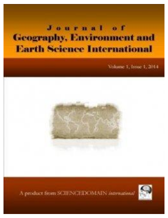

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Elemental Composition of Core Sediments in Niger Delta Mangrove, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author NN designed the study, performed the sampling and statistical analyses, managed the literature searches, wrote the protocol and wrote the draft of the manuscript. Author HI designed and wrote the manuscript with author NN, managed the laboratory and XRF analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

Mangrove core sediments from Choba, Ogbogoro and Isaka in Niger Delta, Nigeria were analyzed to determine their geochemical composition. The ecological risk of the metal concentrations was assessed using Contamination Factor (CF) and Enrichment Factor (EF) while the quality of the sediments was determined using sediment quality guidelines. The results indicated contrasting metal concentrations with depth and location as shown by the box plots and cross sectional graphs. The average concentration of Pb, Zn, Cu, Ni, Cr, V, Nb and Th were found to be most abundant in Choba while As, Sr and TS were most concentrated in Ogbogoro. Compared with the upper continental crust (UCC) values, As, Ni, Cr and V were higher in all the sampled locations. Pb and Th were higher in Choba and Ogbogoro while Zn, Cu and Nb were higher only in Choba. The concentration of biogenic and provenance metals in Isaka are largely geogenic due to strong TiO_2 association with Pb, Zn, Cu, Ni, Cr, V, Sr, Nb and Th. As enrichment in Choba, Ogbogoro and Isaka is anthropogenic. Comparison with the sediment quality guidelines showed that Ni impact in Choba is severe while Cr concentration level in Choba, Ogbogoro and Isaka might have adverse ecotoxic impact on biota.

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Keywords: Mangrove core sediments; geochemistry; heavy metals; sediment quality; Niger delta.

1. INTRODUCTION

Sediments within the mangroves sequestrate heavy metals. In natural environment, heavy metal contamination is a primary concern due to its toxicity, persistence and bioaccumulation potentials [1,2]. Generally, mangrove sediments are fluvial in nature and accumulate gradually with the passage of time carrying contaminants from different sources. These sources include discharge from urban and industrial waste water, leaching from bedrocks and soils, water drainage and runoff from banks [3,4], atmospheric deposition [5] as well as tidal inflow [6]. Depending on the concentration level in mangrove environment, heavy metals may have adverse effect directly on the mangrove flora and funa and indirectly on man.

Coring of mangrove sediments for geochemical analysis can provide an in-depth chronological information on the changes and quality within the mangrove environment. Mangrove sediments are sink for heavy metals [7] and thus contain useful records of the current and background levels of contamination which might be natural or anthropogenic [8]. Researchers on heavy metals in Niger Delta have focused mainly on heavy metals in surface sediments and water [9,10,11, 12,13,14,15,16]. Thus, there is dearth of studies on the cross sectional geochemical variations in Niger Delta mangrove sediments. Mangroves are well known depositional sites because their stems and complex root systems facilitate sedimentation. The high sedimentation rate associated with the mangrove environments might continuously alter their geochemical characteristics annually [17]. Hence the need for a study on the vertical distribution of heavy metal concentrations in core sediments of Niger Delta mangrove to show its recent geochemical trend. Specifically, this study aims at gaining insight into (a) cross sectional geochemical concentration of the core sediments and (b) evaluation of the cross sectional sediment pollution using geostatistical methods and sediment quality guidelines.

2. MATERIALS AND METHODS

2.1 Study Area

The Niger Delta covers about 240 km in distance on its north-south stretch from Onitsha to the barrier islands on the Atlantic Ocean. The east-west stretch of the delta from the Benin River to the Imo River covered about 480 km. Thus, the Niger Delta is rectangular with an approximate area of 46,420 km^2 [18]. However, only about 7,386 km^2 of the Niger Delta are covered by mangroves [19]. This huge wetland area which was formed due to the deposition of sediments by the River Niger is located between latitudes 4°N to 6°N and longitudes 5°E 8°E [20,21]. Thus, it seats directly on the Gulf of Guinea on the Atlantic ocean in southern Nigeria. The Niger Delta has twenty one tidal inlets and as such, it is significantly influenced by tides. Within the mangrove zone, tidal amplitudes ranges between 1 - 3 m in height [9,18]. Tidal influence extends to more than 50 km from the Atlantic coast. The New Kalabar and Bonny Rivers along which the core sediments were sampled are tidal inlets located on the Eastern Niger Delta (Fig. 1). These rivers drain through the areas of hydrocarbon exploration and exploitation. Hence, municipal, industrial and oil related wastes are discharged into these rivers from Port Harcourt and surrounding areas. Geologically, the area consists of mostly alluvial sedimentary basin and basement complex [15]. The climate is equatorial and has high relative humidity while the mean annual rainfall is up to 4,500 mm in the coastal margins in the south and around 2,000 mm in the northern fringe [22]. Temperatures within the Niger Delta ranges between 18°C to 33°C [18].

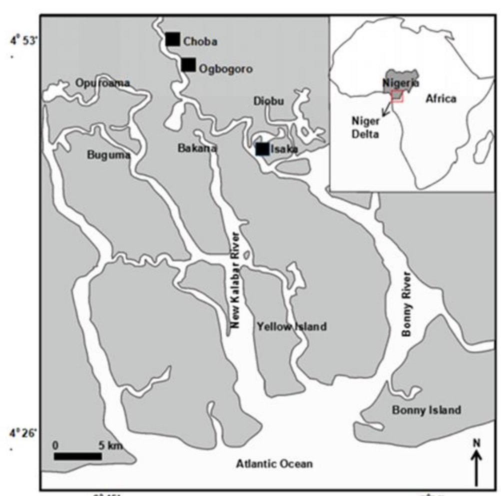

Fig. 1. Map of study area showing sampling locations [16]

2.2 Core Sediment Collection and Preparation

Core sediments were collected within the mangroves along the banks of the New Kalabar River at Choba and Ogbogoro as well as along the Bonny River at Isaka. Six core samples of depth between 31 cm and 35 cm were collected from Choba (n = 2), Ogbogoro (n = 2) and Isaka (n = 2). Samples were collected during the low tide on March 8th and 9th, 2017.

Core samples of the mangrove sediments were collected using a transparent 2-inch diameter PVC pipe which was one meter in length. The pipes were decontaminated using ethanol before coring. The coring points were determined using the CANMORE GP102+ global positioning system (GPS). Coring was done by manually driving the cores into the muddy sediments in the midst of mangrove plants. The cores were pushed into the sediments to ensure that it got to the required depth after which they were carefully and slowly retrieved from the sediments. Once the core bearing sediment was retrieved, it was immediately covered and marked with an arrow to indicate the upward direction. The sediment bearing cores were kept in vertical position in the direction of the arrow while in the field until they were transported out and stored at 4^{o}C. The sediments were recovered from the PVC pipes and the first 10 cm of the core sediments were sliced into 5 at intervals of 2 cm out of which 0 - 2 cm, 4 - 6 cm and 8 - 10 cm slices were selected. The remaining part of the cores were sliced into 5 at 5 cm intervals out of which 15 - 20 cm and 25 - 30 cm slices were selected. Thus, 5 sub-core samples were selected from each of the six cores giving a total of 30 sub-core samples for this study (Table 1). Each of the sub-core samples was homogenized and air dried for 48 hours to reduce weight before they were repackaged in ziplock bags and labeled. Then the sub-core samples were carefully arranged in plastic boxes sealed and exported to the Geoscience Laboratory, Shimane University, Japan for analysis. Approximately 30 g of the sub-core sediments were oven dried at 160°C for 48 hours using the ISUZU Muffle Furnace. Using the Automatic Agate Mortar and Pestle, the dried samples were ground for 20 minutes. Briquettes were made from each of the powdered sediment samples by compressing about 5 g using a force of 200 kN for 60 seconds.

2.3 XRF Analysis

Eleven trace elements; As, Pb, Zn, Cu, Ni, Cr, V, Sr, Nb, Th and TS as well as five oxides; TiO_2, Fe_2O_3, MnO, CaO and P_2O_5 were analyzed using X-ray fluorescence (XRF) RIX-200 spectrometer. In consistence with [23], all the XRF analysis were made from pressed powder briquettes with average errors being less than ± 10%.

2.4 ^{14}C Analysis

Macro fossil wood samples were radiocarbon dated (^{14}C). The samples were retrieved from mangrove core sediments from Ogbogoro and Isaka at depths between 30 - 35 cm. The wood samples were carefully sorted, put in plastic bags, packaged and sent to Beta Analytic Geoscience Laboratory, Nagoya, Japan for analysis.

2.5 Statistical Analysis

The mean concentration of the elements in the sub-core sediment samples, box plots of element concentration with depth and correlation matrix to show the inter-element relationship in the study area were done using Microsoft Excel 2013. The cross sectional graphs and upper continental crust (UCC) normalized graph were done using the Kaleida Graph 4.0.

Table 1. Mangrove core sediment details

Core	Latitude (N)	Longitude (E)	Retrieved core depth (cm)	Number of sub- core samples
CHCS1	4°5319.56	6°5339.21	34	5
CHCS2	4°5319.03	6°5338.79	35	5
OGCS1	4°5052.71	6°5517.15	35	5
OGCS2	4°5055.02	6°5514.66	33	5
ISCS1	4°4418.69	7°0008.23	31	5
ISCS2	4°4419.87	7°0008.02	33	5

CHCS --- Choba core sediment, OGCS --- Ogbogoro core sediment
ISCS ----- Isaka core sediment

2.6 Geostatistical Methods

2.6.1 Contamination factor (CF)

To determine the extent of heavy metal contamination in the sub-core sediments of Niger Delta mangroves, the contamination factor was used. According to [24], contamination factor is expressed thus:

$$CF = C_{metal} / C_{background}$$

Where

C_{metal} is the current metal concentration in the sediments.

$C_{background}$ is the background metal concentration of sediments.

In this study, the upper continental crust proposed by [25] was used as the background metal concentration. The CF is interpreted as follows: CF < 1: signifies low contamination; 1 ≤ CF < 3: signifies moderate contamination; 3 = CF ≤ 6: signifies considerable contamination and CF ≥ 6: signifies very high contamination.

2.6.2 Enrichment factor (EF)

The estimation of the anthropogenic impact of metal enrichment in the sub-core sediments of Niger Delta mangroves was done using the enrichment factor. The enrichment factor adopts a normalized approach where Al, Fe and Si could be used as the normalizing elements [26] as well as Li, Sc, Ti and Zr [27]. In this study, Fe was used as the normalizing element for the computation of the enrichment factor. Fe was chosen as the element for normalization because its anthropogenic sources are small compared to natural sources [28]. Also, Fe is a conservative tracer that could differentiate natural from anthropogenic components [29]. Enrichment factor is expressed as:

$$EF = (X_s / Fe_s)_{sediment} / (X_b / Fe_b)_{background}$$

Where X_s is the element being considered from the sediment sample and Fe_s is the normalizer from the same sample.

X_b is the element being considered from the background while Fe_b is the normalizer from the background.

The UCC by [25] was used as background concentration. The enrichment factor interpretation was based on [30] where; EF < 2 is depletion to minimal enrichment and pollution; EF 2 - 5 is moderate enrichment and pollution; EF 5 - 20 is significant enrichment and pollution; EF 20 - 40 is very high enrichment and pollution while EF > 40 is extreme enrichment and pollution.

3. RESULTS AND DISCUSSION

3.1 Sediment Characteristics

The core sediment sub-samples of depth (0 - 2, 4 - 6, 8 - 10, 15 - 20 and 25 - 30 cm) collected from mangroves along the New Kalabar River at Choba and Ogbogoro as well as Bonny River at Isaka were predominantly composed of muddy, blackish, dark-brown and silty-clay sediments. The first 10 cm of the cores consisted mostly of dark-brown sediments while sediments between 10 - 20 cm were blackish and silty-clay. Below 20 cm, the sediments were blackish and silty-clay but contained fragments of plant stem microfosils. The sediments had unpleasant smell. [31] suggest that the black color and unpleasant smell of sediments are indications of anoxic condition.

3.2 Element-Depth Concentration Assessment

The elemental concentrations relative to depth of the mangrove sediments in Choba, Ogbogoro and Isaka as well as their average concentrations are shown in Table 2. Trace elements and oxides concentrations were compared to the upper continental crust (UCC) values by [25].

3.2.1 Choba

The element and oxide concentrations in the two core samples (CHCS1 and CHCS2) from Choba indicated varying concentration of elements and oxides at different depths and sampling points. However, As, Nb, Th, TiO_2, MnO, CaO and P_2O_5 as well as As, Zn, Cu, Sr, Th, TiO_2, Fe_2O_3, MnO, CaO and P_2O_5 for CHCS1 and CHCS2 respectively have same concentrations in at least two different depths. The average cross sectional concentration of trace elements in cores from Choba have similar pattern and are in the following order; V>Cr>Zn>Sr>Ni>Cu>Pb>Nb>Th>As and V>Cr>Sr>Zn>Ni>Pb>Nb>Cu>Th>As for CHCS1 and CHCS2. However, the concentration order of the oxides were observed to be the same and is as follows; Fe_2O_3>TiO_2>CaO>P_2O_5>MnO. The highest concentration of Pb occurred at 0 - 2 cm; As, Zn, Cu, Ni, Cr, V and Fe_2O_3 at 4 - 6 cm; TS at 8 -10 cm; MnO and CaO at 15 - 20 cm while Sr, Nb, Th, TiO_2 and P_2O_5 were most concentrated at 25 - 30 cm.

3.2.2 Ogbogoro

The elemental concentrations in the two cores sampled at Ogbogoro (OGCS1 and OGCS2) also showed varied concentrations of some elements at different depths. In OGCS1 and OGCS2, As, Zn, Cu, V, Nb, Th, MnO, CaO, P_2O_5 and As, Cu, Sr, Th and MnO were found to have same concentration in at least two different depths respectively. Interestingly, the average concentration of trace elements and oxides followed a similar pattern thus: V>Cr>Sr>Zn>Ni>Pb>Nb>Cu>Th>As and Fe_2O_3>TiO_2>CaO>P_2O_5>MnO. The highest concentration of As, Pb, Zn, Cr, V and P_2O_5 occurred at 0 - 2 cm; Cu, Sr, Nb and Th at 4 - 6 cm; MnO at 8 - 10 cm; TS, Fe_2O_3 and CaO at 15 - 20 cm while Ni and TiO_2 were concentrated most at 25 - 30 cm.

3.2.3 Isaka

The Isaka core samples (ISCS1 and ISCS2) indicated varied elemental concentrations at different depths. As, Pb, Nb, Th, MnO and P_2O_5 were found to have same concentration in at least two different depths in ISCS1 while in ISCS2, As, Zn, Cu, Ni, Th, MnO and P_2O_5 had same concentration in more than one depth. The trends in the average trace element concentrations between the two cores are approximately the same with the difference being on Cr and V concentrations. In ISCS1, the trace element concentration trend is V>Cr>Sr>Zn>Ni>Pb>Nb>Cu>Th>As while in ISCS2, it is Cr>V>Sr>Zn>Ni>Pb>Nb>Cu>Th>As. However, the oxides in both cores had the same concentration sequence thus: Fe_2O_3>TiO_2>CaO>P_2O_5>MnO. The highest concentration of Cr, CaO and P_2O_5 were observed at 4 - 6 cm while As, Pb, Zn, Cu, Ni, V, Sr, Nb, Th, TS, TiO_2, Fe_2O_3 and MnO were found to be most abundant at 25 - 30 cm depth..

Generally, Pb, Zn, Cu, Ni, Cr, V, Nb and Th were observed to be most concentrated in Choba while As, Sr and TS recorded highest concentrations in Ogbogoro. However, Isaka had the least average concentration of all the elements analyzed except TS. Therefore, the mangrove sediments along the New Kalabar River have higher metal concentrations compared to the mangrove sediments along the Bonny River. In comparison with the UCC values of [25], As, Ni, Cr and V were higher in all the sampled locations. Pb and Th were higher in Choba and Ogbogoro while Zn, Cu and Nb were higher only in Choba. Conversely, Sr concentrations in all the locations were lower than the UCC value. The box plots and cross sectional profiles of the concentrations of biogenic metals are shown in Figs. 2 and 3 while Fig. 4 showed metal concentrations normalized to the UCC.

Source rock composition strongly controls sediment composition [32]. Thus, using trace element concentrations, the nature of source rocks could be determined. High average concentrations of Ni, Cr and V in Choba, Ogbogoro and Isaka are indicative of mafic or ultramafic rocks in the source region [33, 34, 35, 36]. The high concentrations of As, Ni, Cr and V in Choba, Ogbogoro and Isaka; Pb and Th in Choba and Ogbogoro as well as Zn, Cu and Nb in Choba might be due to the fine grained nature of the sediments and reducing bottom conditions produced by abundant organic matter [31] or anthropogenically induced [16]. [17] reported that the high sedimentation rate associated with mangroves continuously alter its annual geochemical characteristics. This might in part explain the observed vertical variation of the geochemistry of the mangrove core sediments. However, it could also be attributed to diagenic modifications and precipitation around the redox boundaries [37,38].

3.3 Radiocarbon (^{14}C) Dating Analysis

Radiocarbon (^{14}C) analysis was carried out on two macro fossil wood samples from Isaka and Ogbogoro mangrove core sediments along the Bonny River and New Kalabar River respectively.

Results of the ^{14}C in Isaka (ISCS1) presented in Table 3 above indicate that the wood macro fossil sample deposited at 30 - 35 cm depth has a conventional radiocarbon age of 20 ± 30 BP and d13C of -28.4. At different confidence levels, it was found that the possible range of ages at 95.4% probability include; 1876 - 1918 cal AD (65.3%), 1696 - 1726 cal AD (16.8%), 1813 - 1836 cal AD (11.9%) and 1844 - 1852 cal AD (1.5%). However, it may be 68.2% probable that it dates to the period of 1887 - 1912 cal

Table 2. Depth-concentration of elements and oxides in Niger Delta mangrove core sediments

Core		Trace elements (ppm)											Oxides (wt%)				
		As	Pb	Zn	Cu	Ni	Cr	V	Sr	Nb	Th	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
CHCS1	0-2	7	37	68	21	51	128	203	76	26	16	5892	1.16	7.5	0.02	0.54	0.1
	4-6	10	31	177	107	91	174	210	85	27	17	9096	1.27	8.41	0.02	0.56	0.08
	8-10	7	34	84	22	56	137	204	84	26	18	9098	1.27	6.71	0.02	0.58	0.08
	15-20	7	32	75	19	58	136	207	90	29	18	6653	1.36	6.39	0.03	0.58	0.08
	25-30	7	36	73	23	60	136	201	91	29	17	7084	1.36	6.13	0.02	0.58	0.1
Average		7.6	34	95.4	38.4	63.2	142.2	205	85.2	27.4	17.2	7564.6	1.28	7.0	0.02	0.6	0.09
CHCS2	O-2	6	41	53	23	50	127	195	83	30	18	2901	1.31	6.11	0.02	0.51	0.07
	4-6	6	39	53	21	58	128	193	84	31	17	3728	1.42	3.92	0.02	0.5	0.06
	8-10	8	38	53	20	54	126	201	81	29	16	3929	1.3	5.03	0.02	0.52	0.07
	15-20	8	37	81	20	65	125	189	84	28	17	7720	1.29	4.88	0.02	0.54	0.07
	25-30	7	33	61	20	72	154	209	87	35	20	8056	1.52	4.52	0.02	0.52	0.07
Average		7	37.6	60.2	20.8	59.8	132	197.4	83.8	30.6	17.6	5266.8	1.4	4.9	0.02	0.52	0.07
OGCS1	O-2	9	38	77	24	48	135	213	91	26	16	15135	1.18	8.11	0.02	0.62	0.14
	4-6	9	33	77	25	42	127	194	95	26	17	33370	1.23	9.37	0.02	0.66	0.1
	8-10	8	29	76	24	39	115	193	93	24	16	43074	1.17	10.26	0.03	0.68	0.1
	15-20	6	18	45	15	24	95	183	81	18	13	74833	0.98	13.23	0.03	0.71	0.08
	25-30	8	20	62	14	41	110	194	86	21	14	63395	1.15	9.82	0.03	0.68	0.05
Average		8	27.6	67.4	20.4	38.8	116.4	195.4	89.2	23	15.2	45961.4	1.1	10.2	0.03	0.7	0.09
OGCS2	O-2	10	34	68	24	47	131	208	83	25	16	18996	1.17	9.11	0.02	0.57	0.09
	4-6	8	23	74	17	29	102	192	83	21	13	47028	1.04	12.09	0.02	0.61	0.08
	8-10	7	17	44	14	26	82	146	73	18	12	55438	0.91	9.17	0.02	0.6	0.05
	15-20	9	30	69	21	45	124	197	86	24	16	30364	1.19	9.26	0.02	0.56	0.07
	25-30	7	21	54	17	50	115	200	89	22	15	47632	1.23	8.85	0.02	0.59	0.03
Average		8.2	25	61.8	18.6	39.4	110.8	188.6	82.8	22	14.4	39891.6	1.11	9.7	0.02	0.6	0.06
ISCS1	O-2	7	13	37	12	24	109	85	41	11	8	9967	0.66	3.27	0.01	0.6	0.11
	4-6	6	14	31	9	22	61	56	35	10	7	9658	0.43	1.79	0.01	0.53	0.06
	8-10	7	14	38	13	27	67	69	42	11	8	14661	0.49	2.48	0.01	0.55	0.06
	15-20	10	11	33	10	25	103	99	38	11	7	32817	0.59	4.79	0.01	0.56	0.06
	25-30	13	20	75	22	48	128	219	100	25	16	35316	1.22	9.58	0.03	0.62	0.05
Average		8.6	14.4	42.8	13.2	29.2	93.6	105.6	51.2	13.6	9.2	20483.8	0.7	4.4	0.01	0.6	0.07
ISCS2	O-2	6	15	46	16	33	125	115	43	13	8	11568	0.87	3.15	0.01	0.64	0.11
	4-6	4	7	10	7	12	153	31	11	6	3	15000	0.38	1.14	0.00	0.57	0.05
	8-10	5	11	27	9	18	135	84	24	9	6	24287	0.7	2.71	0.01	0.6	0.07
	15-20	4	8	7	5	12	69	33	15	7	3	18318	0.29	1.93	0.01	0.47	0.03
	25-30	3	9	10	5	17	139	51	17	8	6	18951	0.57	1.75	0.01	0.52	0.05
Average		4.4	10	20	8.4	18.4	124.2	62.8	22	8.6	5.2	17624.8	0.6	2.1	0.01	0.6	0.06
UCC		2	20	71	25	20	35	60	350	25	10.7		0.50	5.00	0.08	4.20	0.16

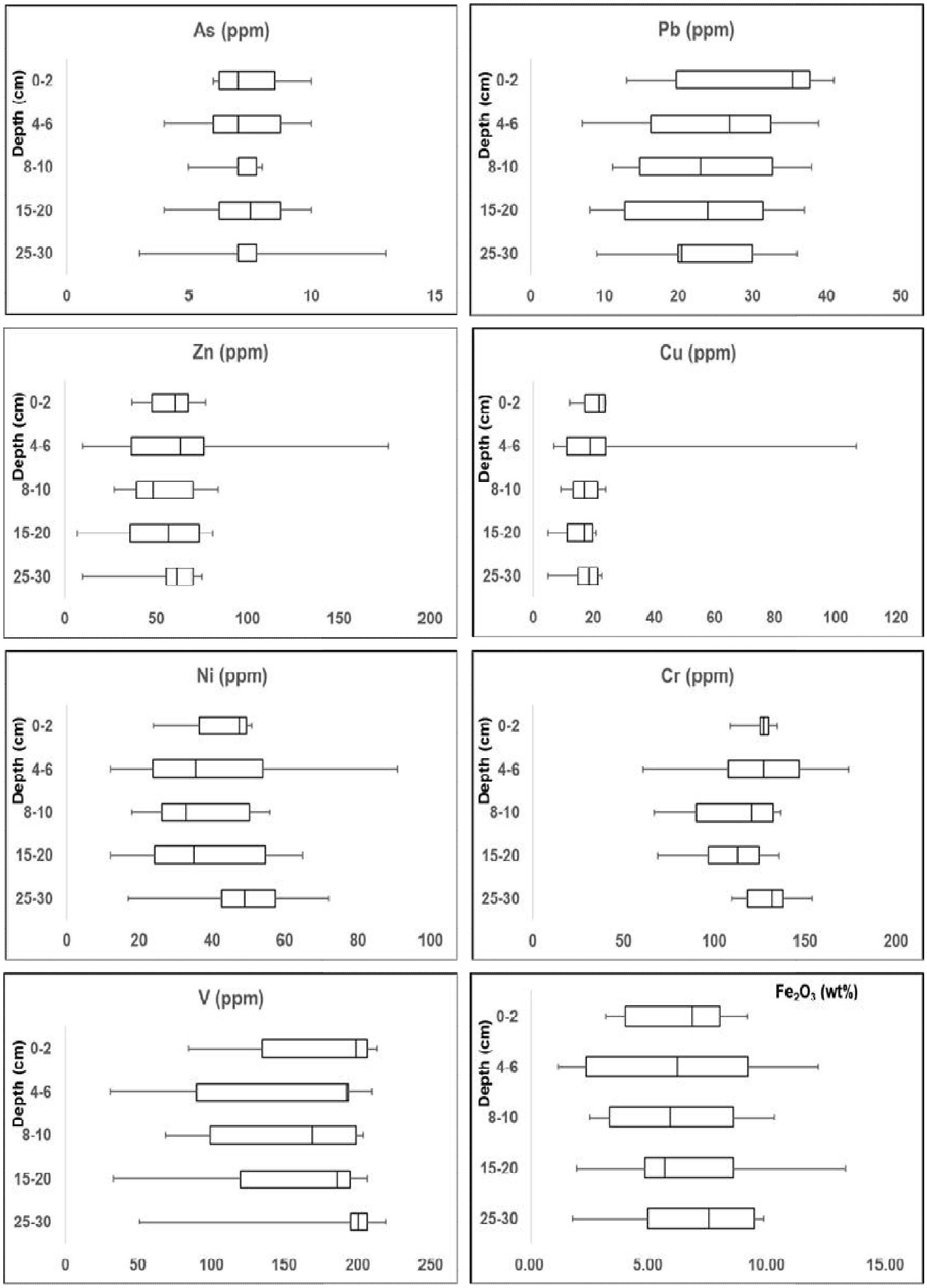

Fig. 2. Box plot showing trace metals and Fe_2O_3 concentrations at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka

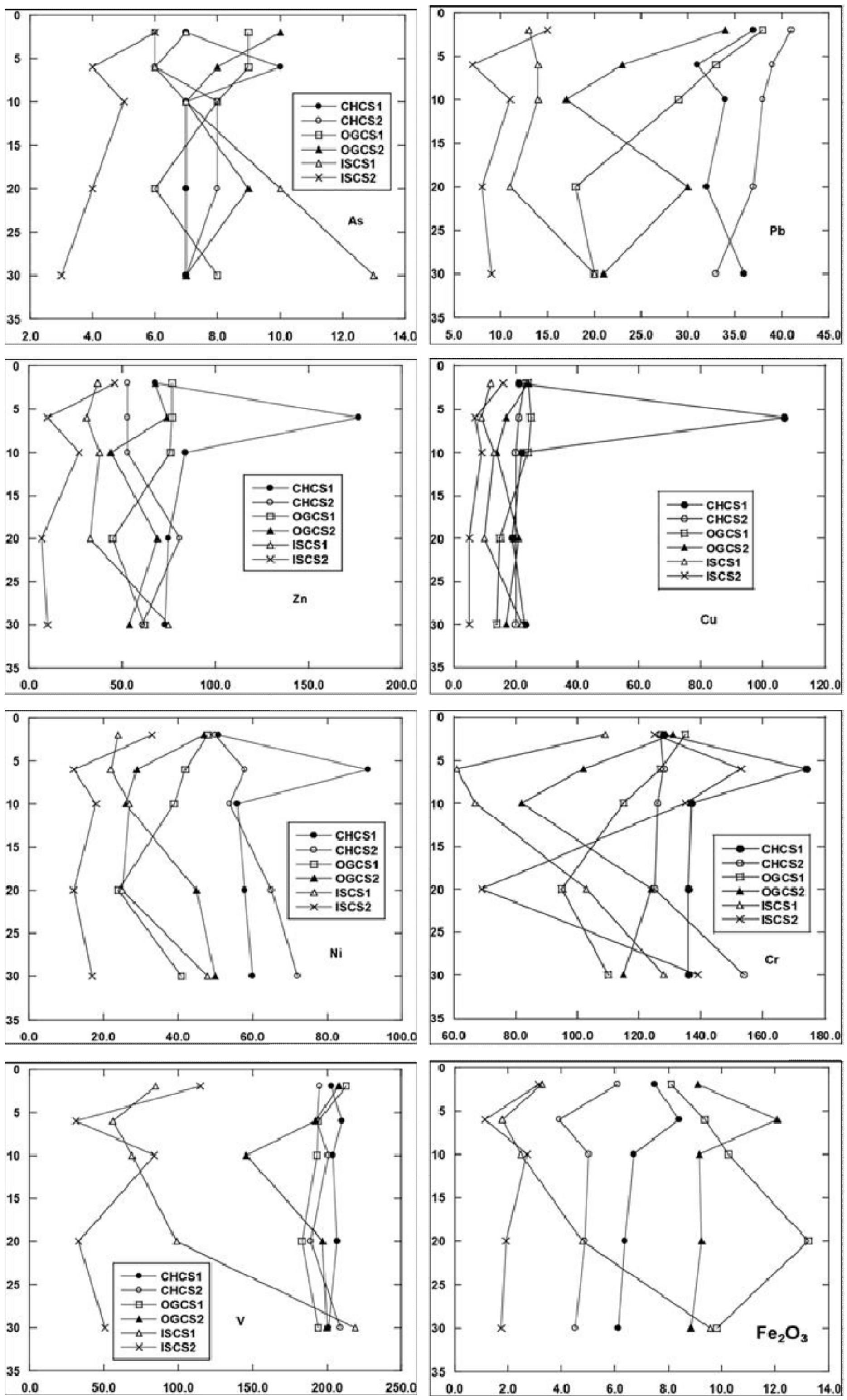

Fig. 3. Cross sectional profile of biogenic and Fe_2O_3 concentrations with depth in mangrove core sediments in Choba, Ogbogoro and Isaka

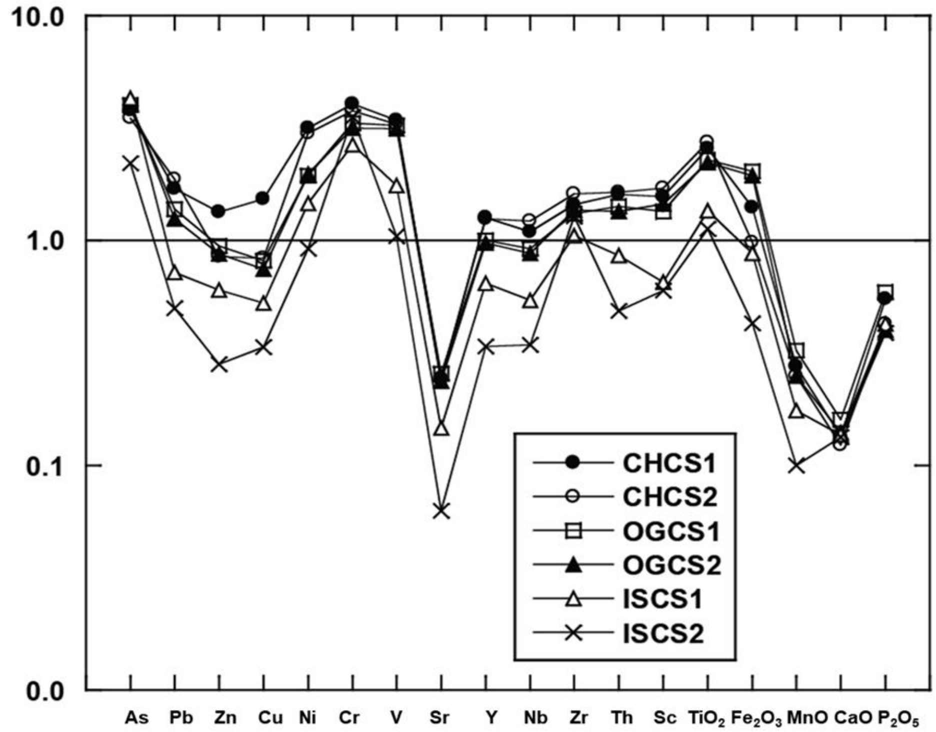

Fig. 4. Comparison of trace elements and oxides concentration in the mangrove core sediments in Choba, Ogbogoro and Isaka. All values were normalized to the UCC of [25]

AD (54.8%), 1708 - 1718 cal AD (8.9%) and 1826 - 1832 cal AD (4.6%). In Ogbogoro (OGCS2), it was found that the wood macro fossil sample has a conventional radiocarbon age of 108.16 ± 0.40 pMC and d13C of -26.5. At 95.4% probability, the possible age ranges are 2000 - 2004 cal AD (88.1%) and 1957 - 1958 cal AD (7.3%) while at 68.2% probability, the age ranged between 2001 - 2003 cal AD (68.2%). The d13C values of the wood samples indicate that they were remains of higher plants.

Wood fossils may not be of the same age compared to the surrounding sediments [39]. However, depending on the residence time of the fossil within the environment, it sometimes exceed the age of the deposits [40]. Interestingly, the wood macro fossils in ISCS1 and OGCS2 at the same depth range (30 - 35 cm) varied greatly in age and belonged to the pre-bomb and post-bomb radiocarbon era respectively. This variation could possibly be due to some geomorphic events such as flooding. It could be that sediment deposition along the banks of the Bonny River around Isaka proceeded gradually while the deposition of sediments on the banks of New Kalabar River around Ogbogoro occurred rapidly.

3.4 Inter-element Relationships

The correlation matrix for the average metal concentrations in the core sediments in Choba, Ogbogoro and Isaka is presented in Table 3. [35, 41] reported that Fe_2O_3 and TiO_2 contents are used as proxies to define elemental sources. These elements are mostly immobile during sedimentary processes [42]. Elements that show strong correlations with TiO_2 should only reflect natural detrital inputs because in sediments,

Tabe 3. Results of radiocarbon (^{14}C) analysis of wood in mangrove core sediments

Core	Layer	Depth (cm)	Material dated	Conventional radiocarbon Age
ISCS1	Mangrove mud	30 - 35	Wood	20 ± 30 BP
OGCS2	Mangrove mud	30 - 35	Wood	108.16 ± 0.40 pMC

BP --- Before Present, pMC --- Percent Modern Carbon lithogenic elements have a linear relationship with TiO_2. However, if there is no correlation between TiO_2 and any metallic element, it suggests that anthropogenic or additional natural processes have contributed to elemental enrichment [43]. In Choba, there is a strong Fe_2O_3-Pb; weak Fe_2O_3-Zn-Cu and negative Fe_2O_3-As-Ni-Cr-V-Sr-Nb-Th-TS-TiO_2 association. This implies that Fe_2O_3 only has influence on the distribution of Pb while it does not affect the distribution of other elements. TiO_2 correlated strongly with Sr, Nb, Th and TS; weakly with As, Zn and Cu; moderately with Ni, Cr and V; and negatively with Pb. The negative TiO_2-Pb shows that Pb concentration is not lithogenic but more anthropogenic while strong TiO_2-Sr-Nb-Th suits suggest that the concentration of provenance metals are lithogenic. In Ogbogoro, Fe_2O_3-TS was moderate but Fe_2O_3-As-Pb-Zn-Cu-Ni-Cr-V-Sr-Nb-Th-TiO_2 was negatively associated. Therefore Fe_2O_3 is not a concentration factor of both the biogenic and provenance elements. However, TiO_2 correlated strongly with Ni, V and Sr; TiO_2-Cr-Nb-Th was moderate while TiO_2-TS was negative. Ni, V and Sr concentrations are therefore largely lithogenic. In Isaka, there is strong Fe_2O_3-As-Ni-V-Sr-Nb-Th-TiO_2 and moderate Fe_2O_3-Pb-Zn-Cu-Cr-TS association. Fe_2O_3 had much influence on the concentration of both biogenic and provenance metals analyzed in this study. TiO_2 associated strongly with Pb, Zn, Cu, Ni, Cr, V, Sr, Nb and Th while it had moderate and weak association with As and TS respectively. The observed concentration of biogenic and provenance metals are largely lithogenic.

The Zn-Nb association in Choba and Isaka is suggestive of the influence of felsic lithology while the Pb-Cu-Ni association in Isaka is indicative of the occurrence of sulphide mineralization [44]. Also, Pb-Zn-Cu-Ni-Cr suits in Isaka implies that these metals have a common source and similar enrichment process [45]. Th-Cu relationship in Ogbogoro and Isaka sediments is suggestive of the existence of granitic/pegmatitic lithology. The Cu:Zn ratio is useful in the description of the redox conditions in sediments [46]. [47] reported that an increase in the Cu:Zn ratio showed a change towards more anaerobic conditions in sediments due to increased organic production which signifies the start of eutrophication. The average core concentrations of Cu:Zn ratio in Choba, Ogbogoro and Isaka yielded 1:2.6, 1:3.3 and 1:2.9 respectively. This implies that Ogbogoro sediments are most anoxic while the Choba sediments are the least anoxic.

4. ECOLOGICAL RISK ASSESSMENT

4.1 Contamination Factor (CF)

The contamination factor of the biogenic elements in the sub core sediments in Choba, Ogbogoro and Isaka is shown in Table 5. The interpretation was based on [24]. The CF of As in the core samples ranged between 3 to 4.75 with an average of 3.65, 4.05 and 3.25 respectively in Choba, Ogbogoro and Isaka. Thus, As is considerably contaminated in the study area. Pb is moderately contaminated in Choba and Ogbogoro with CF averages of 1.79 and 1.32 while in Isaka, it has a low contamination with average CF of 0.61. At depths of 0 - 2, 8 - 10 and 25 - 30 cm, Zn has low contamination in Choba while at depths of 4 - 6 and 15 - 20 cm, it is moderately contaminated. Similarly, at depths of 0 - 2 and 4 - 6 cm, Zn is moderately contaminated in Ogbogoro but at depths of 8 - 10, 15 - 20 and 25 - 30 cm, it has low contamination. In Isaka, Zn concentrations across the depths have low contamination with an average CF of 0.44.

The Cu in Choba was moderately contaminated at 4 - 6 cm depth. Though it had low contamination in other depths, its average CF is 1.18. Ogbogoro and Isaka have low Cu across depths with average CF of 0.78 and 0.43 respectively. At depths of 0 - 2 and 8 - 10 cm in Choba, Ni contamination is moderate while at depths of of 4 - 6, 15 - 20 and 25 - 30 cm, its contamination is considerable. In Ogbogoro, there is a moderate contamination across the depths with average Ni of 1.96. At depths of 0 - 2, 8 - 10 and 25 - 30 cm in Isaka, Ni is moderately contaminated while in other depths, it has low contamination. In Choba and Ogbogoro, Cr across the depths are considerably contaminated with 3.92 and 3.34 CF respective averages. However, at 0 - 2, 4 - 6 and 25 - 30 cm, Cr in Isaka is contaminated considerably but moderately contaminated at depths of 8 - 10 and 15 - 20 cm. With an average V of 3.35, all the core sub samples in Choba are considerably contaminated. In Ogbogoro, the depth of 8 - 10 cm is moderately contaminated by V while the rest depths are considerably contaminated. The depth of 4 - 6 cm in Isaka has low V contamination while the other depths are moderately contaminated.

Table 4. Correlation matix of elements and oxides in mangrove core sediments in Choba, Ogbogoro and Isaka

	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Nb	Th	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
Choba																
As	1															
Pb	-0.68	1														
Zn	**0.83**	-0.45	1													
Cu	0.66	-0.21	**0.94**	1												
Ni	0.71	-0.74	**0.84**	0.76	1											
Cr	0.54	-0.57	0.73	0.76	**0.93**	1										
V	0.07	-0.37	-0.02	0.08	0.35	0.60	1									
Sr	0.32	-0.91	0.18	-0.02	0.63	0.51	0.42	1								
Nb	-0.12	-0.50	-0.01	0.01	0.52	0.62	0.67	0.77	1							
Th	-0.24	-0.53	-0.28	-0.34	0.28	0.32	0.56	**0.82**	**0.92**	1						
TS	0.52	-0.96	0.20	-0.03	0.58	0.45	0.47	**0.93**	0.57	0.66	1					
TiO_2	0.25	-0.80	0.22	0.13	0.71	0.72	0.69	**0.92**	**0.92**	**0.86**	**0.83**	1				
Fe_2O_3	-0.33	**0.88**	0.01	0.23	-0.42	-0.33	-0.52	-0.92	-0.61	-0.76	-0.98	-0.82	1			
MnO	0.20	-0.38	0.01	-0.29	0.00	-0.36	-0.64	0.38	-0.16	0.09	0.35	-0.01	-0.32	1		
CaO	0.24	-0.69	-0.24	-0.52	0.03	-0.17	0.10	0.68	0.19	0.49	**0.80**	0.42	-0.85	0.64	1	
P_2O_5	-0.95	0.45	-0.80	-0.64	-0.52	-0.31	0.19	-0.05	0.42	0.51	-0.26	0.07	0.07	-0.25	-0.11	1

	As	Pb	Zn	Cu	Ni	Cr	V	Sr	Nb	Th	TS	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
Ogbogoro																
As	1															
Pb	**0.97**	1														
Zn	**0.86**	0.79	1													
Cu	**0.90**	**0.95**	**0.81**	1												
Ni	0.54	0.42	0.21	0.15	1											
Cr	**0.89**	**0.84**	0.62	0.64	0.79	1										
V	0.72	0.64	0.47	0.38	**0.84**	**0.95**	1									
Sr	0.53	0.34	0.69	0.21	0.53	0.58	0.65	1								
Nb	**0.99**	**0.94**	**0.87**	**0.85**	0.59	**0.91**	0.76	0.62	1							
Th	**0.96**	**0.93**	0.74	0.77	0.68	**0.98**	**0.88**	0.57	**0.96**	1						
TS	-0.98	-0.99	-0.77	-0.93	-0.50	-0.84	-0.63	-0.36	-0.95	-0.92	1					
TiO_2	0.49	0.33	0.35	0.06	**0.90**	0.75	**0.88**	**0.81**	0.57	0.65	-0.37	1				
Fe_2O_3	-0.48	-0.40	-0.18	-0.28	-0.77	-0.50	-0.39	-0.22	-0.50	-0.46	0.54	-0.49	1			
MnO	-0.47	-0.39	-0.17	-0.28	-0.73	-0.47	-0.35	-0.18	-0.48	-0.43	0.54	-0.45	**1.00**	1		
CaO	-0.89	-0.90	-0.52	-0.74	-0.72	-0.92	-0.77	-0.28	-0.87	-0.92	**0.92**	-0.52	0.65	0.64	1	
P_2O_5	**0.85**	**0.93**	0.75	**0.99**	0.08	0.61	0.36	0.11	0.79	0.74	-0.89	-0.02	-0.17	-0.18	-0.72	1

	As	**Pb**	**Zn**	**Cu**	**Ni**	**Cr**	**V**	**Sr**	**Nb**	**Th**	**TS**	**TiO_2**	**Fe_2O_3**	**MnO**	**CaO**	**P_2O_5**
Isaka																
As	1															
Pb	0.46	1														
Zn	0.55	**0.99**	1													
Cu	0.48	**0.98**	**0.99**	1												
Ni	0.72	**0.94**	**0.96**	**0.94**	1											
Cr	0.41	**0.87**	**0.81**	**0.80**	**0.85**	1										
V	**0.85**	**0.86**	**0.90**	**0.86**	**0.98**	**0.78**	1									
Sr	0.79	**0.89**	**0.90**	**0.86**	**0.98**	**0.86**	**0.99**	1								
Nb	**0.81**	**0.85**	**0.86**	**0.81**	**0.96**	**0.85**	**0.98**	**1.00**	1							
Th	0.72	**0.92**	**0.91**	**0.87**	**0.97**	**0.88**	**0.97**	**0.99**	**0.98**	1						
TS	0.76	-0.04	0.02	-0.08	0.21	-0.02	0.41	0.37	0.43	0.33	1					
TiO_2	0.70	**0.96**	**0.97**	**0.95**	**1.00**	**0.85**	**0.97**	**0.98**	**0.95**	**0.97**	0.21	1				
Fe_2O_3	**0.97**	0.60	0.65	0.59	**0.82**	0.60	**0.92**	**0.89**	**0.92**	**0.85**	0.70	**0.81**	1			
MnO	0.75	0.59	0.57	0.50	0.74	0.77	**0.81**	**0.86**	**0.90**	**0.85**	0.61	0.73	**0.87**	1		
CaO	0.00	**0.82**	**0.81**	**0.86**	0.65	0.61	0.48	0.50	0.42	0.53	-0.56	0.66	0.10	0.06	1	
P_2O_5	-0.15	0.52	0.55	0.63	0.37	0.25	0.20	0.17	0.09	0.17	-0.71	0.37	-0.14	-0.32	**0.88**	1

4.2 Enrichment Factor (EF)

The values of enrichment factor of biogenic metals in the sub core mangrove sediments in Choba, Ogbogoro and Isaka are shown in Table 6. As is moderately enriched in all the depths analyzed in Choba with an average EF of 3.09. In Ogbogoro, As is moderately enriched at 0 - 2 and 25 - 30 cm depth while in other depths, it is minimally enriched. Isaka has the highest EF of As with an average of 5.62 which signifies significant enrichment. The enrichment of Pb, Zn and Cu is minimal in Choba, Ogbogoro and Isaka with average EF of 1.51, 0.67, 1.09; 0.92, 0.46, 0.75 and 0.99, 0.40, 0.75 respectively. Ni enrichment is minimal in Choba at 0 - 2 cm but moderately enriched at other depths. At all depths in Ogbogoro, Ni is minimally enriched and had an average EF of 1.01. In Isaka, Ni is moderately enriched at the upper core but minimally enriched at the lower core. Cr enrichment is moderate across depths in Choba with average EF of 2.61 while in Ogbogoro, Cr is moderately enriched at 0 - 2 cm but minimally enriched in other depths. There is significant enrichment of Cr across the depths in Isaka with average EF of 5.64. At all depths, there is moderate V enrichment in Choba. Ogbogoro has moderate enrichment of V at 0 - 2 cm but minimal enrichment at other depths while Isaka is moderately enriched in V at the upper core but minimally enriched at the lower core.

[48] reported that EF values between 0.5 to 1.5 signify that the metals are derived entirely from geogenic sources while they are derived from anthropogenic sources if the EF values are more than 1.5. Based on the EF values obtained from the core samples, As enrichment is anthropogenic in Choba, Ogbogoro and Isaka. Pb is anthropogenically enriched at depths of 8 - 10, 15 - 20, 25 - 30 and 4 - 6 cm in Choba and Isaka respectively while it is geogenic at other depths and at all the depths in Ogbogoro. Zn and Cu enrichment are geogenic except at 4 - 6 cm in Choba where it is anthropogenic. Ni enrichment is anthropogenic in Choba, geogenic in Ogbogoro and in Isaka, it is anthropogenic in the upper core but geogenic in the lower core. In Choba and Isaka, Cr is enriched anthropogenically while at 0 - 2, 4 - 6 and 25 - 30 cm, it is anthropogenic and geogenic at 8 - 10 and 15 - 20 cm in Ogbogoro. V enrichment is anthropogenic in Choba and Isaka. However, in Ogbogoro it is anthropogenic at 0 - 2, 4 - 6 and 25 - 30 cm but geogenic at 8 - 10 and 15 - 20 cm.

5. CROSS SECTIONAL ASSESSMENT OF SEDIMENT POLLUTION BASED ON SEDIMENT QUALITY GUIDELINES

Primarily, the objective of sediment quality guidelines (SQGs) is the protection of aquatic biota from the harmful and toxic effects related to sediment bound contaminants [49]. Therefore, SQGs are vital instrument employed to determine potential contaminant levels within sediments that are capable of biological effect.

Table 5. CF of metals at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka

Location	Depth (cm)	CF of Metals						
		As	Pb	Zn	Cu	Ni	Cr	V
Choba	0 - 2	3.25	1.95	0.85	0.88	2.53	3.64	3.32
	4 - 6	4.00	1.75	1.62	2.56	3.73	4.31	3.36
	8 - 10	3.75	1.80	0.96	0.84	2.75	3.76	3.38
	15 - 20	3.75	1.73	1.10	0.78	3.08	3.73	3.30
	25 - 30	3.50	1.73	0.94	0.86	3.30	4.14	3.42
Average		3.65	1.79	1.10	1.18	3.08	3.92	3.35
Ogbogoro	0 - 2	4.75	1.80	1.02	0.96	2.38	3.80	3.51
	4 - 6	4.25	1.40	1.06	0.84	1.78	3.27	3.22
	8 - 10	3.75	1.15	0.85	0.76	1.63	2.81	2.83
	15 - 20	3.75	1.20	0.80	0.72	1.73	3.13	3.17
	25 - 30	3.75	1.03	0.82	0.60	2.28	3.21	3.28
Average		4.05	1.32	0.91	0.78	1.96	3.25	3.20
Isaka	0 - 2	3.25	0.70	0.58	0.56	1.43	3.34	1.67
	4 - 6	2.50	0.53	0.29	0.32	0.85	3.06	0.73
	8 - 10	3.00	0.63	0.46	0.44	1.13	2.89	1.28
	15 - 20	3.50	0.48	0.28	0.30	0.93	2.46	1.10
	25 - 30	4.00	0.73	0.60	0.54	1.63	3.81	2.25
Average		3.25	0.61	0.44	0.43	1.19	3.11	1.40

Table 6. EF of metals at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka

Location	Depth (cm)	EF of Metals						
		As	Pb	Zn	Cu	Ni	Cr	V
Choba	0 - 2	2.39	1.43	0.63	0.65	1.86	2.68	2.44
	4 - 6	3.24	1.42	1.31	2.08	3.02	3.50	2.72
	8 - 10	3.19	1.53	0.82	0.72	2.34	3.20	2.87
	15 - 20	3.33	1.53	0.97	0.69	2.73	3.31	2.93
	25 - 30	3.29	1.62	0.89	0.81	3.10	3.89	3.21
Average		3.09	1.51	0.92	0.99	2.61	3.31	2.83
Ogbogoro	0 - 2	2.76	1.05	0.59	0.56	1.38	2.21	2.04
	4 - 6	1.98	0.65	0.50	0.39	0.83	1.52	1.50
	8 - 10	1.93	0.59	0.43	0.39	0.84	1.45	1.45
	15 - 20	1.67	0.53	0.36	0.32	0.77	1.39	1.41
	25 - 30	2.01	0.55	0.44	0.32	1.22	1.72	1.76
Average		2.07	0.67	0.46	0.40	1.01	1.66	1.63
Isaka	0 - 2	5.06	1.09	0.91	0.87	2.22	5.21	2.60
	4 - 6	8.53	1.79	0.99	1.09	2.90	10.43	2.47
	8 - 10	5.78	1.20	0.88	0.85	2.17	5.56	2.46
	15 - 20	5.21	0.71	0.42	0.45	1.38	3.66	1.64
	25 - 30	3.53	0.64	0.53	0.48	1.43	3.37	1.99
Average		5.62	1.09	0.75	0.75	2.02	5.64	2.23

**Highlighted values above 1.50 indicate anthropogenic enrichment.*

Table 7. SQGs and cross sectional concentrations (ppm) of metals in mangrove core sediments in Choba, Ogbogoro and Isaka

Core	Depth (cm)	Elements (ppm)					
		As	Pb	Zn	Cu	Ni	Cr
Choba	0 - 2	6.5	39	60.5	22	50.5	127.5
	4 - 6	8	35	115	64	74.5	151
	8 - 10	7.5	36	68.5	21	55	131.5
	15 - 20	7.5	34.5	78	19.5	61.5	130.5
	25 - 30	7	34.5	67	21.5	66	145
Ogbogoro	0 - 2	9.5	36	72.5	24	47.5	133
	4 - 6	8.5	28	75.5	21	35.5	114.5
	8 - 10	7.5	23	60	19	32.5	98.5
	15 - 20	7.5	24	57	18	34.5	109.5
	25 - 30	7.5	20.5	58	15.5	45.5	112.5
Isaka	0 - 2	6.5	14	41.5	14	28.5	117
	4 - 6	5	10.5	20.5	8	17	107
	8 - 10	6	12.5	32.5	11	22.5	101
	15 - 20	7	9.5	20	7.5	18.5	86
	25 - 30	8	14.5	42.5	13.5	32.5	133.5
LEL		6	31	120	16	16	26
SEL		33	110	270	110	50	110
ISQG		7	30	124	19	na	52
PEL		42	112	271	108	na	160

In order to determine if the observed As, Pb, Zn, Cu, Ni and Cr concentrations at different depths in Choba, Ogbogoro and Isaka mangrove sediments are ecotoxic, they were compared to the sediment quality benchmarks established by the New York State Department of Environmental Conservation [50] and Canadian Council of Ministers of the Environment [51]. The benchmarks are lowest effect level (LEL), severe effect level (SEL) and interim sediment quality guideline (ISQG), probable effect level (PEL) respectively. Metal concentrations that exceed LEL and ISQG values have moderate impact on biota while concentrations that exceed SEL and PEL values have severe impact on biota.

As had a slightly below and above values relative to LEL and ISQG in Choba, Ogbogoro and Isaka (Table 7). The present concentration of As might impact moderately on biota. Pb concentrations in Choba exceeded the values of LEL and ISQG but are below SEL and PEL. However, with the exception of concentrations at 0 - 2 cm, Pb values are lower than LEL and ISQG values in Ogbogoro and Isaka. In all locations and depths, Zn concentrations are lower than the LEL and ISQG values and as such, has no impact on biota. In Choba, Cu exceeded LEL and ISQG values but are below SEL and PEL values. Cu values at 0 - 2 and 4 - 6 cm in Ogbogoro are higher than LEL and ISQG but at 8 - 10 and 15 - 20 cm, it is higher than LEL but within ISQG values while at 25 - 30 cm, it is lower than both LEL and ISQG values. Isaka Cu values are lower than LEL and ISQG and thus have no impact on biota. However, Ni values across locations and depths, exceeded the LEL value. The impact of Ni in Choba is severe given that the values are more than the SEL value while Ogbogoro and Isaka values are below SEL value for Ni. Similarly, Cr concentrations in Choba, Ogbogoro and Isaka might have adverse ecotoxic effect considering that its value exceeded LEL and ISQG values as well as the SEL value particularly in Choba and at some depths in Ogbogoro and Isaka.

6. CONCLUSION

The core mangrove sediment samples have higher concentrations of TS and depleted CaO. Variations were observed on the concentrations of the analyzed elements at different depths. The observed vertical variations might be due to diagenic modifications and precipitation around the redox boundaries. In Choba and Isaka, there is a strong Zn-Nb correlation which is indicative of the influence of felsic lithology while the Pb-Cu-Ni suits in Isaka suggests the occurrence of sulphide mineralization. The Th-Cu association in Ogbogoro and Isaka signifies the existence of granitic/pegmatitic lithology. Pb, Zn, Cu, Ni and Cr in Isaka are correlated and it indicates that these elements have a common source and similar enrichment process.

There is a considerable contamination of As in the mangrove sediments of Choba, Ogbogoro and Isaka. Pb is moderately contaminated in Choba and Ogbogoro but has low contamination in Isaka. Cu has low contamination while Ni, Cr and V are moderately contaminated. The enrichment of Zn and Cu are mostly geogenic while the enrichment of As, Pb, Cr, Ni and V are largely anthropogenic. Concentrations of As, Pb, Zn and Cu were either equal to, below or above LEL and ISQG values. Thus indicating that these elements have low to moderate impact on biota. However, Ni and Cr exceeded the LEL, ISQG and SEL values suggesting a severe ecotoxic potentials. Hence, there is need for remediation and monitoring.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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