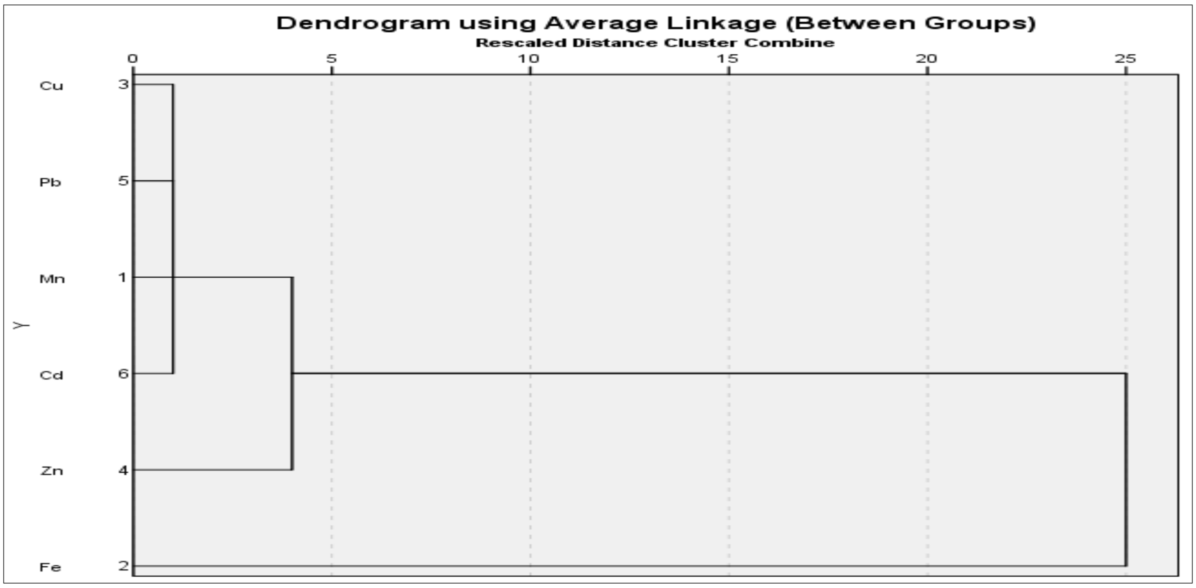


Figure 5 Hierarchical cluster analysis of trace metals in the studied sediments for both seasons resulted in a similar cluster as illustrated in Figure above

Hierarchical cluster analysis (HCA) of trace metals in sediments from rivers investigated for both the dry and wet seasons resulted in a similar pattern as shown in Figure 5. The HCA is tool that reveals parameters with similar source and properties in a media, [26, 81]. Results of HCA in Figure 5 indicate three (3) major clusters namely: Cluster 1 links Mn, Cu, Pb, and Cd together. This represents Factor 1 of PCA analysis during both seasons in Table 4. Cluster two links Zn only while, cluster 3 connects Fe only. Cluster 3 corroborates the finding by Factor 2 of PCA in Table 4 for both the dry and wet seasons. This HCA indicates that, Mn, Cu, Pb, and Cd have originated from a source different from Zn and Fe, [89, 90].

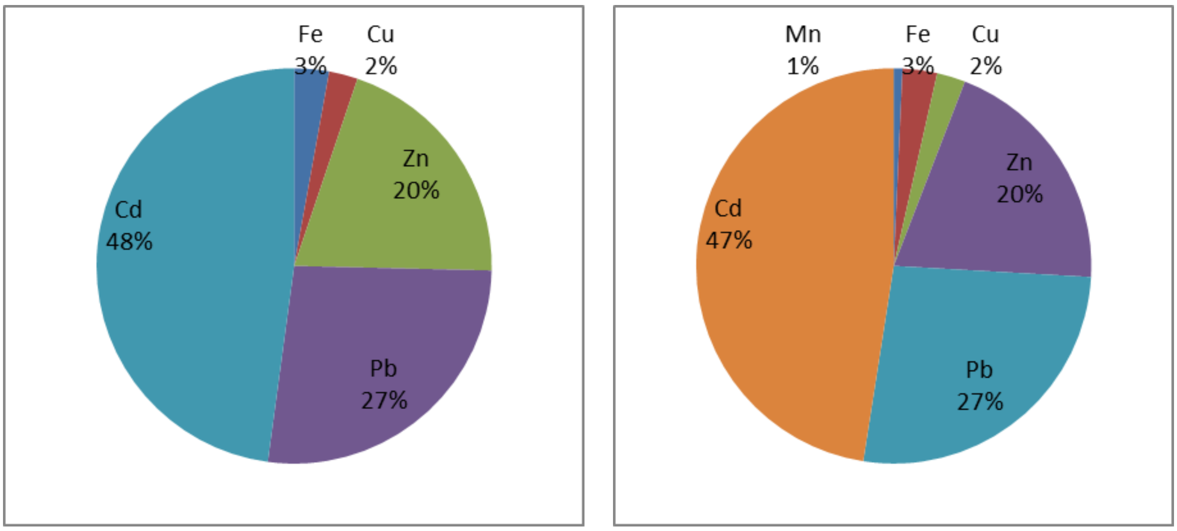
Table 6 Results of Estimated daily intake (EDI) rate, Hazard quotient (HQ), and Hazard index (HI) of Trace Metal in Sediments form the Rivers investigated

	Rfd	**EDI Dry**	**EDI Wet**	**HQ Dry**	**HQ Wet**
Mn	0.14	5.20E-06	5.28E-06	3.91E-05	3.77E-05
Fe	0.70	9.85E-05	1.06E-04	1.41E-04	1.51E-04
Cu	0.04	4.56E-06	4.98E-06	1.14E-04	1.25E-04
Zn	0.30	3.69E-05	4.27E-05	1.23E-04	1.07E-03
Pb	0.0035	4.07E-06	4.97E-06	1.16E-03	1.42E-03
Cd	0.001	2.12E-06	2.54E-06	2.15E-03	2.54E-03
HI				**3.75E-03**	**5.36E-03**

3.3. Non-Carcinogenic Human Health risks Evaluation

The rate of human exposure to trace metals through the ingestion of sediments from the studied river channels was examined by the estimated daily intake (EDI) rate, [91]. The ingestion of trace metals via sediments could be accidentally or intentionally via the consumption of aquatic foods and water from the studied rivers. Results in Table 6 indicate that, for both the dry and wet seasons the mean EDI values obtained were within their recommended oral reference doses (Rfds). Hence, these trace metals may not pose serious human health problems on those exposed to them through sediments from the studied rivers.

The hazard quotients (HQs) of the metals in the studied sediments for both seasons are less than one (1) although the values for wet season were relatively higher (Table 6). Consequently, exposure to these sediments may not result in non-carcinogenic health problems however; the wet season samples had higher potential of causing human health risks than the dry.



A B

Figure 6 Hazard quotient of trace metals for the Dry (A) and Wet (B) seasons

The results for the hazard indices (HI) of trace metals via exposure to the studied sediments are in Table 6. The mean HI values for the dry and wet seasons were 3.73E-03 and 5.34E-03, respectively. The values for both seasons were below one hence; these trace metals may not have the potential of causing non-carcinogenic health risks on those exposed to them via the studied sediments. The results obtained showed higher potential for the wet season samples. Figure 6A indicates that, Pb and Cd contributed 89% of the total HI value reported during the dry season. However, during the wet season Zn, Pb, and Cd contributed 20, 27, and 47% to the HI recorded (Figure 6B).

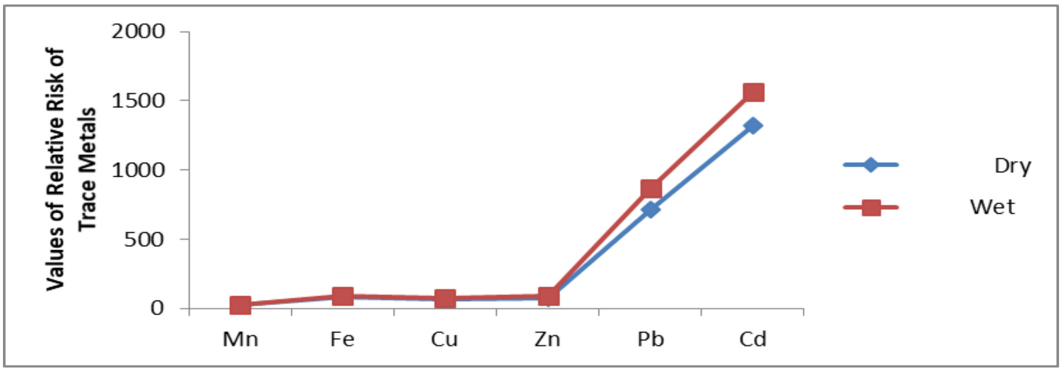


Figure 7 The Relative Risk of Trace Metals in Sediments during the Dry and Wet seasons

The relative risk (RR) of trace metals for both the dry and wet seasons are in Figure 7. The sequence for RR values of trace metals in sediments is Cd > Pb > Fe > Cu = Zn > Mn for the dry season. During the wet season, the RR values for trace metal varied as Cd > Pb > Fe = Cu = Zn > Mn. Consequently, Cd and Pb contributed 89 and 90 % of the total RR value obtained during the dry and wet seasons, respectively. In both seasons, Cd contributed the highest percentage (58) of the total RR value recorded. Thus, Cd was the metal in the studied sediments with the highest tendency to cause non-carcinogenic health problems on those exposed to these sediments, followed by Pb, [92]. The high Cd enrichment observed in this study is similar to the findings by Wang *et al*. [93] and Liu *et al*. [94]. Cd and Pb are highly toxic metals hence; their enrichments in the studied aquatic channels should be closely examined for forestall serious health issues along the food chain, [95- 97].

4. Conclusion

The study has revealed the potentials of environmental indices in evaluating suspected polluted environment. The status of the study areas has also been established and the probable sources of the contaminants identified. Higher levels of all the metals were obtained during the wet than in dry season indicating the negative impact of runoff from adjoining farmlands. The high levels of Cd in all the studied locations in both the dry and wet seasons are indicative of pollution threat traceable primarily to anthropogenic and natural factors. The relative high wet season concentrations of the metals also reflected in the higher EDI, HQ, and HI values recorded during the season. Although the all the parameters related to human health risks assessment were within safe levels, the high risks potentials of Pb and Cd in the studied rivers calls for concern.

Significance statement

This research has evaluated the concentrations of trace metals in sediments from five (5) major rivers in the Niger Delta Region of Nigeria. The impact of oil exploration and exploitation activities on the quality of the aquatic ecosystems within the area has been assessed. The environmental and human risks related to long term exposure to the studied river channels have also been highlighted. Results revealed anthropogenic factor as the major fundamental source of contaminants in the studied aquatic environment. Pb and Cd were identified as the contaminants with very high potentials of affecting human health adversely over time.

Compliance with ethical standards

Acknowledgements

We wish to acknowledge the efforts of the Technical Staff Department of Pure and Applied Chemistry, University of Calabar. We also wish to appreciate all those who contributed in one way or the other towards the successful completion of this research, we say thank you remain blessed.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

[1] Ebong, G. A., H. S. Etuk, A. O. Okon, I. B. Anweting, A. E. Ekot and J. P. Essien, 2023. Air Quality Index of some Commercial Centres in Uyo Metropolitan Area, Akwa Ibom State, Nigeria. British Journal of Earth Sciences Research, 11(3): 28-46. http://dx.doi.org/10.37745/bjesr.2013/vol11n32846

[2] Tombere, V. P., A. O. Okon, G. A.Ebong and A. W. Akpan, 2023. Physicochemistry of Iko River Channel in Nigeria and the Related Human Health Problems. Asian Journal of Biological Sciences, 16 (4): 417-437. https://doi.org/10.17311/ajbs.2023.417.437

[3] Saleem, M., J. Iqbal, G. Akhter and M. H. Shah, 2018. Fractionation, bioavailability, contamination and environmental risk of heavy metals in the sediments from a freshwater reservoir, Pakistan. Journal of Geochemical Exploration, 184: 199-208. https://doi.org/10.1016/j.gexplo.2017.11.002

[4] Essien, J. P., D. I. Ikpe, E. D. Inam, A. O. Okon, G. A. Ebong and N. U. Benson, 2022. Occurrence and spatial distribution of heavy metals in landfill leachates and impacted freshwaterecosystem: An Environmental andHuman Health Threat. PLoS ONE, 17(2): e0263279. Doi: 10.1371/journal.pone.0263279

[5] Ebong, G. A., B. N. Ita, A. B. Nyong and N. U.Benson, 2004a. Seasonal changes in the Water quality of Qua IboeRiver Estuary and its associated creeks in Ibeno, Nigeria. Journal of Applied Sciences, 9 (2): 6469 – 6482.

[6] Okoli, C. Nkiruka,Egobueze, Anthony and D. A. Briggs, 2020. waste management policy implementation in Nigeria: a study of Rivers State waste management agency. Int. J. Adv. Res., 8(02): 755 -765. Doi: 10.21474/IJAR01/10506

[7] Noiki, A. A., S. A. Afolalu, O. O. Yusuf, M. E. Emetere, S. O.Ongbali, O. R. Oloyede, O. O. Joseph and S. O. Banjo, 2021. Impact Assessment of the Current Waste Management Practices in Nigeria. IOP Conf. Series: Materials Science and Engineering 1107: 012172.Doi:10.1088/1757-899X/1107/1/012172

[8] Ebong, G. A., E. I. Udoessien and B. N. Ita, 2004b. Seasonal Variations of Heavy metal concentrations in Qua Iboe River Estuary, Nigeria. Global Journal of Pure and Applied Sciences, 10 (4):611-618. Doi: 10.4314/gjpas.v10i4.16446

[9] Ebong, G. A. and H. S. Etuk, 2016. Fractionation Status and Uptake Potentials of Trace Metals in Water Bodies within Niger Delta Region, Nigeria. International Research Journal of Pure & Applied Chemistry, 13(2): 1-18. Doi: 10.9734/IRJPAC/2016/29408

[10] Zhao, G., S. Ye, H. Yuan, X. Ding and J. Wang, 2017. Surface sediment properties and heavy metal pollution assessment in the Pearl River Estuary, China. Environmental Science and Pollution Research, 24(3): 2966-2979. Doi:https://doi.org/10.1007/s11356-016-8003-4

[11] Olowu, R.A., O.O. Ayejuyo, G.O. Adewuyi, I.A. Adejoro, A.A.B. Denloye, A.O. Babatunde and A.L. Ogundajo, 2010. Determination of heavy metals in fish tissues, water and sediment from Epe and Badagry Lagoons, Lagos, Nigeria. E-Journal Chemistry, 7(1): 215–221. Doi:10.1155/2010/676434

[12] Saha, N., M.S. Rahman, M.B. Ahmed, J.L. Zhou, H.H. Ngo and W. Guo, 2017. Industrial metal pollution in water and probabilistic assessment of human health risk. J Environ Manage., 185:70-78. Doi: 10.1016/j.jenvman.2016.10.023.

[13] Chaudhary, V.K., S.K. Singh, A.L. Srivastav, A. Singh, N. Patel and A. Patel, 2020.Chemical water contaminants: Potential risk to human health and possible remediation. Contamination of Water, 157-172. https://doi.org/10.1016/B978-0-12-824058-8.00001-3

[14] Pandey, S. and N. Kumari, 2022. Impact assessment of heavy metal pollution in surface water bodies. Metals in Water, 129-154. https://doi.org/10.1016/B978-0-323-95919-3.00004-5

[15] Ustaoğlu, F. and Y.Tepe, 2019. Water quality and sediment contamination assessment of Pazarsuyu Stream, Turkey using multivariate statistical methods and pollution indicators. International Soil and Water Conservation Research, 7(1): 47-56. https://doi.org/10.1016/j.iswcr.2018.09.001.

[16] Varol, M. 2020.Environmental, ecological and health risks of trace metals in sediments of a large reservoir on the Euphrates River (Turkey). Environmental Research, 187:109664.https://doi.org/10.1016/j.envres.2020.109664.

[17] Akan, J.C., F.L. Abdulrahman, O.A. Sodipo, A.E. Ochanya and Y.K. Askira, 2010. Heavy metals in sediments from River Ngada, Maiduguri Metropolis, Borno State, Nigeria. Journal of Environmental Chemistry and Ecotoxicology, 2(9): 131-140.

[18] Akintade, O.O., G.E. Ogunleye, R. Oderinde, A. Ogbesejana and W.B. Agbaje, 2022. Heavy Metals Pollution Assessment of Asa River Sediments in Ilorin, Kwara State, Nigeria. American Journal of Applied and Industrial Chemistry, 6(1): 20-30. Doi: 10.11648/j.ajaic.20220601.14

[19] Ezewudo, B.I., B.O. Mgbenka, Md.S.L. Ram Proshad and G.E. Odo, 2023. Appraisal of metal contamination in sediments of lower reaches of Niger River, Nigeria, using contamination indices and sediment quality guidelines. International Journal of Environmental Analytical Chemistry, 103(11): 2616-2635. Doi: 10.1080/03067319.2021.1895140

[20] Jolaosho, T.L., I.O. Elegbede, P.E. Ndimele, G.O. Mekuleyi, I.O. Oladipupo and A.A. Mustapha, 2023. Comprehensive geochemical assessment, probable ecological and human health risks of heavy metals in water and sediments from dredged and non-dredged Rivers in Lagos, Nigeria. Journal of Hazardous Materials Advances, 12:100379. https://doi.org/10.1016/j.hazadv.2023.100379.

[21] Ololade, I.A., A. Apata, N.A.Oladoja, B.A.Alabi and O.O. Ololade, 2023. Appraisal of river sediments in southwestern Nigeria with a special focus on trace metals: Occurrence, seasonal variation, sources, and health risks. Acta Ecologica Sinica, https://doi.org/10.1016/j.chnaes.2023.08.004

[22] Osakwe, O. (2013). Evaluation of Heavy Metals in Sediments of River Ethiope, Delta State, Nigeria.IOSR Journal of Applied Chemistry, 4(2):1-4. Doi: 10.9790/5736-0420104

[23] Bubu, A., C.P. Ononugbo and G.O. Avwiri, 2017. Determination of Heavy Metal Concentrations in Sediment of Bonny River, Nigeria. Archives of Current Research International, 11 (4): 1-11.Doi: 10.9734/ACRI/2017/38841

[24] Ekwere, A. (2019). Heavy Metal Concentration of Sediments from the Eastern Niger Delta Basin, South-East Nigeria. In: Doronzo, D., Schingaro, E., Armstrong-Altrin, J., Zoheir, B. (eds) Petrogenesis and Exploration of the Earth's Interior. CAJG 2018. Advances in Science, Technology & Innovation, Springer, Cham. https://doi.org/10.1007/978-3-030-01575-6_21

[25] Hassan, R.O., H.O. Othman, D.S.Ali, F.O.Abdullah and D.A. Darwesh, 2023. Assessment of the health riskposed by toxic metals in commonly consumed legume brands in Erbil, Iraq. Journal of Food Composition and Analysis, 120: 105282.https://doi.org/10.1016/j.jfca.2023.105282.

[26] Ebong, G.A., H.S. Etuk, I.B. Anweting, A.E. Ekot and A.E. Ite, 2023b. Relationship between traffic density, metal accumulation, pollution status, and human health problems in roadside soils and vegetables within the South-South Region of Nigeria. International Journal of Environment, Agriculture and Biotechnology, 8(3): 65 -79. Doi:10.22161/ijeab.83.8

[27] Murtala, A.I., P.G. Oguntunde, A.S. Akinwumiju and O.O. Olubanjo, 2020. Rainfall Analysis over the Niger Central Hydrological Area, Nigeria: Variability, Trend, and Change point detection. Scientific African, 8:e00419. Doi:10.1016/j.sciaf.2020.e00419

[28] Kemela, B. and A. Phoebe, 2021. Assessment of Climate Variability in the Niger Delta Region of Nigeria. International Journal of Chemistry and Chemical Engineering Systems, 6: 17 – 28.

[29] Ebong, G.A., E.S.Ettesam and E.U. Dan, 2020. Impact of Abattoir Wastes on Trace Metal Accumulation, Speciation, and Human Health–Related Problems in Soils within Southern Nigeria. Air, Soil and Water Research, 13: 1–14. Doi: 10.1177/1178622119898430

[30] Etuk, H.S., A.O. Okon, G.A. Ebong, B.O.Ekpo and A.A. Ayi, 2023a. Seasonal and Tidal variations of DO, BOD, and Nutrients in Major Rivers within Eastern Niger Delta, Nigeria. World Journal of Advanced Research and Reviews, 20(01), 243–257. Doi: https://doi.org/10.30574/wjarr.2023.20.1.2014

[31] Maanan, M., M. Saddik, M. Maanan, M. Chaibi, O. Assobhei and B. Zourarah, 2015. Environmental and Ec]ological Risk Assessment of heavy metals in sediments of Nador Lagoon, Morocco. Ecological Indicators, 48: 616 - 626.

[32] Barakat A, M. El Baghdadi, J. Rais and S. Nadem, 2012 Assessment of heavy metals in surface sediments of Day River at Beni-Mellal region, Morocco. Research Journal of Environmental and Earth Sciences, 4(8):797–806.

[33] Jia, Z.,S. Li, Q. Liu, F. Jiang and J. Hu, 2021. Distribution and partitioning of heavy metals in water and sediments of a typical estuary (Modaomen, South China): The effect of water density stratification associated with salinity. Environmental Pollution, 287: 117277. https://doi.org/10.1016/j.envpol.2021.117277.

[34] USEPA (2007) Method 7000B: Flame Atomic Absorption Spectrophotometry. Downloaded on 08/11/2011 from http://www.epa.gov/osw/hazard/ testmethods/sw846/pdfs/7000b.pdf

[35] Mendham, J., R.C. Denney, J.D. Barnes and M.J.K. Thomas, 2000. Vogels quantitative chemical analysis. 6th edition, Pearson education (Singapore), Delhi. pp. 357–359.

[36] Enuneku, A.A. and F. Ineh, 2019. Assessment of Human Health Risk for Surface Sediments of Ikpoba River Contaminated by Heavy Metals. J. Appl. Sci. Environ. Manage., 23 (11) 2013-2017.Doi: https://dx.doi.org/10.4314/jasem.v23i11.17

[37] Guo, W.,X, Liu, Z. Liuand G. Li, 2010. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. Procedia Environ. Sci., 2: 729 –736. Doi:10.1016/j.proenv.2010.10.084

[38] Liu, P., W. Hu, K. Tian, B. Huang, Y. Zhao, X. Wang and J.S. Khim, 2020. Accumulation and ecological risk of heavy metals in soils along the coastal areas of the Bohai Sea and the Yellow Sea: A comparative study of China and South Korea. Environ. Int., 137: 105519. Doi: 10.1016/j.envint.2020.105519

[39] Turekian, K.K. and K.H. Wedepohl, 1961. Distribution of the elements in some major units of the earth's crust. Bulletin of Geological Society of America, 72: 175–192. https://doi.org/10.1130/0016-7606

[40] Achi, C., A. Omoniyi and A.O. Coker, 2021. Distribution of Selected Toxic Elements in Water Phases of River Ogbere, Ibadan, Nigeria. Journal of Environmental Protection, 12(07):429 – 437. Doi:10.4236/jep.2021.127026

[41] Hakanson, L. 1980.An ecological risk index for aquatic pollution control. A Sedimentol. Approach. Water Res., 14, 975–1001. Doi: 10.4236/jamp.2022.1010199

[42] Saha, N., M.S. Rahman, M.B. Ahmed, J.L. Zhou, H.H. Ngo and W. Guo, 2017. Industrial metal pollution in water and probabilistic assessment of human health risk. J Environ Manage., 185:70-78. Doi: 10.1016/j.jenvman.2016.10.023.

[43] Huang, X., X. Wang, X. Zhang, C. Zhou, J. Ma and X. Feng, 2022. Ecological risk assessment and identification of risk control priority areas based on degradation of ecosystem services: A case study in the Tibetan Plateau. Ecological Indicators, 141: 109078. https://doi.org/10.1016/j.ecolind.2022.10907

[44] Mahabadi, H.M., M. Ramroudi, M.R. Asgharipour, H.R. Rahmani and M. Afyuni,2020. Evaluation of the ecological risk index (Er) of heavy metals (HMs) pollution in urban field soils. SN Appl. Sci., 2: 1–8. Doi: 10.1007/s42452-020-03219-7

[45] Rostami, S., H. Kamani, S. Shahsavani and M. Hoseini, 2021. Environmental monitoring and ecological risk assessment of heavy metals in farmland soils. Hum. Ecol. Risk Assess. Int. J., 27: 392 – 404. Doi: 10.1080/10807039.2020.1719030

[46] Cao, H.C., Z.Q. Luan, J.D.Wang and X.L. Zhang, 2007. Potential ecological risk of cadmium, lead and arsenic in agricultural black soil in Jilin province, China. Stochastic Environmental Research and Risk Assessment, 23: 57 - 64. Doi: 10.1007/s00477-007-0195-1

[47] Ebong, G.A., E.A. Moses, O.A.Akpabio,and R.B. Udombeh, 2022a. Physicochemical properties, total concentration, geochemical fractions, and health risks of trace metals in oil-bearing soils of Akwa Ibom State, Nigeria. Journal of Materials & Environmental Sustainability Research, 2(4): 1-18. Doi: https://doi.org/10.55455/jmesr.2022.009

[48] Hu, Y., X. Liu, J. Bai, K. Shih, E.Y. Zeng and H. Cheng, 2013. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environ. Sci. Pollut. Res., 20, 6150–6159. Doi: https://doi.org/10.1007/s11356-013-1668-z

[49] Kang, Z., S. Wang, J. Qin, R. Wu and H. Li, 2020. Pollution characteristics and ecological risk assessment of heavy metals in paddy fields of Fujian province, China. Sci. Rep., 10, 12244. Doi: https://doi.org/10.1038/s41598-020-69165-x

[50] USEPA. (2002). Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites; Office of Emergency and Remedial Response: Washington, DC, USA, 2002.

[51] Enuneku, A., O. Omoruyi, I. Tongo, E. Ogbomida, O.Ogbeide andL. Ezemonye,2018. Evaluating the potential health risks of heavy metal pollution in sediment and selected benthic fauna of Benin River, Southern Nigeria. Applied Water Science, 8: 224. https://doi.org/10.1007/s13201-018-0873-9

[52] USEPA (2000). Risk-Based Concentration Table. Phil adelphi a PA. United St a tes Environmental Protection Agency, Washington DC, USA.

[53] Adebiyi, F.M., O.T. Ore and I.O. Ogunjimi, 2020. Evaluation of human health risk assessment of potential toxic metals in commonly consumed crayfish (Palaemonhastatus) in Nigeria. Heliyon, 6: e03092. https://doi.org/10.1016/j.heliyon.2019.e03092

[54] SAl-Asadi, S.A.R. and H.M.A. Al-Kafari, 2022. Levels and sources of heavy metals pollution in the water and sediments of Al-Diwaniyah River, Iraq. Sustainable Water Resources Management, 8:101. https://doi.org/10.1007/s40899-022-00692-3

[55] Utete, B. and B.T. Fregene, 2020. Heavy metal concentrations in surface water, sediments and fish and their potential toxicity in highly degraded multipurpose periurban Eleyele Lake, Ibadan City, Oyo State, south-western Nigeria. Cogent Environmental Science, 6(1): 1785137. https://doi.org/10.1080/23311843.2020.1785137

[56] Iwegbue, C.M.A., B. Lari, S.A. Osakwe, G.O. Tesi, G.E. Nwajei and B.S. Martincigh, 2018. Distribution, sources and ecological risks of metals in surficial sediments of the Forcados River and its Estuary, Niger Delta, Nigeria. Environmental Earth Sciences, 77:227.https://doi.org/10.1007/s12665-018-7344-3

[57] Sojka, M. and J. Jaskuła, 2022. Heavy Metals in River Sediments: Contamination, Toxicity, and Source Identification—A Case Study from Poland. Int. J. Environ. Res. Public Health, 19: 10502. https:// doi.org/10.3390/ijerph191710502

[58] Omotugba, S.K., K.M. Adelakun, T.A.Ampitan, K.O.Babatunde, A.T. AbdulKadir, E.A. Oluwole and M.H. Garba, 2020. Heavy metals in water, fish and sediment from a gold mine polluted river, Nigeria. Journal of Forestry Research and Management, 17(2): 101-108.

[59] Osakwe, S.A. and B.O. Peretiemo-Clarke, 2013. Evaluation of Heavy Metals in Sediments of River Ethiope, Delta State, Nigeria. IOSR Journal of Applied Chemistry, 4(2): 01-04.

[60] Ekwere, A. 2019. Heavy Metal Concentration of Sediments from the Eastern Niger Delta Basin, South-East Nigeria. In: Doronzo, D., Schingaro, E., Armstrong-Altrin, J., Zoheir, B. (eds) Petrogenesis and Exploration of the Earth's Interior. CAJG 2018. Advances in Science, Technology & Innovation. Springer, Cham. https://doi.org/10.1007/978-3-030-01575-6_21

[61] Jaskuła, J., M. Sojka, M. Fiedler and R. Wrózy´nski, 2021. Analysis of Spatial Variability of River Bottom Sediment Pollution with Heavy Metals and Assessment of Potential Ecological Hazard for the Warta River, Poland. Minerals, 11: 327. https://doi.org/10.3390/ min11030327

[62] Varol, M. 2020. Environmental, ecological and health risks of trace metals in sediments of a large reservoir on the Euphrates River (Turkey). Environmental Research, 187: 109664.https://doi.org/10.1016/j.envres.2020.109664.

[63] WHO. (2004).World Health Organization. Guidelines for drinking water quality. 3rd edition. p. 515.

[64] USEPA. (1999).United States Environmental Protection Agency. Screening level ecological risk assessment protocolfor hazardous waste combustion facilities. Appendix E. Toxicity Reference Values. 3.

[65] Desai, D.K., F.D. Desai and J. Laroche, 2012. Factors influencing the diversity of iron uptake systems in aquatic microorganisms. Front Microbiol.. 18: 3:362. Doi: 10.3389/fmicb.2012.00362.

[66] Crans, D.C. and K. Kostenkova, 2020. Open questions on the biological roles of first-row transition metals. Commun Chem., 3: 104. https://doi.org/10.1038/s42004-020-00341-w

[67] Uwah, I.E., S.F. Dan, R.A. Etiuma and U.E. Umoh, 2013. Evaluation of Status of Heavy Metals Pollution of Sediments in Qua-Iboe River Estuary and Associated Creeks, South-Eastern Nigeria. Environment and Pollution, 2(4): 110 - 122. Doi:10.5539/ep.v2n4p110

[68] Gavhane, S.K., J.B. Sapkale, N.K.Susware and S.J. Sapkale, 2021. Impact of Heavy Metals in Riverine and Estuarine Environment: A review. Research Journal of Chemistry and Environment, 25 (5): 226 – 233.

[69] Smith, S.L., D.D. MacDonald, K.A. Keenleyside, C.G. Ingersoll and J. Field, 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. J. Great Lakes Res., 22: 624–638.

[70] Persaud, D.R., R. Jaagumagi and A. Hayton, 1993. Guidelines for the protection and management of aquatic sediments in Ontario. Standards Development Branch. Ontario Ministry of Environment and Energy, Toronto, Canada.

[71] MacDonald, D.D.,C.G. Ingersoll and T.A. Berger, 2000. Development and evaluation of consensus-based sediment quality guideline for freshwater ecosystems. Arch. Environ. Contam. Toxicol., 39: 20–31.

[72] Long, E.R., L.J. Field and D.D. MacDonald, 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ Toxicol Chem., 17:714–727

[73] Edokpayi, J.N., J.O. Odiyo, E.O.Popoola and T.A.M. Msagati, 2017. Evaluation of temporary seasonal variation of heavy metals and their potential ecological risk in Nzhelele River, South Africa. Open Chem., 2017; 15: 272–282. https://doi.org/10.1515/chem-2017-0033

[74] Hong, H., B. Zhang and H. Lu, 2021. Seasonal Variation and Ecological Risk Assessment of Heavy Metal in an Estuarine Mangrove Wetland. Water 2021, 13: 2064. https://doi.org/10.3390/w13152064

[75] Apau, J., J. Osei-Owusu, A. Yeboah, O. Gyamfi, G. Darko, O. Akoto and M. Dodd,2022. Distribution of heavy metals in sediments, physicochemical and microbial parameters of water from River Subin of Kumasi Metropolis in Ghana. Scientific African, 15:e01074. https://doi.org/10.1016/j.sciaf.2021.e01074.

[76] Yargholi, B., S. Sepehri and E. Kanani, 2023. Removal of heavy metals from agricultural runoff using constructed wetland; traces pollutants in reed bed sediments and plant biomass. Wetlands Ecol Manage., https://doi.org/10.1007/s11273-023-09922-7

[77] Wang, J., J. Ge, X. Yang, D. Cheng, C. Yuan, Z. Liu, S. Yang, Y. Guo and Y. Gu, 2023. Distribution and ecological risk assessment of heavy metals in sediments of Dajiuhu Lake Wetland in Shennongjia, China. Environ Sci Pollut Res., 30: 25999 – 26011. https://doi.org/10.1007/s11356-022-23952-3

[78] Hu, Y., X. Liu, J.Bai, K. Shih, E.Y. Zeng and H. Cheng, 2013. Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. Environ. Sci. Pollut. Res., 20, 6150–6159. Doi: https://doi.org/10.1007/s11356-013-1668-z

[79] Mugoša, B., D. Đurovic, M. Nedovic´-Vukovic´,S. Barjaktarovic´-Labovic´ and M. Vrvic´, 2016. Assessment of ecological risk of heavy metal contamination in coastal municipalities of Montenegro. International Journal of Environmental Research and Public Health, 13 (4): 393–405. Doi: 10.3390/ijerph13040393

[80] Ediagbonya, T.F. and O.T. Balogun, 2020. Potential risk assessment and spatial distribution of elemental concentrations in sediment. Applied Water Science, 10:176.https://doi.org/10.1007/s13201-020-01260-w

[81] Etuk, H.S., G.A. Ebong, I.B. Anweting, A.O. Okon and A.E. Ekot, 2023b. Sources and health risks of inorganic toxicants in Gallus gallus domesticus (broilers) in Uyo, Nigeria. British Journal of Multidisciplinary and Advanced Studies: Sciences, 4(5):1-30 Doi: https://doi.org/10.37745/bjmas.2022.0302

[82] Ebong, G.A., Moses, E.A., Akpabio, O.A. and Inam, I. (2022a). Impact of Seasonal Variations and Oil Activities on the Total Concentrations, Geochemical Fractions, And Human Health Problems of Trace Metals in Soils within the Oil-Bearing Communities of South-South Region of Nigeria. British Journal of Environmental Sciences, 10(6): 29-65.

[83] Ebong, G.A., H.S. Etuk, E.U. Dan and M.A. Onukwubiri, 2019a. Waste management: impact on metal accumulation and speciation in Aba River channel, Nigeria, Geosystem Engineering, 24(1): 46-60. Doi: 10.1080/12269328.2019.1663278

[84] Xia, X., Y. Teng and Y. Zhai, 2022. Biogeochemistry of Iron Enrichment in Groundwater: An Indicator of Environmental Pollution and Its Management. Sustainability, 14(12):7059. https://doi.org/10.3390/su14127059

[85] Elrashidi, M.A., C.A. Seybold and D.A. Wysocki, 2015. Effects of Annual Precipitation on Heavy Metals in Runoff from Soils in the US Great Plains. Water Air Soil Pollut., 226:417. https://doi.org/10.1007/s11270-015-2684-z

[86] Zhang, T., Y. Xiao, D.Liang, H. Tang, S. Yuan and B. Luan, 2020. Rainfall Runoff and Dissolved Pollutant Transport Processes Over Idealized Urban Catchments. Front. Earth Sci., 8:305. Doi: 10.3389/feart.2020.00305

[87] Sun, X., D. Fana, M. Liu, Y. Tiana, Y. Pang and H. Liao, 2018. Source identification, geochemical normalization and influence factors of heavy metals in Yangtze River Estuary sediment. Environmental Pollution, 241: 938–949. https://doi.org/10.1016/j.envpol.2018.05.050.

[88] Ebong, G.A., H.S. Etuk and E.U. Dan, 2019b. Multivariate Statistical Evaluation of Ecological Risks Associated with the Uncontrolled Tipping Method of Urban Wastes at Uyo Village Road, Akwa Ibom State, Nigeria. Singapore Journal of Scientific Research, 9 (1): 1-12. Doi: 10.3923/sjsres.2019.1.12

[89] Ebong, G.A.; H.S. Etuk and E.U. Dan, 2018. Distribution, pollution index and associated Health risk of trace metals in waste-impacted soils within Akwa Ibom State, Nigeria. Geosystem Engineering, 21(3): 121 – 134. Doi: 10.1080/12269328.2017.1376291

[90] Mehta, V., S. Bawa and J. Singh, 2021. WEClustering: word embeddings based text clustering technique for large datasets. Complex & Intelligent Systems, 7(6): 3211–3224. https://doi.org/10.1007/s40747-021-00512-9

[91] Ebong, G.A., E.A. Moses, O.A. Akpabio and R.B. Udombeh, R.2022b. Physicochemical properties, total concentration, geochemical fractions, and health risks of trace metals in oil-bearing soils of Akwa Ibom State, Nigeria. Journal of Materials & Environmental Sustainability Research, 2(4): 1-18.

[92] Furtak, G., M. Kozłowski, S. Kwiatkowski and A. Cymbaluk-Płoska, 2022. The Role of Lead and Cadmium in Gynecological Malignancies. Antioxidants, 11: 2468. https://doi.org/10.3390/antiox11122468

[93] Wang, B., Y. Liu, H. Wang, L. Cui, Z. Zhang, J. Guo, S. Liu and W. Cui, 2020. Contamination and health risk assessment of lead, arsenic, cadmium, and aluminum from a total diet study of Jilin Province, China. Food Sci Nutr., ;8(10):5631-5640. Doi: 10.1002/fsn3.1851.

[94] Liu, P., W. Hu, K. Tian, B. Huang, Y. Zhao, X. Wang and J.S. Khim, 2020. Accumulation and ecological risk of heavy metals in soils along the coastal areas of the Bohai Sea and the Yellow Sea: A comparative study of China and South Korea. Environ. Int., 137: 105519. Doi: 10.1016/j.envint.2020.105519

[95] Adesiyan, I.M., M. Bisi-Johnson, O.T. Aladesanmi, A.I. Okoh and A.O. Ogunfowokan, 2018. Concentrations and human health risk of heavy metals in rivers in Southwest Nigeria. Journal of health & pollution, 8(19): 180907. https://doi.org/10.5696/2156-9614-8.19.180907

[96] Wang, J. and Geng, L. (2019). Effects of Socioeconomic Status on Physical and Psychological Health: Lifestyle as a Mediator. Int J Environ Res Public Health, 16(2):281. doi: 10.3390/ijerph16020281.

[97] Kumar, A., Kumar, A., Cabral-Pinto, M. M. S.,Chaturvedi, A. K., Shabnam, A. A., Subrahmanyam, G., Mondal, R., Gupta, D. K., Malyan, S. K., Kumar, S. S. A., Khan, S. and Yadav, K. K. (2020). Lead Toxicity: Health Hazards, Influence on Food Chain, and Sustainable Remediation Approaches. International Journal of Environmental Research and Public Health, 17(7): 2179. https://doi.org/10.3390/ijerph17072179