Shimane University

Doctoral Thesis

Environmental Risk Assessment of Geochemical Composition and Spatial Dynamics in Sediments of Niger Delta Mangrove, Nigeria

(ナイジェリアのニジェールデルタマングローブ堆積物における地球化学組成と空間的動態の環境リスクアセスメント)

By

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Abstract

The geochemical evaluation of the mangrove environment in Niger Delta, Nigeria was carried out using trace and major element compositions of surface sediments, core sediments as well as *Rhizophora racemosa* sampled at Choba, Ogbogoro and Isaka. Fifteen surface sediment samples (Choba, n = 5; Ogbogoro, n = 5 and Isaka, n = 5) were collected. Six core sediment samples ranging from 31 - 35 cm in depth were collected. Each of the core sediments was subdivided into five. This yielded thirty sub core samples thus: Choba, n = 10; Ogbogoro, n = 10 and Isaka, n =10. Also, the leaves, stems and roots of *R. racemosa* and *A. germinans* were collected and it gave a total of twenty seven samples (Choba, n = 9; Ogbogoro, n = 9 and Isaka, n = 9) and twelve samples (Ogbogoro, n = 3; Isaka, n = 9) respectively. The surface sediment, core sediment and *R. racemosa* samples were analysed using X-ray fluorescence (XRF). The XRF data of the surface sediments was used to evaluate their geochemical compositions, inter-element relationships and potential ecological impact. Results show that the highest mean concentrations in parts per million (ppm) of Pb, Zn, Cu, Ni, Cr, Y, Nb, Th and Sc in Choba sediments were 36.2, 65.2, 19.6, 47.4, 121.6, 21.4, 23.0, 13.8 and 16.8; As, V, Sr, Zr, TS and F in Ogbogoro sediments were 6.4, 192.3, 70.0, 273.4, 14627.0 and 104.8 while Br, I and Cl in Isaka sediments were 27.4, 41.4 and 4189.6, respectively. Box plots of the elements show contrasting concentrations in different sampling locations. Compared to the upper continental crust (UCC), As and Ni were higher in Choba, Ogbogoro and Isaka. The abundance of Pb was found to be higher in Choba and Ogbogoro. Though Th and Sc were more concentrated in Choba and Ogbogoro relative to the UCC, they were found to be lower in Isaka. However, Zn, Cu, Cr, V, Sr and Zr concentrations in the UCC were found to be higher than the mean concentrations of these elements in Choba, Ogbogoro and Isaka mangrove sediments. Most of the trace elements correlated positively and strongly with Fe_2O_3. This implies that Fe_2O_3 is important in controlling metal concentrations in the area. The concentrations of As and Zn were either equal to or below the low effect level (LEL) and interim sediment quality guideline (ISQG). Pb, Cu and Ni were found to be higher than LEL and ISQG in Choba while Cr concentrations in Choba, Ogbogoro and Isaka all exceeded the LEL, ISQG and severe effect level (SEL) values but below probable effect level (PEL) value; thus indicating potentials for moderate to severe ecological harm. The XRF data of the core sediments was used to determine the element-depth geochemical composition and inter-element relationships. The ecological risk of the metal concentrations was assessed using Contamination Factor (CF) and Enrichment Factor (EF), Pollution Load Index (PLI) Geoaccumulation (Igeo) 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 plot and cross sectional graph. 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 was severe while Cr concentration level in Choba, Ogbogoro and Isaka might have adverse ecotoxic impact on biota. The XRF data of the *R. racemosa* and *A. germinans* was used in comparison to the core sediment data to determine heavy metals distribution and pattern in mangrove plant species. The results showed contrasting heavy metal concentrations in the sediments, *R. racemosa* and *A. germinans*. As, Pb, Cu, Ni, Y, Nb and Zr had higher concentrations in the sediments while the concentrations of Zn, Sr, Cl, TS, MnO, CaO and P_2O_5 were more in *R. racemosa* and *A.*

germinans tissues. However, Cr, V and TiO_2 which had relatively high concentrations in the sediments were not detected in *R. racemosa* and *A. germinans*. Graphical analyses revealed a correlation between concentrations in sediment and *R. racemosa* as well as a similar pattern of heavy metal concentrations in the *R. racemosa* leaves, stems and roots in Choba, Ogbogoro and Isaka. But variations were found in the leaf/stem and leaf/root upward transport relationship. Most heavy metals were found to concentrate in *R. racemosa* roots while the least concentrations were found in the leaves. Similarly, PLI results showed that *R. racemosa* and *A. germinans* have root>stem>leaf pollution load.

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CHAPTER ONE

Background of the Study

1.1 General Introduction

The Niger Delta is located at the extreme southern part of Nigeria and thus, sits directly on the coasts of the East Atlantic Ocean. It is predominantly a wetland and consists mostly of salt-water swamp (mangroves) and fresh water swamp. The mangroves stretched through the entire coastline of the Niger Delta and extended more than 50 km inland in some parts. Hence, occupying a huge intertidal zone approximately 7, 386 km^2 (UNEP, 2007). The Niger Delta is a classified Global 200 ecoregion and provides habitat for many locally and globally endangered species (UNDP, 2012). It contains between 60 - 80% of all plant species and animal species found in Nigeria (Mayers *et al*., 2000; Okonkwo *et al*., 2015). Also over 60% of the fish caught between the Gulf of Guinea (formally known as the Bight of Biafra) and Angola breed in the mangroves of the Niger Delta (UNEP, 2007).

The exploration, discovery and exploitation of abundant petroleum resources in Niger Delta which began in the 1950s opened it up to uncontrolled rapid urbanization and industrialization. This in turn, exposed Niger Delta to various scales of pollution. Though it is among ten most important wetland and marine ecosystems in the world (FME *et al.*, 2006), the unsustainable approach to oil exploration and exploitation has made it one of the five most severely damaged ecosystems in the world by petroleum (Kadafa, 2012a). According to UNDP (2006), a total of 6,817 oil spills occurred between 1976 to 2001, with a loss of approximately three million barrels of oil out of which about 70% of the spilled oil was not recovered. For instance, the blow up of the Funiwa Well No. 5 in 1980 spilled an estimated 421,000 barrels of oil into the surrounding environment and it led to the destruction of about 836 acres of mangrove forest within six miles offshore (Ukoli, 2001). Spills equally occur through the complex and extensive network of oil pipelines that crisscross the Niger Delta due to failures of pipelines and storage facilities (Kadafa, 2012b). Also, the persistent gas flaring going on in the Niger Delta for decades greatly contributes to the pollution of the environment. Similarly, some of the estuarine rivers in the area are used for the discharge both point and non-point wastes or as means of transportation (Uzukwu *et al.,* 2014). Given that the mangroves trap sediments from the upland and sediments carried by tides, they provide sink for heavy metals and other pollutants (Duarte *et al*., 2013; Machado *et al*., 2016). As such, the extent of metal contamination in mangrove environment is influenced by land use within its catchment (Brady *et al*., 2014). Polluted mangroves could in turn become pollution source. This, particularly hampers mangrove development given that they have very poor regeneration potential (Chindah *et al.,* 2007). It is against this backdrop that this study seeks to assess the present geochemical status of the mangrove sediments and plant species (*R. racemosa; A. germinans*) as well as the associated environmental risks in Niger Delta, Nigeria.

1.2 Objectives of the Study

This study was carried out to determine the present geochemical status of the Niger Delta mangrove environment in Nigeria. The following are the specific objectives:

(a) To determine the geochemical composition of the surface sediments in Niger Delta mangrove.

(b) To assess the element-depth concentrations of the Niger Delta mangrove core sediments.

(c) To evaluate the ecological risk of Niger Delta mangrove sediment geochemical concentrations.

(d) To determine the elemental concentrations and distributions in *R. racemosa* and *A. germinans.*

(e) To determine the heavy metals uptake patterns in *R. racemosa* and *A. germinans.*

1.3 Significance of the Study

This study is considered significant in the following ways:

(a) Generation of data on the present geochemical concentrations in mangrove sediments in Niger Delta.

(b) Production of baseline data on the bioaccumulation and translocation of heavy metals in *R. racemosa* and *A. germinans* in Niger Delta.

(c) Determination of the ecological risks of heavy metal concentrations in Niger Delta mangrove sediments and plant species (*R. racemosa* and *A. germinans*).

1.4 Study Area

The Niger Delta covers about 240 km in distance on its north-south stretch from Onitsha to the barrier islands on the East 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 (UNDP, 2012). However, only about 7,386 km^2 of the Niger Delta are covered by mangroves (UNEP, 2007). This huge wetland area is located between latitudes 4^{o}N to 6^{o}N and longitudes 5^{o}E 8^{o}E (Dada *et al*., 2015; Opafunso, 2007). Thus, it seats directly on the Gulf of Guinea (formally known as the Bight of Biafra) on the Atlantic ocean in southern Nigeria. The samples for this study were collected from the eastern Niger Delta mangroves along the banks of the New Kalabar River in Choba and Ogbogoro as well as from mangroves on the banks of the Bonny River at Isaka. Population density and human activities are more pronounced in Choba and least pronounced in Isaka. However, both the New Kalabar and Bonny Rivers are among the most stressed rivers in Niger Delta (Uzukwu *et al.*, 2014; Dienye and Woke, 2015). These rivers are used for the disposal of both point and non-point wastes as well as means of transportation. Also, illegally obtained petroleum products are ferried through these rivers; thus exposing them to spillage.

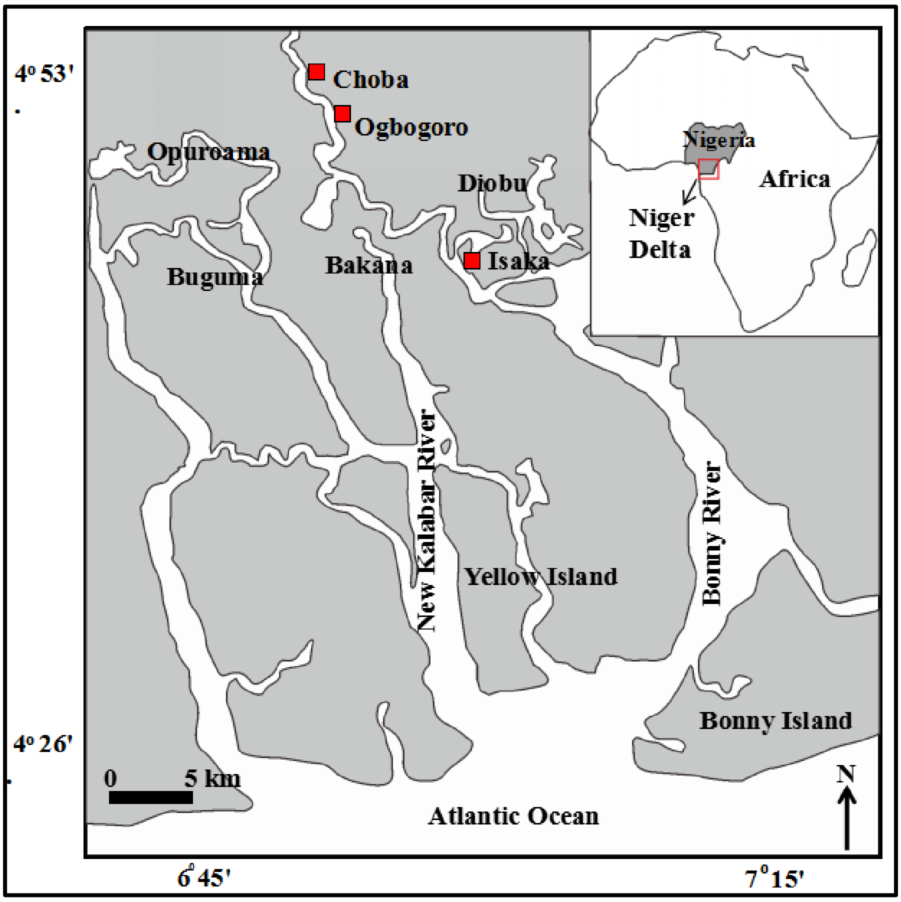

Figure 1.1 Map of study area showing sampling locations.

1.5 Climate and Vegetation of Niger Delta

The climate of Niger Delta is equatorial. It has a high mean annual temperature due to its location in the tropics and an all year round high humidity due to the warm Guinea current that prevails on its coast. The temperature ranges from 18ºC to 33ºC (UNDP 2012) while the relative humidity decreases from 85% within the coastal margins to 80% around its northern fringe (Adejuwon 2012). The coastal margins of the Niger Delta receives rainfall throughout the year. However, the mean annual rainfall decreases from about 4,500 mm within the coastal margins to about 2,000 mm around its northern fringe (Adejuwon 2012). The vegetation of the Niger Delta consists of four main distinct vegetation types namely; mangrove forest, fresh water swamp forest, lowland forest and barrier island swamp forest (Chindah *et al.*, 2007).

1.6 Hydrological Settings in Niger Delta

The Niger River basin emptied into the Atlantic Ocean through the Niger Delta. With a length of 4,200 km, drainage area of 2.27 million square kilometers and discharge rate of 9,570 m^3/s, the Niger river is the third longest river in Africa and its basin is the ninth largest in the world (Oyebande and Odunuga 2010; Dada *et al*., 2015). The basin is shared among ten countries (Oyebande and Odunuga 2010). Through its multiple distributaries, the Niger River discharges its sediment load at the Niger Delta (Abam 1999; Abam 2001). Thus, the Niger Delta sediments originate from diverse sources given that these sediments were transported from different countries within the catchment of River Niger. The Niger Delta has twenty one tidal inlets (Dada *et al*., 2015) and as such, it is significantly influenced by tides. Within the mangrove zone, tidal amplitudes ranges between 1 - 3 m in height (Chinda *et al.*, 2009; UNDP, 2012). Tidal influence extends to more than 50 km from the Atlantic coast.

Figure 1.2 Hydrological map of Niger Delta. Source: Google Earth (2018).

1.7 Geological Settings in Niger Delta

Geologically, the Niger Delta evolved as a result of the drifting apart of the African and South American plates at the site of the triple junction in the late Jurassic and continued into the Cretaceous (Burke *et al*., 1971; Kulke 1995; Emujakporue and Ngwueke 2013). The geologic sequence of the Niger Delta consists of three main subsurface lithostratigraphic units which are overlain by different types of Quaternary deposits and range in age from Tertiary to recent (Short and Stauble 1967; Burke *et al*., 1971; Reijers 2011; Emujakporue and Ngwueke 2013; Ola and Alao 2013; Dada *et al*., 2015; Didei and Akana 2016). The lithostratigraphic units are the Akata Formation, Agbada Formation and Benin Formation. At the base of the Niger Delta sequence is the Akata Formation. It is overlain by the Agbada Formation. The Akata Formation consists of thick shale turbidite sands and small amounts of silt and clay with an estimated thickness of 7,000 meters (Tuttle *et al*., 1999; Asadu *et al*., 2015). The Agbada Formation underlies the Benin Formation. It is made up of an alternation of sands (fluviatile, coastal and fluviomarine), silt, clay and marine shale (Asadu *et al*., 2015). This is the major oil-producing formation in the Niger Delta basin (Chukwu 1999; Asadu *et al*., 2015). Its thickness is estimated to be 3,700 meters (Tuttle *et al*., 1999). The Benin Formation is the topmost stratigraphic layer of the Niger Delta and consists mainly of alternating sequence of gravel, sand, silt, clay and alluvium estimated to be up to 2,000 meters thick (Tuttle *et al.,* 1999; Ekwere *et al.,* 2013).

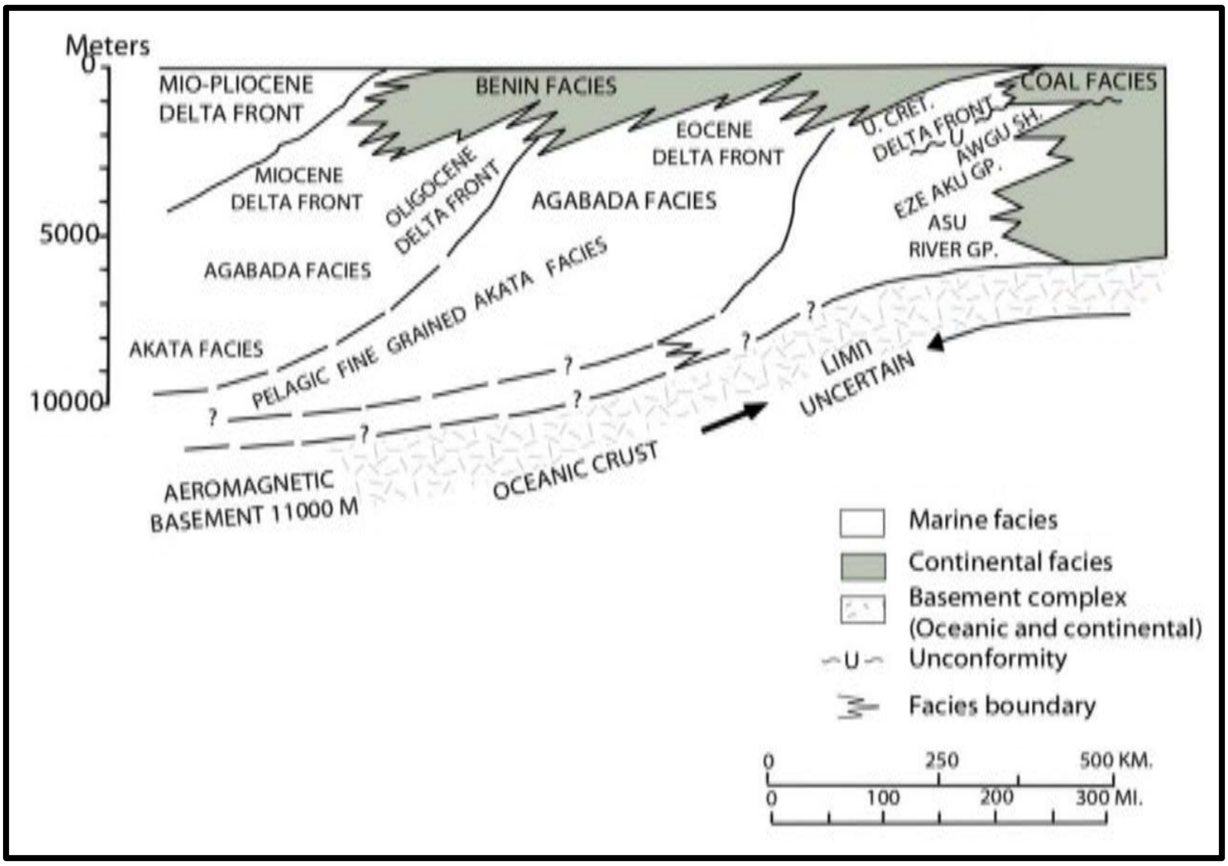

Figure 1.3 Lithostratigraphic map of Niger Delta showing the Akata, Agbada and Benin Formations (Tuttle *et al*., 1999).

CHAPTER TWO

Geochemical Evaluation of Mangrove Surface Sediments

2.1 Introduction

Mangroves are highly specialized ecosystems found between latitudes 30^o north and south of the equator. They thrive in saline and brackish environment. Sediments in mangrove are mostly in anaerobic condition with high concentrations of sulfides and organic matter (Silva *et al.,* 1990). As a sink, mangrove therefore favours the retention of water-borne heavy metals. In the aquatic ecosystem, trace metals are among the most persistent pollutants (Arnason and Fletcher, 2003). Increased concentration of heavy metals in mangrove environment is mostly due to discharge of urban and industrial waste-waters, leaching from bedrocks and soils as well as water drainage and runoff from banks (Soares *et al.,* 1999; Wan *et al.,* 2012). Thus, the records of both the natural watershed conditions and changes caused by human activities are embedded in the mangrove sediments (Arnason and Fletcher, 2003).

The mangrove of Niger Delta in Nigeria is the largest in Africa with estimated area coverage of 7,386 km^2 (UNEP 2007). In recent years, attention has been paid to the sedimentology and organic geochemical studies of Niger Delta (Ntekim *et al.,* 1993; Ekwere *et al.,* 2013; Oni *et al.,* 2014; Vincent-Akpu and Yanadi, 2014; Onojake *et al.,* 2015). However, these studies used few geochemical elements (Zn, Pb, Cd, Co, Cr, Fe and Ni) in their assessment of heavy metal concentrations in Niger Delta. The present study of surface sediments of the New Kalabar and Bonny Rivers in eastern Niger Delta was undertaken to evaluate their environment and to obtain a deeper understanding of the present geochemical status of Niger Delta. Specifically, this study aims at gaining insight into (a) geochemical composition of the surface sediments, including trace and major element concentrations, (b) evaluation of sediment source composition and (c) evaluation of sediment pollution.

2.2 Materials and Methods

2.2.1 Mangrove Surface Sediment Sample Collection and Preparation

Surface sediment samples were collected in the mangrove areas along the New Kalabar River at Choba and Ogbogoro and Bonny River at Isaka. Fifteen sediment samples were collected from Choba (n = 5), Ogbogoro (n = 5) and Isaka (n = 5). Samples were collected during low tide on March 8th and 9th, 2017.

Figure 2.1 Sampling points in Choba mangroves. Source: Google Earth (2018).

Figure 2.2 Sampling points in Ogbogoro mangroves. Source: Google Earth (2018)

Figure 2.3 Sampling points in Isaka mangroves. Source: Google Earth (2018).

The surface sediment samples were collected using bucket auger. Sediment samples weighing about 200 g were packaged in plastic bags in the field and stored in a cooler at 4°C. The samples were homogenized and air dried for 48 hours to reduce weight before repackaging them in ziplock bags and placed them in plastic boxes. The samples were exported to Earth Science laboratory, Shimane University, Japan for analysis. About 50 g of each sediment sample was oven dried at 160°C for 48 hours. The dried samples were ground for 20 minutes using automatic agate mortar and pestle grinder. Then, about 5 g of each of the powdered sediment samples were compressed into briquettes using a force of 200 kN for 60s.

2.2.2 XRF Analysis

Selected trace elements (As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, Zr, Th, Sc, TS, F, Br, I and Cl) as well as major elements (TiO_2, Fe_2O_3, MnO, CaO and P_2O_5) concentrations were determined using X-ray fluorescence (XRF) RIX-2000 spectrometer. In line with the method of Ogasawara (1987), all analysis was made on pressed powder briquettes. Relatively, average errors for all elements are less than ± 10%.

2.2.3 Loss on Ignition

The Loss on Ignition (LOI) for the samples was determined by igniting sub-samples using an Isuzu Muffle Furnace at 1,050°C for 4 hours. Net weight loss was used to calculate the gravimetric LOI.

2.2.4 Statistical Analysis

The mean and standard deviation were established using IBM SPSS version 20. The UCC normalized graph and scatter plots were done using KaleidaGraph 4.0 while box plots of element concentration and correlation matrix computed in Microsoft Excel 2013 were used to analyze the inter-element relationship of the elements in the study area.

2.3 Results and Discussion

2.3.1 Mangrove Surface Sediment Characteristics

The surface sediment samples (0 - 2 cm) collected from the New Calabar River at Choba and Ogbogoro and Bonny river at Isaka consisted mainly of soft, blackish, dark brown, silty-clay and sandy sediments. The sandy sediments were observed at sampling points CH5 and OG5 along the New Calabar river and IS1 along the Bonny River. The measured pH and ORP values of surface sediment samples at 25^{o}C yielded (pH: 5.75 to 6.36 for Choba; 5.84 to 6.31 for Ogbogoro and 6.19 to 7.03 for Isaka while ORP was - 285 to - 199 mV for Choba; - 289 to 93 mV for Ogbogoro and - 229 to - 15 mV for Isaka). This indicates that the sediments are slightly acidic and in anoxic condition. The black color and unpleasant smell of the surface sediments are evidence of these conditions (Ahmed *et al.,* 2012).

2.3.2 Concentrations of Elements in the Mangrove Surface Sediments

Trace element compositions of the surface sediments in New Calabar and Bonny rivers sampled at Choba, Ogbogoro and Isaka respectively are presented on Table 2.1 in comparison with the UCC from Taylor and McLennan (1985). These elements had contrasting concentrations at different sampling locations as indicated by the box plot in Figure 2.4.

The average concentrations of the trace elements obtained from the mangrove sediments in Choba showed that the metal concentrations in the surface sediments was in the following order; TS>Zr>V>Cr>F>Zn>Sr>Ni>Pb>I>Br>Nb>Y>Cu>Sc>Th>As. In Ogbogoro, the average concentration trend was TS>Cl>Zr>V>Cr>F>Sr>Zn>Ni>Br>Pb>I>Nb>Y >Sc>Cu>Th>As while the trend in Isaka was TS>Cl>Zr>Cr>F>V>I>Zn>Sr>Br>Ni>Pb>Nb>Cu>Sc>Y>Th>As, respectively. The concentrations of trace elements in the surface sediments were comparatively higher in Choba along the New Kalabar River though Cl was not detected in Choba sediments. The highest mean concentrations of Pb, Zn, Cu, Ni, Cr, Y, Nb, Th and Sc were recorded in Choba. As, V, Sr, Zr, TS and F were more abundant in Ogbogoro along the New Calabar River. However, the highest concentrations of Br, I and Cl were observed on sediments in Isaka along the Bonny River. High concentrations of As, Ni and Cr in Choba, Ogbogoro and Isaka as well as the high concentrations of Pb and V in Choba and Ogbogoro are suggestive of anthropogenically induced huge organic load of the New Calabar and Bonny rivers. Many industries within the catchment of these rivers discharge effluents with little or no treatment (Vincent-Akpu and Yanadi, 2014). Also, the enrichment of Ni and Cr could be indicative that the sediments were derived from ultramafic rocks (Garver *et al.,* 1996; Armstrong-Altrin *et al.,* 2001). The high TS content of the sediments is indicative of the redox conditions (Ishiga and Diallo, 2016). The values of LOI are important for the determination of the organic matter content of sediments and are related to TS values. Choba has the highest mean LOI while Ogbogoro has the lowest mean LOI. The concentrations of the trace elements showed pronounced variations between elements and locations as well as variations in pattern. Compared to the UCC, As and Ni were higher in Choba, Ogbogoro and Isaka. The abundance of Pb was found to be higher in Choba and Ogbogoro. Though Th and Sc were more concentrated in Choba and Ogbogoro relative to the UCC, they were found to be lower in Isaka. However, Zn, Cu and Sr concentrations in the UCC were found to be lower than the mean concentrations of these elements in Choba, Ogbogoro and Isaka mangrove sediments (Table 2.1).

Table 2.1: Trace element geochemical compositions of surface sediments of New Kalabar River at Choba; Ogbogoro and Bonny river at Isaka in Niger Delta, Nigeria.

Area		**Trace Elements (ppm)**																		**wt%**
		As	**Pb**	**Zn**	**Cu**	**Ni**	**Cr**	**V**	**Sr**	**Y**	**Nb**	**Zr**	**Th**	**Sc**	**TS**	**F**	**Br**	**I**	**Cl**	**LOI**
Choba SS (n=5)	Range	3-7	9-45	58-63	7-25	7-65	88-135	4-215	10-85	4-30	4-32	80-354	2-18	4-22	3061-7289	63-114	2-32	8-50	nd	5-14
	Mean	6.0	36.2	65.2	19.6	47.4	121.6	158.4	61.4	21.4	23.0	272.8	13.8	16.8	4912.5	88.5	23.2	24.2		7
	SD	1.7	15.9	5.8	7.2	23.0	19.3	87.1	29.6	10.1	10.9	110.3	6.7	7.3	1754.8	36.1	12.4	15.9		3.8
Ogbogoro SS (n=5)	Range	2-9	6-32	51-60	2-24	9-47	50-132	161-227	58-82	4-24	4-26	157-371	3-17	3-24	485-27450	17-280	3-46	15-41	372-2573	1-6
	Mean	6.4	22.6	55.8	16.0	33.4	108.8	192.3	70.0	17.2	19.0	273.40	12.4	16.2	14627.0	104.8	23.4	22.4	1318.8	4
	SD	2.9	9.9	4.9	8.3	14.5	34.1	34.6	11.8	7.9	8.8	77.4	5.7	7.9	10091.6	111.4	16.0	10.9	922.4	2.1
Isaka SS (n=5)	Range	2-7	6-17	12-49	4-13	13-29	74-148	20-109	10-50	5-13	6-13	174-313	4-9	4-13	3650-16948	49-192	13-47	37-47	2009-7436	3-6
	Mean	4.2	12.2	29.0	9.0	21.4	118.6	59.4	27.6	8.6	10.0	249.6	6.6	8.8	8329.0	104.2	27.4	41.4	4189.6	5
	SD	1.9	4.7	17.4	4.1	8.1	30.3	37.1	17.1	3.6	3.7	49.6	2.1	4.1	5333.5	57.0	13.6	4.7	2186.5	1.5
UCC	Mean	2	20	71	25	20	35	60	350	22	25	190	10.7	11						

nd ---- not detected, SS ---- surface sediments, UCC ---- upper continental crust

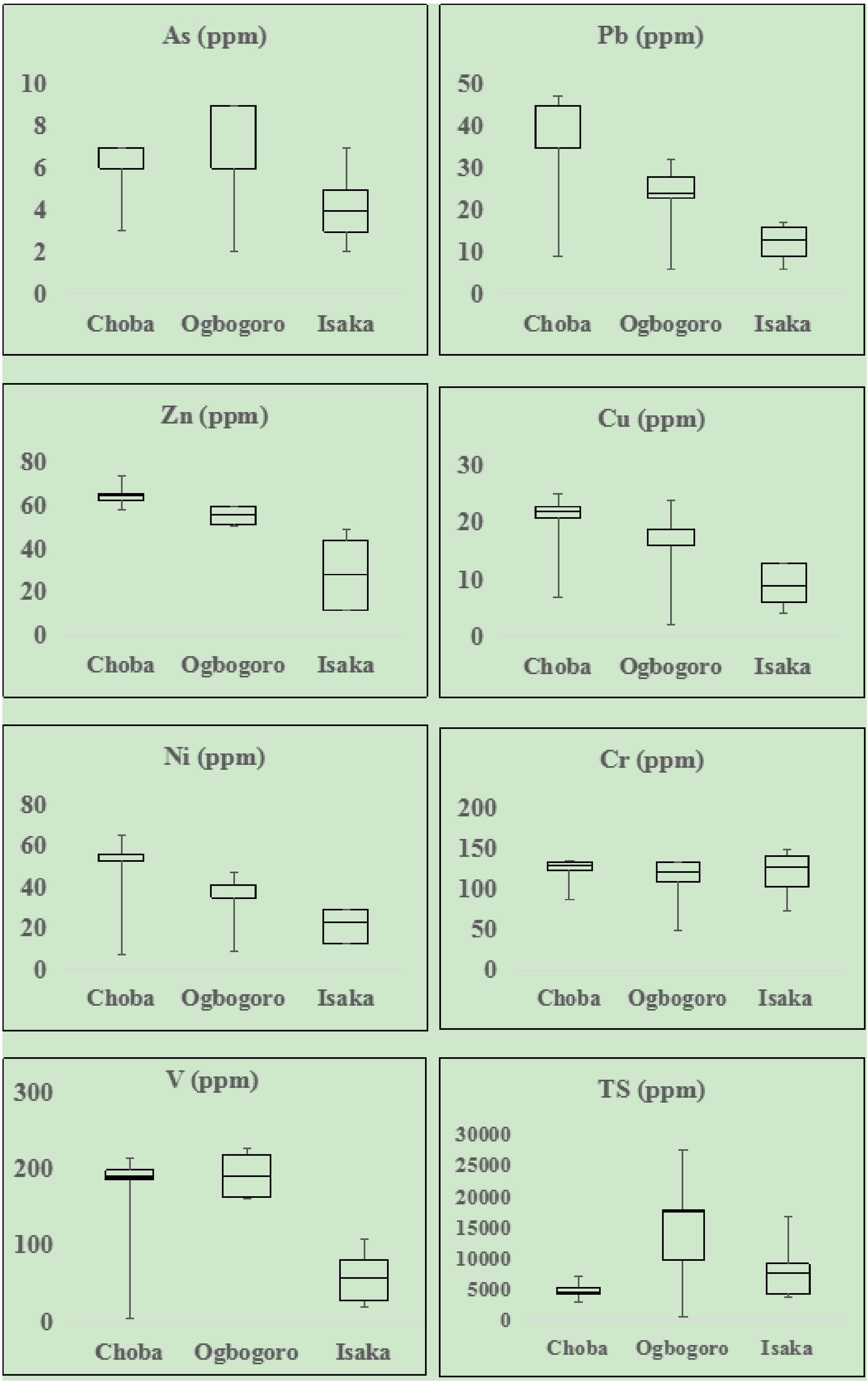

Figure 2.4 Box plot summary of trace metal concentrations in surface sediments in New Kalabar River at Choba; Ogbogoro and Bonny River at Isaka. Vertical lines of the plots indicate the range while boxes enclose 50% of data and illustrates the 25% quartile, median (horizontal bar) and 75% quartile.

Table 2.2 Major element geochemical compositions of surface sediments of New Kalabar River at Choba; Ogbogoro and Bonny River at Isaka in Niger Delta, Nigeria.

Area		Major Elements (wt%)				
		TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
Choba (n=5)	Range	0.05-1.39	0.69-7.47	0.02-0.03	0.49-0.57	0.05-0.14
	Mean	0.80	4.80	0.02	0.51	0.07
	SD	0.45	2.28	0.01	0.55	0.04
Ogbogoro (n=5)	Range	0.08-1.22	6.39-10.12	0.01-0.03	0.41-0.54	0.01-0.06
	Mean	0.80	8.25	0.02	0.50	0.04
	SD	0.45	2.06	0.01	0.55	0.02
Isaka (n=5)	Range	0.28-0.73	0.66-3.84	0.01-0.01	0.46-0.54	0.03-0.06
	Mean	0.60	2.20	0.01	0.49	0.05
	SD	0.55	1.30	0.00	0.20	0.01
UCC	Mean	0.50		0.08	4.20	0.16

Table 2.2 shows that sediments in Choba have the highest concentration of of CaO and P_2O_5 while TiO_2 and MnO have equal mean concentrations in both Choba and Ogbogoro. However, Fe_2O_3 is most abundant in Ogbogoro. Compared to the UCC concentrations, TiO_2 is higher in Choba, Ogbogoro and Isaka while Fe_2O_3 has a higher concentration in Ogbogoro. Average concentrations of MnO, CaO and P_2O_5 in the UCC were found to be higher than concentrations in Choba, Ogbogoro and Isaka sediments (Figure 2.5).

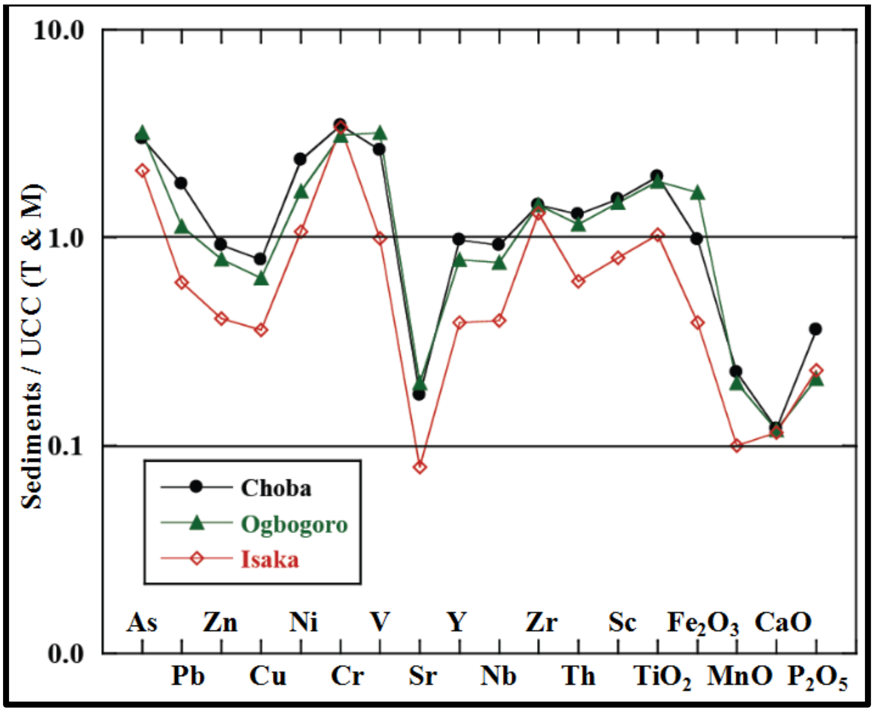

Figure 2.5 Comparison of concentrations of trace and major elements in surface sediments from Choba, Ogbogoro and Isaka. All values were normalized to the UCC values of Taylor and McLennan (1985).

2.3.3 Inter-element Relationships in Mangrove Surface Sediments

Table 2.3 Correlations between elements in mangrove surface sediments in Choba.

	As	Pb	Zn	Cu	Ni	Cr	V	TS	F	Br	I	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
Choba (n = 5)																
As	1															
Pb	0.91	1														
Zn	0.77	0.46	1													
Cu	0.98	0.93	0.73	1												
Ni	0.98	0.88	0.82	0.97	1											
Cr	0.99	0.90	0.78	1.00	0.98	1										
V	0.97	0.94	0.71	1.00	0.98	0.99	1									
TS	0.06	-0.86	0.78	-0.34	0.80	-0.02	-0.33	1								
F	-1	-1	-1	-1	-1	-1	-1	0	1							
Br	0.96	0.88	0.78	0.92	0.97	0.93	0.93	0.72	-1	1						
I	-0.79	-0.93	-0.41	-0.87	-0.82	-0.82	-0.90	0.53	1	-0.76	1					
TiO_2	0.97	0.89	0.81	0.96	1.00	0.97	0.97	0.93	-1	0.99	-0.82	1				
Fe_2O_3	0.87	0.95	0.46	0.94	0.85	0.90	0.94	-0.90	-1	0.77	-0.95	0.83	1			
MnO	0.33	-0.98	0.97	0.10	0.96	0.38	0.10	0.90		0.57	0.62	0.94	-0.70	1		
CaO	-0.90	-0.97	-0.47	-0.95	-0.86	-0.92	-0.95	0.98	1	-0.81	0.92	-0.85	-0.99	0.82	1	
P_2O_5	-0.98	-0.93	-0.74	-0.97	-0.99	-0.97	-0.98	-0.66	1	-0.99	0.85	-0.99	-0.86	-0.58	0.89	1

Table 2.4 Correlations between elements in mangrove surface sediments in Ogbogoro.

	As	Pb	Zn	Cu	Ni	Cr	V	TS	F	Br	I	TiO_2	Fe_2O_3	MnO	CaO	P_2O_5
Ogbogoro (n = 5)																
As	1															
Pb	0.84	1														
Zn	1.00	0.24	1													
Cu	0.93	0.98	0.72	1												
Ni	0.96	0.95	0.90	0.99	1											
Cr	0.95	0.93	0.95	0.98	0.98	1										
V	0.99	0.30	0.99	0.75	0.95	0.90	1									
TS	0.69	0.54	0.07	0.61	0.66	0.77	-0.05	1								
F	0.26	0.41	-0.18	0.40	0.30	0.45	-0.32	0.53	1							
Br	0.87	0.88	0.74	0.91	0.89	0.84	0.77	0.32	0.27	1						
I	-0.88	-0.86	-0.32	-0.89	-0.93	-0.92	-0.42	-0.78	-0.19	-0.67	1					
TiO_2	0.92	0.94	0.97	0.97	0.97	0.99	0.94	0.78	0.44	0.79	-0.95	1				
Fe_2O_3	0.99	0.07	0.97	0.58	0.85	0.87	0.97	0.18	-0.32	0.60	-0.52	0.90	1			
MnO	0.71	-0.50	0.66	0.00	0.43	0.46	0.66	0.55	-0.46	0.03	-0.80	0.50	0.81	1		
CaO	0.75	0.77	-0.25	0.79	0.80	0.88	-0.38	0.94	0.59	0.50	-0.88	0.91	-0.19	0.19	1	
P_2O_5	0.79	0.99	0.00	0.95	0.93	0.90	0.12	0.50	0.30	0.82	-0.88	0.92	-0.11	-0.50	0.75	1

Table 2.5 Correlations between elements in mangrove surface sediments in Isaka.

	As	Pb	Zn	Cu	Ni	Cr	V	TS	F	Br	I	TiO_2	Fe_2O_3	CaO	P_2O_5
Isaka (n = 5)															
As	1														
Pb	0.86	1													
Zn	0.87	0.95	1												
Cu	0.86	0.99	0.98	1											
Ni	0.90	0.97	0.98	0.98	1										
Cr	-0.51	-0.55	-0.43	-0.47	-0.58	1									
V	0.96	0.97	0.93	0.96	0.95	-0.52	1								
TS	0.90	0.61	0.65	0.64	0.65	-0.16	0.79	1							
F	-0.29	-0.15	-0.40	-0.22	-0.37	0.23	-0.16	-0.15	1						
Br	0.97	0.88	0.83	0.85	0.89	-0.68	0.95	0.80	-0.19	1					
I	-0.89	-0.94	-0.93	-0.93	-0.98	0.73	-0.93	-0.60	0.41	-0.92	1				
TiO_2	0.91	0.95	0.99	0.97	0.99	-0.52	0.95	0.69	-0.42	0.88	-0.96	1			
Fe_2O_3	0.98	0.94	0.92	0.94	0.94	-0.49	1.00	0.84	-0.19	0.96	-0.91	0.94	1		
CaO	0.96	0.85	0.83	0.86	0.84	-0.33	0.95	0.93	-0.08	0.91	-0.79	0.85	0.97	1	
P_2O_5	0.81	0.94	0.93	0.96	0.90	-0.23	0.92	0.69	-0.09	0.76	-0.80	0.90	0.91	0.88	1

Tables 2.3, 2.4 and 2.5 show the correlation matrix for elements in the Choba, Ogbogoro and Isaka mangrove sediments, respectively. A strong positive relationship was observed in Choba between the concentrations of Fe_2O_3 and As, Pb, Cu, Ni, Cr, V and TiO_2. Also, TS is strongly related positively with Ni, TiO_2, MnO and CaO. In Ogbogoro, Fe_2O_3 has strong positive relationship with As, Zn, Ni, Cr, V, TiO_2 and MnO while TS and CaO have strong positive relationship. In Isaka, Fe_2O_3 and As, Pb, Zn, Cu, Ni, V, TS, TiO_2, CaO and P_2O_5 have strong positive relationship while TS is strongly and positively related to As, Br, Fe_2O_3 and CaO. The As-Fe_2O_3, Pb-Fe_2O_3, Zn-Fe_2O_3 and Cu-Fe_2O_3 diagrams (Figure 2.6) show the behaviour of element correlations with Fe_2O_3 in the sediment samples.

Relationships among the elements in the study area show that biogenic and provenance metals on the average are strongly and positively correlated with Fe_2O_3. This suggests that Fe_2O_3 may have a great influence on the metal concentrations in the Choba-Ogbogoro-Isaka mangrove sediments. The strong positive correlation matrices of a suite of metals (As, Pb, Cu, Zn, Ni and Cr in Choba; As, Zn, Ni and Cr in Ogbogoro and As, Pb, Zn and Cu in Isaka) with V indicates the possibility of formation of complexes with organic matter (Ahmed *et al.*, 2012). The very strong correlation between Th and Cu suggests the existence of granitic or pegmatitic lithology in the area. The Pb-Ni-Cu association is indicative of the occurrence of sulphide mineralization while the positive Zn-Nb correlation suggests the presence and influence of felsic lithology (Odokuma-Alonge and Adekoya, 2013). Strong negative correlations were observed between F and many elements in Choba. In Ogbogoro, I had a varying negative correlation with all the elements while Cr, F and I also had varying negative correlations with the elements analyzed in Isaka. Therefore, it might be that Cr, F and I have a different source.

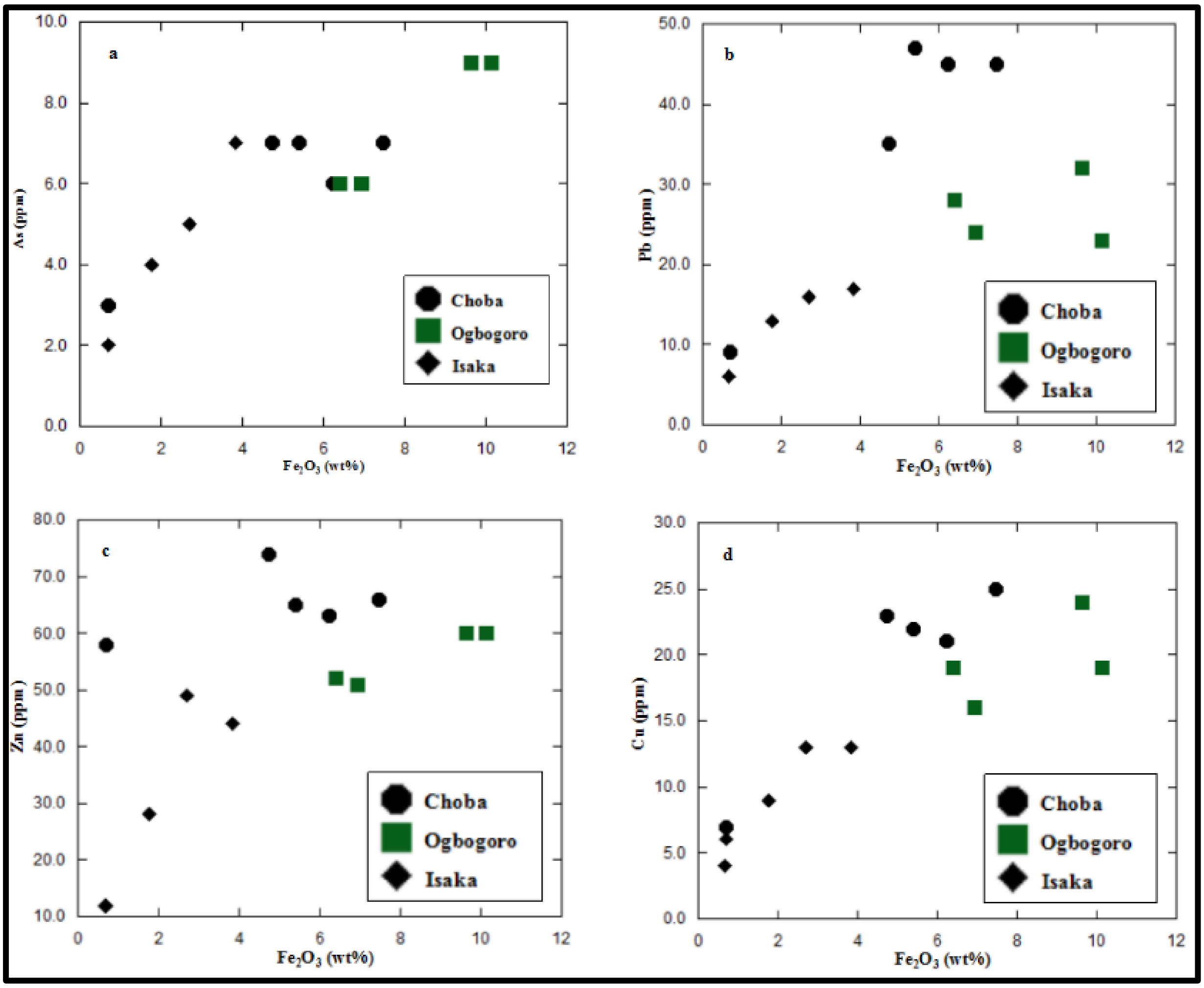

Figure 2.6 **a-d**. Correlations between Fe_2O_3 and As, Pb, Zn and Cu in Choba, Ogbogoro and Isaka.

2.3.4 Comparison of Metal Concentrations in Mangrove Surface Sediments with Sediment Quality Guidelines (SQGs)

Through natural processes or anthropogenic activities, chemical substances are released into the environment which may later enter the aquatic ecosystems. These substances may be deposited into the bed sediments where the contaminants may accumulate over time (CCME 1998). In order to assess the toxicity level of the present metal concentrations in Choba, Ogbogoro and Isaka along the New Calabar and Bonny Rivers, respectively; the concentrations of As, Pb, Zn, Cu, Ni and Cr were compared with the sediment quality guidelines developed by New York State Department of Environmental Conservation (NYSDEC, 1999) and Canadian Council of Ministers of the Environment (CCME, 1998).

Table 2.6 Sediment quality criteria and metal concentrations (ppm) in Choba, Ogbogoro and Isaka mangrove surface sediments

Metals	LEL[1]	SEL[2]	IQSG[3]	PEL[4]	CHO	OGB	ISA
As	6	33	7	42	6	6	4
Pb	31	110	30	112	36	23	12
Zn	120	270	124	271	65	56	29
Cu	16	110	19	108	20	16	9
Ni	16	50	na	na	47	33	21
Cr	26	110	52	160	122	109	119

CHO (Choba), OGB (Ogbogoro), ISA (Isaka) and na (not available)

[1] Lowest effect level (LEL;NYSDEC,1999)

[2] Severe effect level (SEL;NYSDEC,1999)

[3] Threshold effect level (TEL) or Interim sediment quality guideline (ISQG; SAIC, 1998)

[4] Probable effect level (PEL; SAIC, 1998)

na ---- not available

The mean concentrations of As in the surface sediments in Isaka is lower than LEL while Choba and Ogbogoro values are the same with LEL and slightly lower ISQG benchmarks. This suggests no adverse effect on biota. In Choba, Pb (36) is higher than both LEL and ISQG but lower than SEL and PEL. This implies that Pb concentrations in Choba is significantly enriched and might impact moderately on the health of biota. However, concentrations of Pb in Ogbogoro and Isaka are lower than LEL and ISQG, thus an indication of no adverse impact on these locations. Zn concentrations in Choba, Ogbogoro and Isaka are all below the LEL and

ISQG. This implies no adverse effect on the health of biota. The concentrations of Cu in Choba are higher relative to LEL and ISQG values. This indicates that Cu concentration in Choba may moderately impact on biota health. However, Cu concentrations in Ogbogoro and Isaka are both below the values of LEL and ISQG. Thus it has no adverse effect on biota. The concentration of Ni in all the sampled locations is higher than the LEL value but lower than SEL value. This indicated that Ni might be enriched in the area and thus may moderately impact on biota health. The Cr concentrations in Choba (122), Ogbogoro (109) and Isaka (119) exceeded the Cr values of LEL (26), ISQG (52) and SEL (110) but below PEL (160). This indicates that Cr might be greatly enriched in Choba, Ogbogoro and Isaka. Therefore, the concentrations of Cr could have adverse effect on the mangrove flora and fauna in area.

2.3.5 Comparison of Metal Concentrations in Parts of Niger Delta as well as Niger Delta Mangrove Sediments with Concentrations in Mangrove Sediments in other Countries.

The biogenic metal concentration values in sediments from different parts of Niger Delta based on previous studies were compared to the concentration values of the biogenic metals obtained in this study and presented in Table 2.7. It was found that Zn, Cu and Ni were highest in Calabar River sediments (184, 64 and 67) and lowest in Isaka (29, 9 and 21), respectively. Pb was most concentrated in Okirika Island (42) and least in Isaka (12). The highest concentration of Cr was in Choba (122) while the lowest was in Okirika Island (21).

However, the biogenic metal concentrations in mangrove sediments of Niger Delta, Nigeria were compared with the biogenic metal concentrations in mangrove sediments in Japan, Tanzania and Sri Lanka as shown in Table 2.8. As was found to be most concentrated in Japan (13.8) and least concentrated in Sri Lanka (5.4). Pb, Zn and Cu were most concentrated in

Tanzania (44.5, 162.3, 51.0) and least concentrated in Japan (13.3, 49.5, 14.5), respectively. Ni and Cr had highest concentrations in Nigeria (34.1, 116.3) while Japan had the least concentrations (12.8, 59.5), respectively. However, Sri Lanka had the highest concentration of V (197.0) while the least concentration of 91.3 was in Japan.

Table 2.7 Comparison of Biogenic Metal Concentrations in Choba, Ogbogoro and Isaka Mangrove Sediments with Concentrations in other parts of Niger Delta

Location	As	Zn	Pb	Cu	Cr	Ni	Source
Calabar River	-	184	20	64	65	67	Ntekim *et al.*, 1993.
Cross River Estuary	-	53	25	28	39	39	Ntekim *et al.*, 1993.
Okirika Island	-	-	42	26	21	34	Erakhrumen, 2015.
Choba	6	65	36	19	122	47	This Study
Ogbogoro	6.4	55	23	16	109	33	This Study
Isaka	4.2	29	12	9	119	21	This Study

*Values in ppm

Table 2.8 Biogenic Metal Concentrations in Mangrove Sediments in Nigeria, Japan, Tanzania and Sri Lanka

	As	Pb	Zn	Cu	Ni	Cr	V	Sources
Nigeria	5.5	23.7	50.0	14.9	34.1	116.3	136.7	This study
Japan	13.8	13.3	49.5	14.5	12.8	59.5	91.3	Ishiga & Diallo, 2016.
Tanzania	7.0	44.5	162.3	51.0	25.5	105.5	128.4	Ishiga *et al.*, 2016.
Sri Lanka	5.4	20.6	86.9	33.5	18.3	93.1	197.0	Adikaram *et al.*, 2016.

*Values in ppm

2.4 Conclusion

In this study, the results show that the highest mean concentrations (ppm) of Pb (36.20), Zn (65.20), Cu (19.60), Ni (47.40), Cr (121.60), Y (21.40), Nb (23.00), Th (13.80), and Sc (16.80) were recorded in Choba. As (6.40), V (192.25), Sr (70.00), Zr (273.40), TS (14627.00) and F (104.80) were found to be most abundant in Ogbogoro while Br (27.40), I (41.40) and Cl

(4189.60) were most concentrated in Isaka. Most of the trace elements correlated positively and strongly with Fe_2O_3. This implies that Fe_2O_3 is important in controlling metal concentrations in the area. The concentrations of As and Zn were either equal to or below the LEL and ISQG. Pb, Cu and Ni were found to be higher than LEL and ISQG in Choba while Cr concentrations in Choba, Ogbogoro and Isaka all exceeded the LEL, ISQG and SEL values but below PEL value; thus indicating potentials for moderate to severe ecological harm.

CHAPTER THREE

Geochemical Assessment of Mangrove Core Sediments

3.1 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 (Pekey, 2006; Nemati *et al.*, 2011). Generally, mangrove sediments are fluvial in nature and accumulate 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 (Soares *et al.,* 1999; Wan *et al.,* 2012), atmospheric deposition (Machado *et al.*, 2016) as well as tidal inflow (Tam and Wong, 2000). Depending on the concentration level in mangrove environment, heavy metals may have adverse effect directly on the mangrove flora and fauna and indirectly on human.

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 sinks for heavy metals (Arnason and Fletcher, 2003) and thus contain useful records of the current and background levels of contamination which might be natural or anthropogenic (Al-Mur *et al.*, 2017). Researchers on heavy metals in Niger Delta have focused mainly on heavy metals in surface sediments and water (Chindah *et al.,* 2009; Ephraim and Ajayi, 2014; Vincent-Akpu and Yanadi, 2014; Onojake *et al.,* 2015; Vincent-Akpu *et al.,* 2015; Wala *et al.*, 2016; Bubu *et al.,* 2018; Nwawuike and Ishiga, 2018). Thus, there is dearth of studies on the cross sectional geochemical variations in Niger Delta mangrove sediments. Mangroves are well known depositional sites because its stems and complex root systems facilitate sedimentation. The high sedimentation rate associated with the mangrove environment might continuously alter its geochemical characteristics annually (Liu *et al.,* 2011). 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.

3.2 Materials and Methods

3.2.1 Mangrove 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°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 5cm 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 3.1). 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 Earth Science 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.

Table 3.1 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

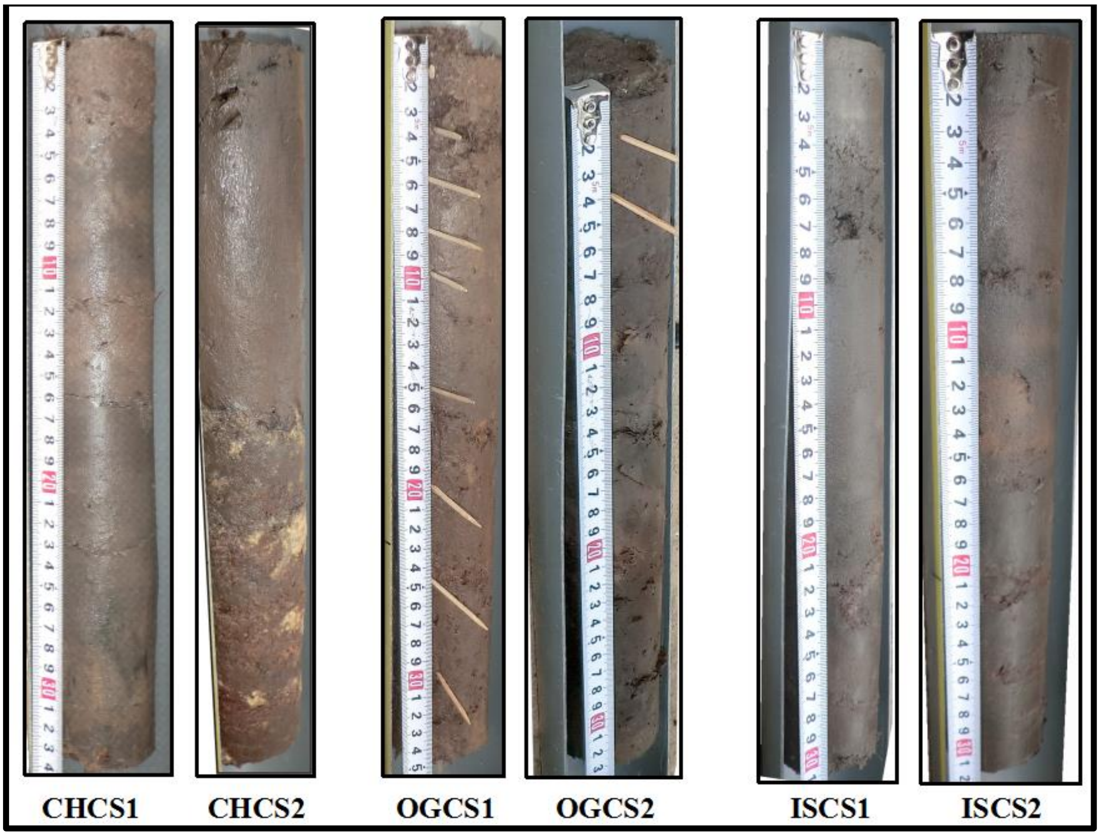

Figure 3.1 Mangrove Core Sediment Samples from Choba, Ogbogoro and Isaka.

3.2.2 XRF Analysis

Eleven trace elements; As, Pb, Zn, Cu, Ni, Cr, V, Sr, Nb, Th and TS as well as five major elements; TiO_2, Fe_2O_3, MnO, CaO and P_2O_5 were analyzed using X-ray fluorescence (XRF) RIX-200 spectrometer. In consistence with Ogasawara (1987), all the XRF analysis were made from pressed powder briquettes with average errors being less than ± 10 %.

3.2.3 ^{14}C Analysis

Macrofossil 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.

3.2.4 Statistical Analysis

The mean concentrations 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 KaleidaGraph 4.0.

3.2.5 Geostatistical Methods

3.2.5.1 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. Thomilson *et al.,* (1980) expressed contamination factor 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 Taylor and McLennan (1985) was used as the background metal concentration. The CF is interpreted as follows: CF < 1: signifies low contamination; $1 \leq CF < 3$: signifies moderate contamination; $3 = CF \leq 6$: signifies considerable contamination and $CF \geq 6$: signifies very high contamination.

3.2.5.2 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 (Seshan *et al.,* 2010) as well as Li, Sc, Ti and Zr (Reimann and DeCaritat, 2000). 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 anthropogenic sources are small compared to natural sources (Helz, 1976). Also, Fe is a conservative tracer that could differentiate natural from anthropogenic components (Goher *et al.,* 2014). 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 Taylor and McLennan (1985) was used as background concentration. The enrichment factor interpretation was based on Sutherland (2000) 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.

3.2.5.3 Pollution Load Index (PLI)

To determine the pollution load of heavy metal concentrations at different depths in the core sediments samples, the pollution load index was applied. According to Tomlinson *et al.,* (1980), pollution load index is given as:

$PLI = \sqrt[n]{CF_1 \times CF_2 .... \times CF_n}$

Where:

n is the number of metals and CF is the contamination factor.

PLI value < 1 is unpolluted, PLI = 1 indicates metal load that approximates to the background concentrations while PLI > 1 is polluted (Caberera *et al.,* 1999).

3.2.5.4 Geo-accumulation (Igeo)

The geo-accumulation index proposed by Muller (1969) was used to also determine the extent of metal contamination in the Niger Delta mangrove core sediments. The Igeo is given as:

$Igeo = \log_2[(C_{metal}/1.5C_{metal(background)})]$

Where:

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

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

The upper continental crust proposed by Taylor and McLennan (1985) was used as the background metal concentration. To offset the lithogenic effect, 1.5 is used as the compensating factor of the background data. The interpretation of the geo-accumulation index in line with Muller, (1981): $Igeo < 0$ is class 0 (uncontaminated/unpolluted), $0 \leq Igeo < 1$ is class 1 (unpolluted to moderately polluted), 1 ≤ Igeo < 2 is class 2 (moderately polluted), 2 ≤ Igeo < 3 is class 3 (moderately to highly polluted), 3 ≤ Igeo < 4 is class 4 (highly polluted), 4 ≤ Igeo < 5 is class of 5 (highly to extremely polluted) and Igeo ≥ 5 is class of 6 (extremely polluted).

3.3 Results and Discussion

3.3.1 Mangrove Core 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. The sediments had unpleasant smell. Ahmed *et al.* (2012) suggest that the black color and unpleasant smell of sediments are indications of anoxic condition.

3.3.2 Element-Depth Concentration Assessment of Mangrove Core Sediments (EDCA)

The elemental concentrations relative to depth of the mangrove core sediments in Choba, Ogbogoro and Isaka as well as their average concentrations are shown in Table 3.2. Trace and major element concentrations were compared to the upper continental crust (UCC) values by Taylor and McLennan (1985).

3.3.2.1 EDCA in Choba

The elemental concentrations in the two core samples (CHCS1 and CHCS2) from Choba indicated varying concentration of elements 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 major elements 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.

3.3.2.2 EDCA in 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 and major elements 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.

3.3.2.3 EDCA in 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 and major 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 major elements 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 4-6cm 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.

Table 3.2 Depth-Concentration of Elements 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	0-2	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	0-2	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	0-2	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	0-2	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	0-2	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

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 Taylor and McLennan (1985), 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 Figures 3.1 and 3.2 while Figure 3.3 showed metal concentrations normalized to the UCC.

Source rock composition strongly controls sediment composition (Johnson, 1993). 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 (Garver *et al.*, 1996; Roser *et al.*, 1996; Ishiga *et al.*, 1999; Armstrong-Altrin *et al.*, 2001). 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 (Ahmed *et al.*, 2009) or anthropogenically induced (Nwawuike and Ishiga, 2018). Liu *et al* (2011) 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 (Lee and Cundy, 2001; Soto-Jimenez and Paez-Osuna, 2001).

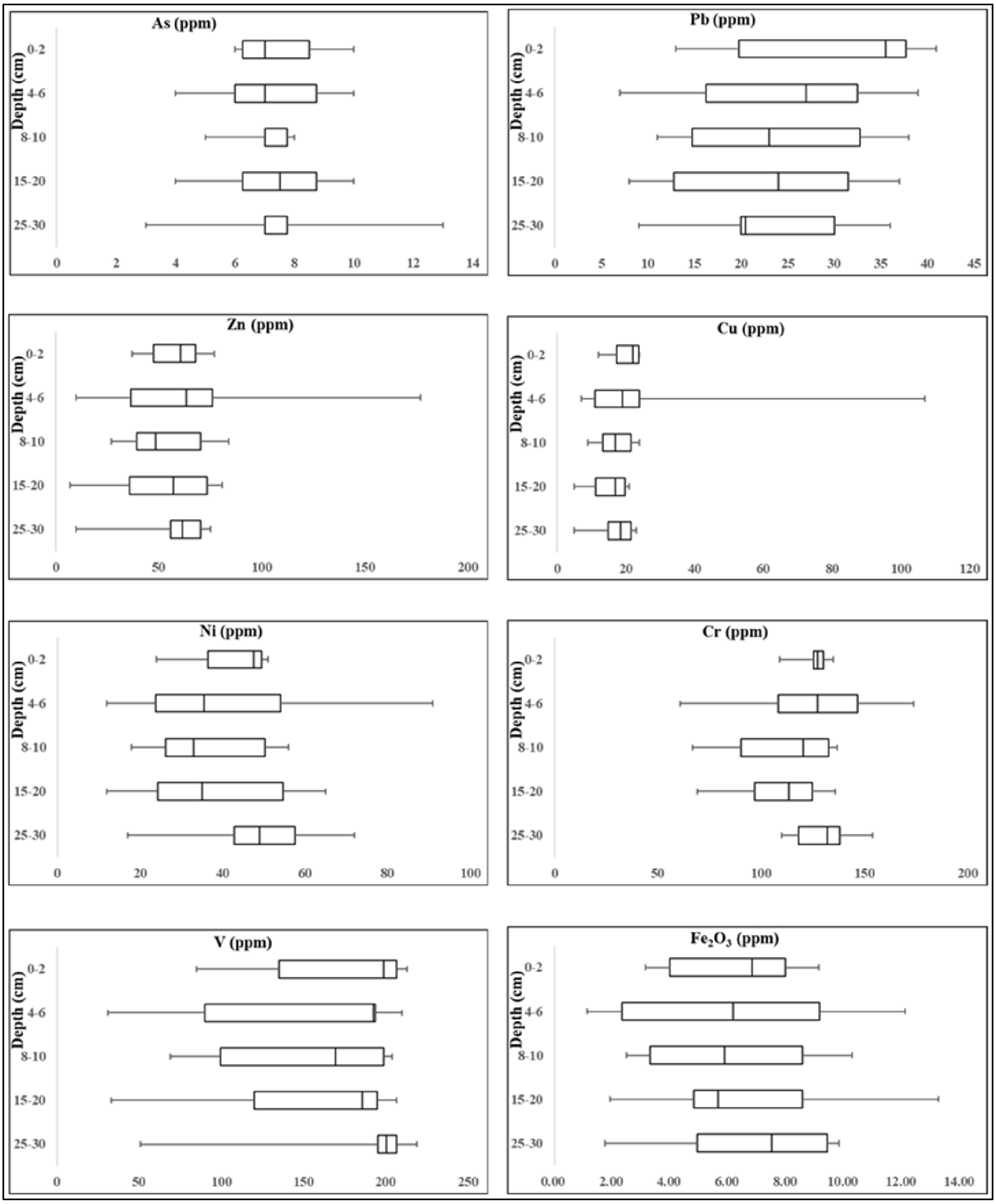

Figure 3.2 Box plot showing metal concentrations at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka.

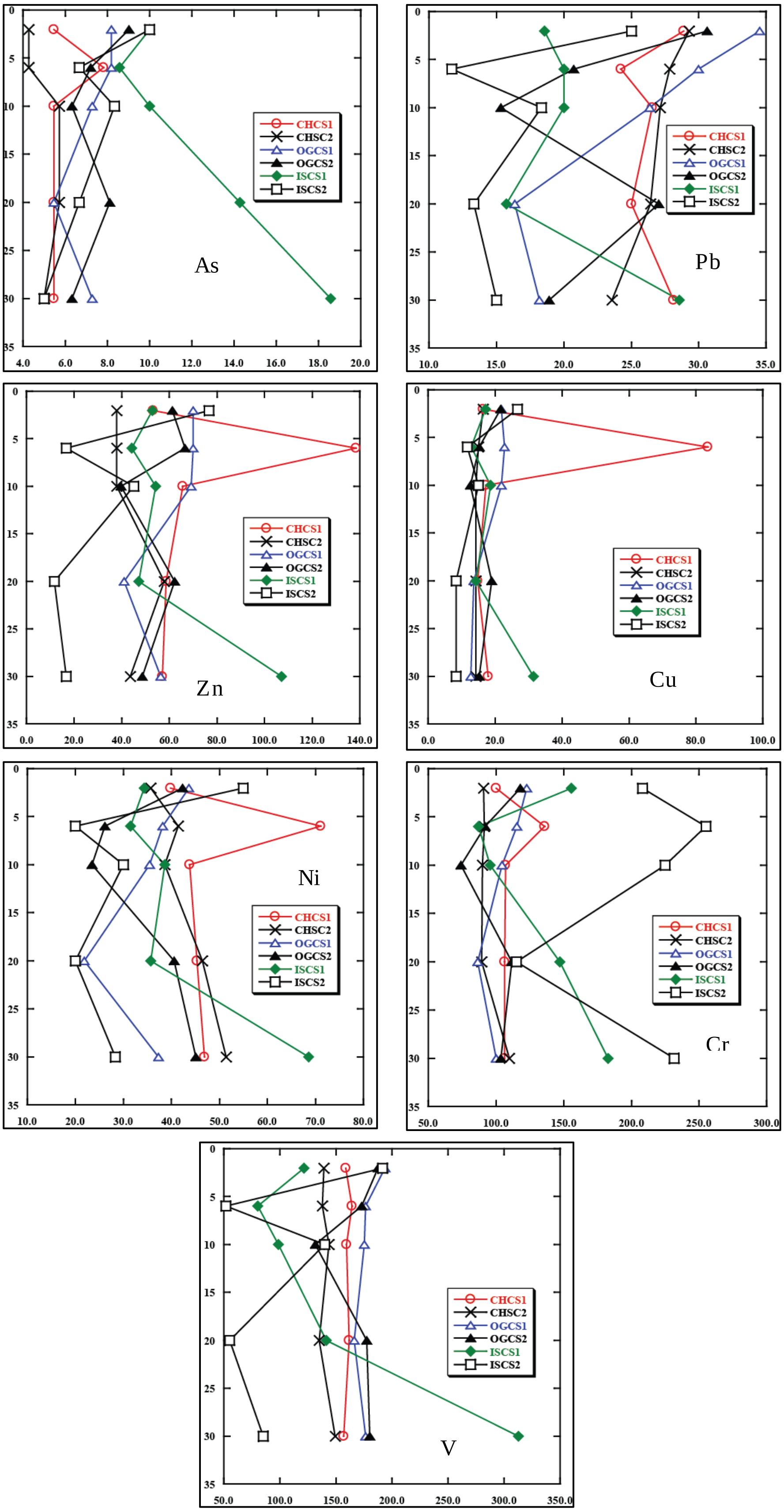

Figure 3.3 TiO_2 normalized cross sectional profile of biogenic concentrations with depth in mangrove core sediments in Choba, Ogbogoro and Isaka.

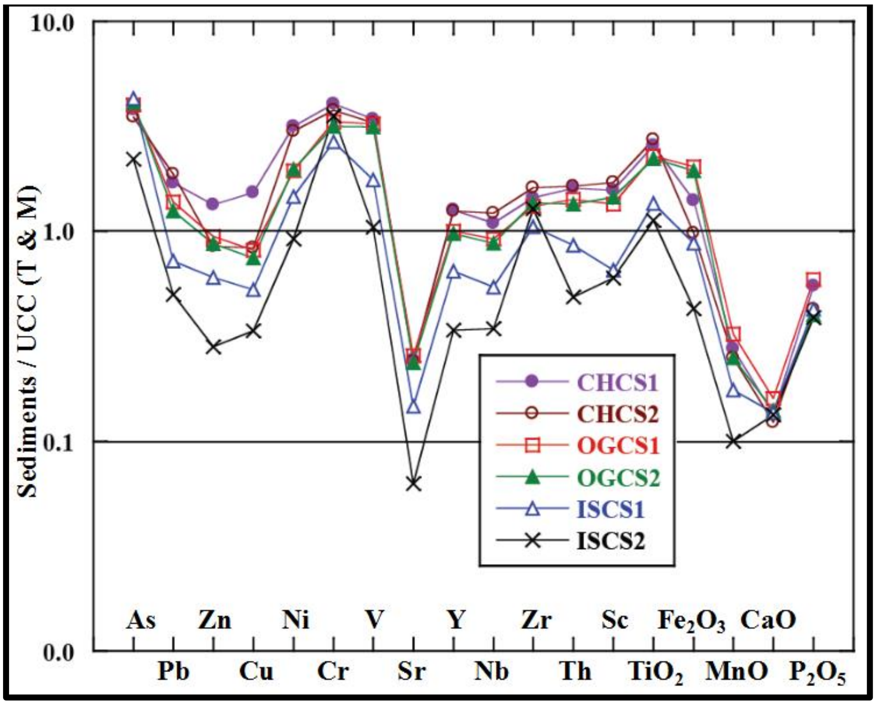

Figure 3.4 Comparison of trace and major element concentrations in the mangrove core sediments (30 cm) from Choba, Ogbogoro and Isaka. All values were normalized to the UCC of Taylor and McLennan, 1985.

3.3.3 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.

Table 3.3 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

Results of the ^{14}C in Isaka (ISCS1) presented in Table 3.3 above indicate that the wood macrofossil 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 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 macrofossil 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. The radiocarbon plot for ISC1 and OGC2 are shown in figures 3.5 and 3.6.

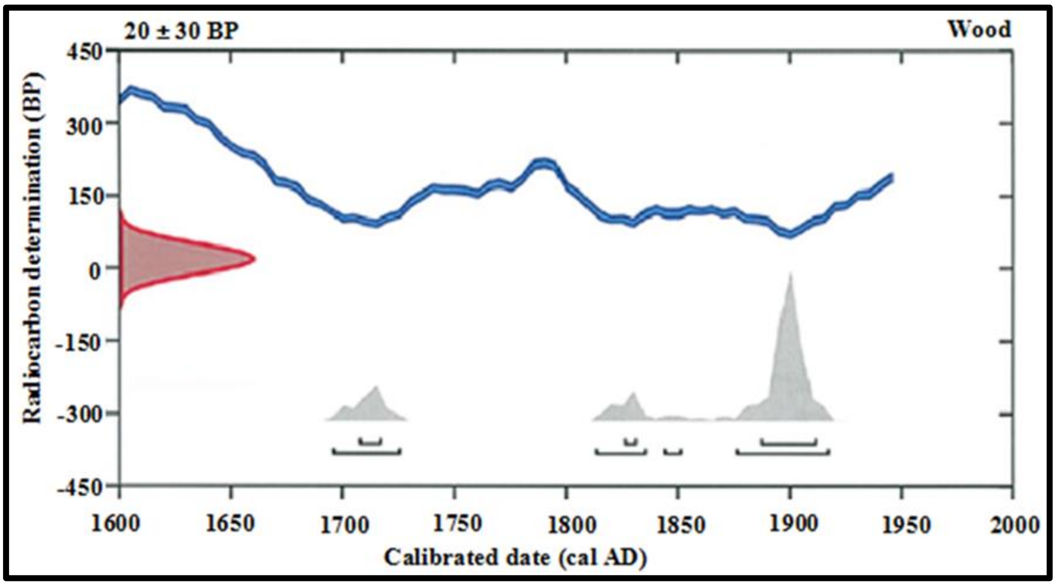

Figure 3.5 Radiocarbon plot of wood macro fossil in ISC1

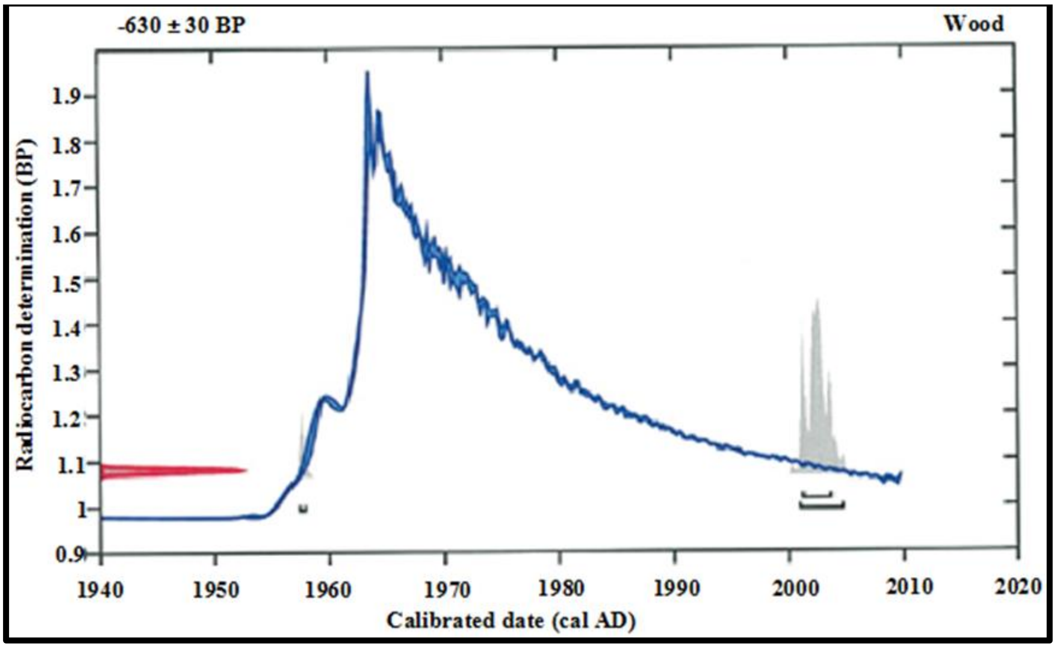

Figure 3.6 Radiocarbon plot of wood macro fossil in OGC2

Wood fossils may not be of the same age compared to the surrounding sediments (Hervé *et al.*, 2007). However, depending on the residence time of the fossil within the environment, it sometimes exceed the age of the deposits (Ely *et al.*, 1992). 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.

3.3.4 Inter-element Relationships in Mangrove Core Sediments

The correlation matrix for the average metal concentrations in the core sediments in Choba, Ogbogoro and Isaka is presented in Tables 3.4 to 3.6. Ishiga *et al.* (1999) and (Roser, 2000) 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 (Skilbeck and Cawood, 1994). Elements that show strong correlations with TiO_2 should only reflect natural detrital inputs because in sediments, 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 (Dalai and Ishiga, 2013). 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 (Odokuma-Alonge and Adekoya, 2013). Also, Pb-Zn-Cu-Ni-Cr suits in Isaka implies that these metals have a common source and similar enrichment process (Dialo and

Ishiga, 2016). 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 (Tolonen and Merilainen, 1983). Kauppila *et al* (2005) 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.

Table 3.4 Correlation matrix of elements in mangrove core sediments in Choba

	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

Table 3.5 Correlation matrix of elements in mangrove core sediments in Ogbogoro

	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

Table 3.6 Correlation matrix of elements in mangrove core sediments in Isaka

	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

3.3.5 Ecological Risk Assessment of Mangrove Core Sediments

3.3.5.1 Contamination Factor (CF)

The contamination factor of the biogenic elements in the sub core sediments in Choba, Ogbogoro and Isaka is shown in Table 3.7. The interpretation was based on Thomilson *et al* (1980). The CF of As in the core samples range 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. Pb is moderately contaminated in Choba and Ogbogoro with CF average 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 are 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 CuCF 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 NiCF 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

VCF 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 3.7 CF of metals at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka.

Location	Depth (cm)	Elements						
		AsCF	PbCF	ZnCF	CuCF	NiCF	CrCF	VCF
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

3.3.5.2 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 3.8. 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.

Zhang and Liu (2002) reported that EF values between 0.5 and 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 its 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; anthropogenic in the upper core but geogenic in the lower core in Isaka. 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.

Table 3.8 EF of metals at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka.

Location	Depth (cm)	Elements						
		AsEF	PbEF	ZnEF	CuEF	NiEF	CrEF	VEF
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.

3.3.5.3 Pollution Load Index (PLI)

The pollution load index of biogenic metals in the sub core mangrove sediments in Choba, Ogbogoro and Isaka are shown in Table 3.9. The PLI assessment was based on Cabrera *et al.* (1999) which states that PLI < 1 is unpolluted, PLI = 1 indicates metal load that approximates to the background concentrations while PLI > 1 is polluted. Given that the analysed mangrove core sediments at different depths in Choba and Ogbogoro all have PLI above 1, it implies that the sediments are polluted. In Isaka, the PLI at depths of 0 - 2, 8 - 10 and 25 - 30 cm are above 1 and as such, polluted. However, at depths of 4 - 6 and 15 - 20 cm, the PLI is below 1 and thus unpolluted.

Table 3.9 PLI at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka.

Location	Depth (cm)	PLI of Core Sediments	Status
Choba	0 - 2	2.04	Polluted
	4 - 6	2.86	Polluted
	8 - 10	2.12	Polluted
	15 - 20	2.15	Polluted
	25 - 30	2.17	Polluted
Ogbogoro	0 - 2	2.22	Polluted
	4 - 6	1.93	Polluted
	8 - 10	1.67	Polluted
	15 - 20	1.72	Polluted
	25 - 30	1.73	Polluted
Isaka	0 - 2	1.29	Polluted
	4 - 6	0.81	Unpolluted
	8 - 10	1.07	Polluted
	15 - 20	0.86	Unpolluted
	25 - 30	1.45	Polluted

3.3.5.4 Geo-accumulation Index (Igeo)

Table 3.10 presents the geo-accumulation of the mangrove core sediments at different depths. It was found that in Choba, Ogbogoro and Isaka, As had Igeo values greater than 1 with the exception of 4 - 6 cm (0.74) depth in Isaka. This implies that As is moderately polluted. The Igeo of Pb in Choba is less than 1 across depths and connotes the class of 1 (unpolluted to moderately polluted). However in Ogbogoro and Isaka, Pb has an Igeo of less than 0 with exception of 0 - 2 cm (0.26) in Ogbogoro. Thus, Pb is unpolluted in Ogbogoro and Isaka. With the exception of 4 - 6 cm (0.11, 0.77) Zn and Cu, respectively; Igeo values were below 0 and thus unpolluted. At depths of 0 - 2 cm (0.75) and 8 - 10 (0.87) in Choba, Ni was unpolluted. But at depths of 4 - 6, 15 - 20 and 25 - 30 cm, Ni was moderately polluted. In Ogbogoro, Ni had Igeo values of less than 1 across depths and thus in class 1 (unpolluted to moderately polluted). This is similar with the depth of 25 - 30 cm (0.12) in Isaka. However, at depths of 0 - 2 up to 15 - 20 cm in Isaka, Ni Igeo values were below 0 and as such, unpolluted. In Choba, Cr and V had Igeo values in class of 2 and so are moderately polluted at other depths with Igeo above 1. In Isaka, Cr is moderately polluted at depths of 0 - 2, 4 - 6 and 25 - 30 cm but unpolluted to moderately polluted at depths 8 - 10 and 15 - 20 cm. However, V was unpolluted to moderately polluted at depths 0 - 2 and 25 - 30 cm while its in the class of 0 at depths of 4 - 6, 8 - 10 and 15 - 20 cm.

Table 3.10 Igeo at different depths in mangrove core sediments in Choba, Ogbogoro and Isaka.

Location	Depth (cm)	Igeo						
		As	Pb	Zn	Cu	Ni	Cr	V
Choba	0 - 2	1.12	0.39	-0.82	-0.77	0.75	1.28	1.14
	4 - 6	1.41	0.22	0.11	0.77	1.31	1.52	1.16
	8 - 10	1.32	0.26	-0.64	-0.84	0.87	1.32	1.17
	15 - 20	1.32	0.20	-0.45	-0.94	1.04	1.31	1.14
	25 - 30	1.22	0.20	-0.67	-0.80	1.14	1.47	1.19
Ogbogoro	0 - 2	1.66	0.26	-0.56	-0.64	0.66	1.34	1.23
	4 - 6	1.50	-0.10	-0.50	-0.84	0.24	1.12	1.10
	8 - 10	1.32	-0.38	-0.83	-0.98	0.12	0.91	0.91
	15 - 20	1.32	-0.32	-0.90	-1.06	0.20	1.06	1.08
	25 - 30	1.32	-0.55	-0.88	-1.28	0.60	1.09	1.13
Isaka	0 - 2	1.12	-1.10	-1.36	-1.42	-0.07	1.16	0.15
	4 - 6	0.74	- 1.51	-2.38	-2.23	-0.82	1.03	-1.05
	8 - 10	1.00	-1.27	-1.71	-1.77	-0.42	0.94	-0.23
	15 - 20	1.22	-1.66	-2.42	-2.32	-0.70	0.71	-0.45
	25 - 30	1.41	-1.05	-1.33	-1.47	0.12	1.35	0.58

3.3.6 Cross Sectional Assessment of Core Sediment Pollution Based on Sediment Quality Guidelines

Primarily, the objectives of sediment quality guidelines (SQGs) is the protection of aquatic biota from the harmful and toxic effects related to sediment bound contaminants (Spencer and Macleod, 2002). Therefore, SQGs are vital instrument employed to determine potential contaminant levels within sediments that are capable of biological effect.

Table 3.11 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	39.0	60.5	22.0	50.5	127.5
	4 - 6	8.0	35.0	115.0	64.0	74.5	151.0
	8 - 10	7.5	36.0	68.5	21.0	55.0	131.5
	15 - 20	7.5	34.5	78.0	19.5	61.5	130.5
	25 - 30	7.0	34.5	67.0	21.5	66.0	145.0
Ogbogoro	0 - 2	9.5	36.0	72.5	240	47.5	133.0
	4 - 6	8.5	28.0	75.5	21.0	35.5	114.5
	8 - 10	7.5	23.0	60.0	19.0	32.5	98.5
	15 - 20	7.5	24.0	57.0	18.0	34.5	109.5
	25 - 30	7.5	20.5	58.0	15.5	45.5	112.5
Isaka	0 - 2	6.5	14.0	41.5	14.0	28.5	117.0
	4 - 6	5.0	10.5	20.5	8.0	17.0	107.0
	8 - 10	6.0	12.5	32.5	11.0	22.5	101.0
	15 - 20	7.0	9.5	20.0	7.5	18.5	86.0
	25 - 30	8.0	14.5	42.5	13.5	32.5	133.5
LEL		6.0	31.0	120.0	16.0	16.0	26.0
SEL		33.0	110.0	270.0	110.0	50.0	110.0
ISQG		7.0	30.0	124.0	19.0	na	52.0
PEL		42.0	112.0	271.0	108.0	na	160.0

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 (NYSDEC, 1999) and Canadian Council of Ministers of the Environment (CCME, 1998). 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 3.9). 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 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. Thus, the concentrations of Ni and Cr could impact severely on the flora and fauna in the area.

3.4 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 or 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. The assessment of the pollution load indicated that the core sediments are polluted across depths and locations. Similarly, the Igeo of As and Cr informed that they are moderately polluted across depths and locations. Ni and V are moderately polluted in Choba and Ogbogoro but are unpolluted in Isaka. Also, the Igeo of Pb, Zn and Cu are in the class of 0 and thus, unpolluted. 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.

CHAPTER FOUR

Heavy Metal Concentrations in Mangrove Sediments and Distribution in *Rhizophora racemosa*

4.1 Introduction

Mangroves are unique floral assemblage found in the inter-tidal zones of tropical and sub-tropical regions of the world. They are mostly shrubs that grow in the marine or estuarine environments and thus are halophytic. As an adaptive strategy, the mangroves have complex root system that enable them cope with saline water and wave action. Mangroves function as a significant sink for clastics, CO_2, detritus as well as anthropogenic pollutants. It stabilizes shorelines by trapping sediments, contributes to climate protection by sequestrating carbon and also provides valuable breeding ground for fish and other organisms that inhabit the ecoregion.

Niger Delta mangrove forest is the largest concentration of mangroves in Africa. It has an estimated size of about 7,386 km^2 (UNEP, 2007). This huge wetland area was formed due to sediment deposition by the River Niger and located between longitudes 5^oE to 8^oE and latitudes 4^oN to 6^oN (Opafunso, 2007; Dada *et al.,* 2015). According to (UNEP, 2007), the Niger Delta mangroves provide breeding ground for over 60% of the fishes caught between the Gulf of Guinea and Angola.

Despite its importance, mangroves are degraded due to natural and anthropogenic pollution from urban and industrial waste, leaching from bedrocks and soils (Soares *et al.,* 1999), atmospheric deposition (Machado *et al.,* 2016) and tidal inflow (Tam and Wong, 2000). Although mangroves are referred to as sink for pollutants, changing physio-chemical conditions within the ecosystem could turn them into pollution sources (Harbinson, 1986).

Hence the need to investigate the heavy metal concentration in mangrove sediment and *R. racemosa* in Niger Delta mangroves. Specifically, this study seeks to: (a) determine the concentration of trace and major elements in Niger Delta mangrove sediments, (b) determine the concentration of trace and major elements in *R. racemosa* roots, stems and leaves and (c) determine if the *R. racemosa* in different locations within Niger Delta mangroves have the same heavy metal uptake pattern.

4.2 Materials and Methods

4.2.1 Study Species

R. racemosa also known as red mangroves is the mangrove species used for this study. It belongs to the family of Rhizophoraceae. This species is limited to the Atlantic East Pacific (AEP) with largest concentration on the Atlantic coast of West Africa (Lo *et al.*, 2014). In Niger Delta, the *R. racemosa* is locally called Angala or Ngala. It is the most predominant species and consists of about 90% of the mangrove forest (Chima and Larinde, 2016; Jackson and Lewis, 2000). *R. racemosa* is a pioneer species with numerous aerial stilt roots and can grow to a height of 45 m (Abere and Ekeke, 2011). The locals mostly exploit it for firewood and timber.

Figure 4.1 *Rhizophora racemosa* at the bank of New Kalabar River at Choba, Niger Delta.

Figure 4.2 *Rhizophora racemosa* at the bank of New Kalabar River at Ogbogoro, Niger Delta.

Figure 4.3 *Rhizophora racemosa* at the bank of Bonny River at Isaka, Niger Delta.

4.2.2 Mangrove Core Sediment Collection and Preparation

Sediment core samples of 10 cm depth were collected from Choba, Ogbogoro and Isaka. Two core samples were collected from each location (n = 2). Thus, a total of 6 core sediment samples were collected. The cores were taken using a transparent 2-inch diameter PVC pipe. Prior to coring, the PVC pipes were decontaminated using ethanol. The cores were manually driven into the muddy mangrove sediments and carefully retrieved. Homogenization of the retrieved core sediment samples was done after which they were placed in ziplock bags, labeled and transported out and stored at 4^{o}C. The samples were air dried for 48 hours to reduce weight before repackaging and putting them in plastic box for export to the Earth Science Laboratory, Shimane University, Japan.

About 30 g each of the sediment samples were put in decontaminated beakers and covered with aluminum foil and using the ISUZU Muffle Furnace, they were oven dried at 160°C for 48 hours. Sediment grinding was done using the Automatic Agate Mortar and Pestle for 20 minutes. The powdered sediments were made into briquettes by compressing about 5 g each using 200 kN for 60 seconds.

4.2.3 *R. racemosa* Sample Collection and Preparation

The *R. racemosa* samples were equally collected from Choba, Ogbogoro and Isaka. The stilt aerial roots, stems and leaves of three *R. racemosa* plants were sampled in each location ($n = 3$). Thus, a total of nine *R. racemosa* samples were collected. The samples were cut into smaller sizes and placed in plastic ziplock bags and labeled. The samples were immediately taken to the Nigerian Stored Products Research Institute (NSPRI) Port-Harcourt where they were dried at 80°C for 24 hours. Then, they were repackaged and carefully arranged in plastic boxes, sealed and exported to the Earth Science Laboratory, Shimane University, Japan.

About 20 g of the root, stem and leaf samples each was put in decontaminated beakers, covered with aluminum foil and using the ISUZU Muffle Furnace, they were oven dried at 110°C for 24 hours and later at 160°C for 48 hours. They were ground using the Automatic Agate Mortar and Pestle for 20 minutes. Also, the powdered *R. racemosa* samples were made into briquettes by compressing about 5 g each using 200 kN for 60 seconds.

4.2.4 XRF Analysis

Thirteen trace elements; As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, Zr, Cl and TS as well as four major elements; TiO_2, MnO, CaO and P_2O_5 were analyzed for both sediment and *R. racemosa* samples using X-ray fluorescence (XRF) RIX-200 spectrometer. In accordance with (Ogasawara, 1987), all the XRF analysis were made from pressed powder briquettes with average errors being less than ± 10 %.

4.2.5 Statistical Analysis

The mean concentrations of the trace and major elements in sediment and *R. racemosa* samples were done using Microsoft Excel 2013. The KaleidaGraph 4.0 was used to plot the concentration graphs for trace and major elements in the sediments and *R. racemosa* roots, stems and leaves.

4.2.6 Biological Methods

4.2.6.1 Bio-Concentration Factor (BCF)

To determine the extent of heavy metal concentrations on the roots of the *R. racemosa* plant samples from the Niger Delta mangroves, the bio-concentration factor was employed. According to Yoon *et al* (2006), bio-concentration factor is expressed thus:

$BCF = R_{mc} / S_{mc}$

Where:

R_{mc} is the root metal concentration and

S_{mc} is the soil metal concentration.

Bio-Concentration Factor greater than (>) 1 is an indication of hyperaccumulation (Cluis, 2004).

4.2.6.2 Bio-Accumulation Factor (BAF)

The estimation of the extent to which *R. racemosa* shoots (leaves and stems) bio-accumulate metals in the Niger Delta mangroves was done using the bio-accumulation factor. In line with Yanqun *et al* (2005), bio-accumulation factor is given as:

$BAF_{leaf} = L_{mc} / S_{mc}$

$BAF_{stem} = St_{mc} / S_{mc}$

Where:

L_{mc} and St_{mc} are metal concentrations in leaves and stems respectively and

S_{mc} is the soil metal concentration.

4.2.6.3 Bio-Translocation Factor (BTF)

The rate at which metals concentrated on the Niger Delta R. racemosa roots was transferred to the leaves and stems was calculated using the bio-translocation factor. Also, according to Yanqun *et al* (2005), bio-translocation factor is expressed as:

$BTF_{leaf} = L_{mc} / R_{mc}$

$BTF_{stem} = St_{mc} / R_{mc}$

Where:

L_{mc} and St_{mc} are metal concentrations in leaves and stems respectively and

R_{mc} is the root metal concentration.

Bio-translocation factor greater than (>) 1 indicates effective translocation (Baker and Brooks, 1989; Rezvani and Zaefarian, 2011; Fitz and Wenzel, 2002).

4.3 Results

4.3.1 Concentration of Heavy Metals in Sediments

The mean concentration and standard deviations of trace elements and major elements in the mangrove core sediments in Choba, Ogbogoro and Isaka are presented in Table 4.1 For the sediment characteristics, see (Nwawuike and Ishiga, 2018a; Nwawuike and Ishiga, 2018b). Choba sediments have higher concentrations of elements compared to Ogbogoro and Isaka sediments. The highest concentrations of Zr, V, Cr, Zn, Ni, Pb, Cu, Nb and Y were all recorded in Choba sediments. Though Cl and TS were most concentrated in Isaka, however, Isaka sediments are the least contaminated of the three locations sampled. TiO_2 concentrated more in Choba sediments, CaO and P_2O_5 were more concentrated in Ogbogoro sediments while MnO is equally concentrated Choba and Ogbogoro sediments. Interestingly, similar heavy metal concentration pattern was observed in the sampled sediments. The sequence of elemental concentration in Choba is Zr>V>Cr>Sr>Zn>Ni>Pb>Cu>Nb>Y>As; Zr>V>Cr>Sr>Zn>Ni>Pb>Nb>Y>Cu>As in Ogbogoro and Zr>Cr>V>Sr>Zn>Ni>Pb>Cu>Nb>Y>As in Isaka. The major elements have same concentration sequence in all the locations; TiO_2>CaO>P_2O_5>MnO. Figure 4.4 shows the graphical representation of the heavy metal concentration sequence in the study area.

Table 4.1 Concentration of trace and major elements in Niger Delta mangrove sediments in Choba, Ogbogoro and Isaka.

Trace Elements	Choba	Ogbogoro	Isaka
As	7.33 ± 1.51	8.50 ± 1.05	5.83 ± 1.17
Pb	36.67 ± 3.61	29.00 ± 7.77	12.33 ± 2.94
Zn	81.33 ± 48.47	69.33 ± 12.86	31.50 ± 12.37
Cu	35.67 ± 34.96	21.33 ± 4.63	11.00 ± 3.29
Ni	60.00 ± 15.48	38.50 ± 9.18	22.67 ± 7.26
Cr	136.67 ± 18.72	115.33 ± 20.28	108.33 ± 37.24
V	201.00 ± 6.23	191.00 ± 23.71	73.33 ± 28.63
Sr	82.17 ± 3.31	86.33 ± 8.26	32.67 ± 12.75
Y	27.17 ± 1.47	22.17 ± 1.94	9.83 ± 2.79
Nb	28.17 ± 2.14	23.33 ± 3.20	10.00 ± 2.37
Zr	285.67 ± 19.69	272.50 ± 21.68	238.17 ± 42.23
Major Elements			
TiO_2	1.29 ± 0.08	1.12 ± 0.12	0.59 ± 0.19
MnO	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
CaO	0.54 ± 0.03	0.62 ± 0.04	0.58 ± 0.04
P_2O_5	0.08 ± 0.01	0.09 ± 0.03	0.08 ± 0.03

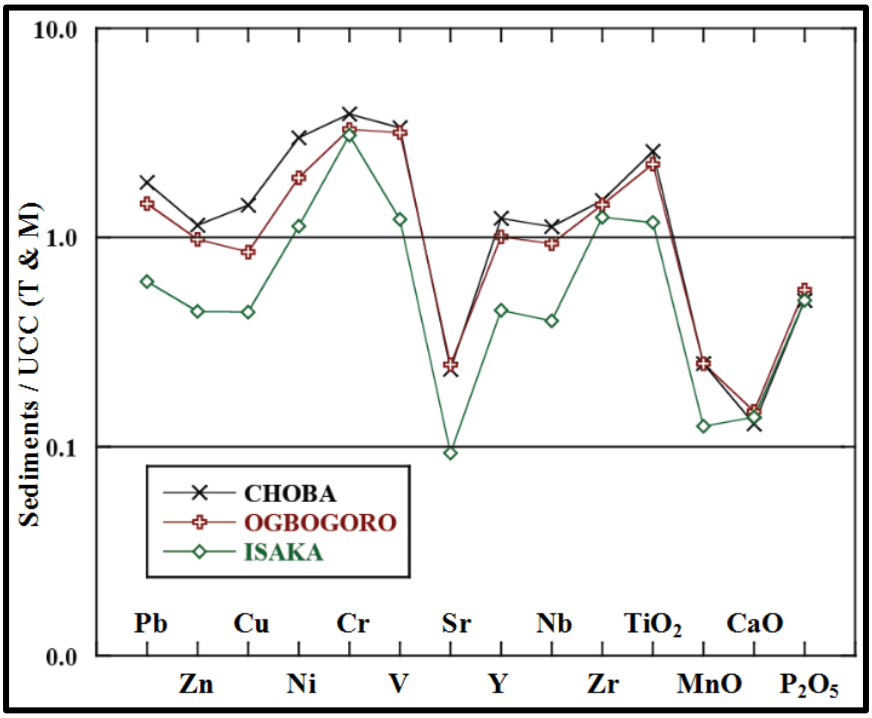

Figure 4.4 Pattern of heavy metal concentrations in core sediments (10 cm) from Choba, Ogbogoro and Isaka mangrove sediments normalized to the UCC values of (Taylor and McLennan, 1985).

4.3.2 Heavy Metals Distribution in *R. racemosa*

Table 4.2 shows the heavy metal concentrations in the leaves, stems and roots of *R. racemosa* samples from Choba, Ogbogoro and Isaka mangroves. Among the eleven trace elements and four major elements tested for, Cr, V and TiO_2 were not detected.

4.3.2.1 Heavy Metals Distribution in *R. racemosa* in Choba

The *R. racemosa* leaves, stems and roots sampled at Choba mangroves along the banks of the New Kalabar River showed varied concentrations of both trace and major elements. As (2.2, 1.0) and Pb (8.6, 5.0) had highest concentrations in the roots and least concentrations in the leaves. Zn (170.2, 47.1) and Ni (24.7, 15.0) concentrated most in the stems but least in the leaves. The highest and least concentrations of Cu (7.0, 3.1) and P_2O_5 (0.7, 0.4) were found in the leaves and roots respectively while Cl (63973.3, 11590.0) an TS (14779.7, 3501.0) were most concentrated in the leaves and least in the stems. Sr (102.0, 53.2), Zr (27.7, 22.2), MnO (0.2, 0.1) and CaO (2.7, 1.8) were found to concentrate mostly in the stems and minimally in the roots while Y (3.5, 2.5) and Nb (2.5, 1.9) concentrated more in the roots and least in the stems.

4.3.2.2 Heavy Metals Distribution in *R. racemosa* in Ogbogoro

The trace and major elements concentrations in *R. racemosa* leaves, stems and roots sampled in Ogbogoro mangroves also along the banks of the New Kalabar River showed different concentrations. As (2.0, 1.0), Pb (7.7, 5.4), Zn (151.8, 41.8) and Nb (2.2, 1.9) were concentrated most in the roots and least in the leaves. The concentrations of Cu (3.2, 1.0) and Ni (23.0, 12.9) were highest in the stems and lowest in the leaves. Sr (171.5, 69.2), Zr (39.6, 23.5), CaO (4.5, 2.1) and P_2O_5 (0.6, 0.4) had most concentrations in the leaves and least concentrations in the roots while Cl (56087.0, 10943.0) an TS (16430.3, 3233.3) were most concentrated in the leaves and least in the stems. Y (3.0, 2.4) was found to be most concentrated in the roots and least concentrated in the stems while MnO (0.1, 0.0) had the highest and lowest concentrations in the stems and roots respectively.

4.3.2.3 Heavy Metals Distribution in *R. racemosa* in Isaka

The trace and major elements concentrations in *R. racemosa* leaves, stems and roots sampled in Isaka mangroves along the banks of the Bonny River indicated variations in concentration. As (1.5, 1.0), Zn (187.5, 30.8), Ni (18.0, 4.0) and Nb (2.0, 1.7) had the highest concentrations in the roots and lowest in the leaves. The concentrations of Pb (6.8, 4.2) and Cu (3.8, 2.5) were most in the stems and least in the leaves. Sr (283.1, 149.4), Zr (53.0, 36.0), CaO (6.9, 3.6) were found to have the most concentrations in both stems and least concentrations in the roots. The concentration of Y (2.6, 2.4) and Cl (77597.5, 17386.3) were highest in the leaves and lowest in the stems while TS (13239.3, 3382.3), MnO (0.2, 0.1) and P_2O_5 (0.6, 0.3) were highest in the leaves and lowest in the roots.

Generally, it is interesting to note that *R. racemosa* sampled in Choba, Ogbogoro and Isaka mangroves were found to have similar heavy metal uptake and concentration pattern in their leaves, stems and roots. However, the leaf / stem and leaf / root upward transport relationship showed some variations. These are shown in Figures 4.5 to 4.9.

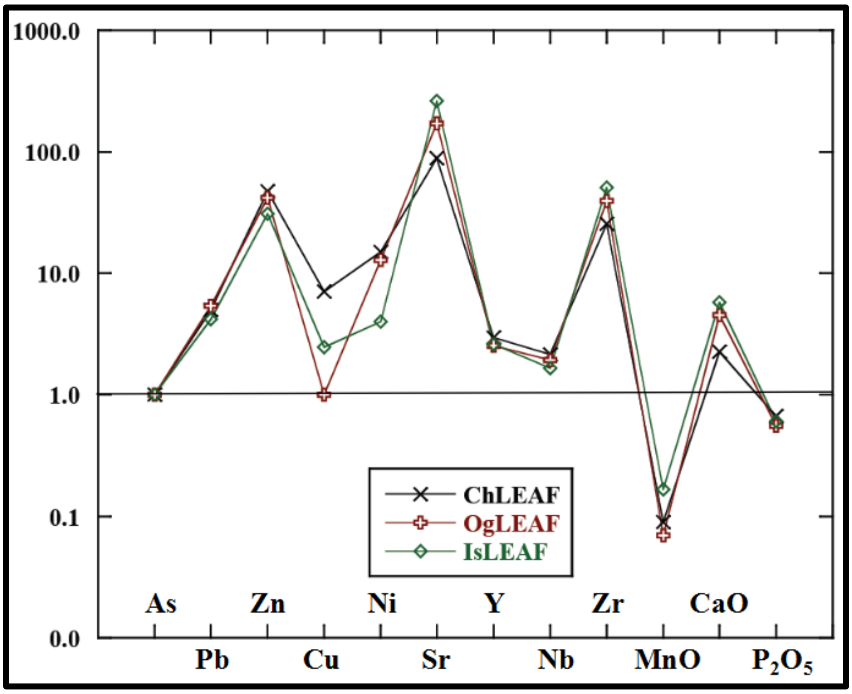

Figure 4.5 Concentration pattern of Heavy metals in *R. racemosa* leaves in Choba, Ogbogoro and Isaka (Ch --- Choba, Og --- Ogbogoro, Is --- Isaka).

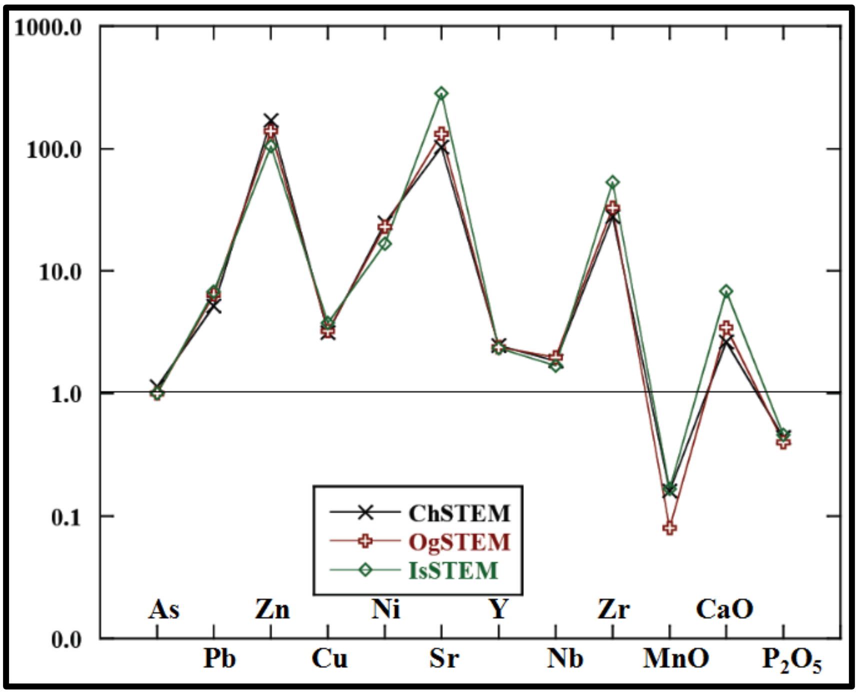

Figure 4.6 Concentration pattern of Heavy metals in *R. racemosa* stems in Choba, Ogbogoro and Isaka (Ch --- Choba, Og --- Ogbogoro, Is --- Isaka).

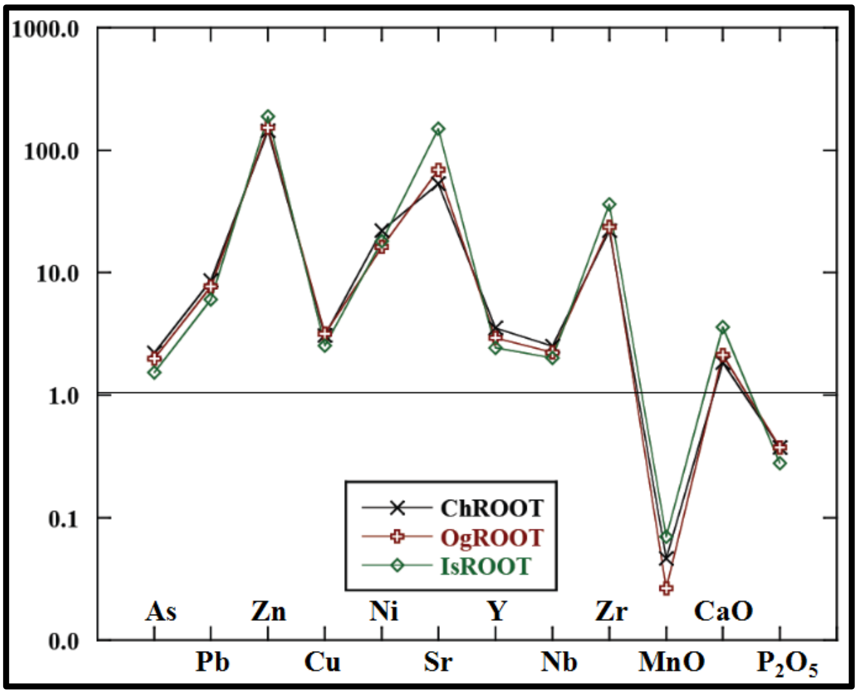

Figure 4.7 Concentration pattern of Heavy metals in *R. racemosa* roots in Choba, Ogbogoro and Isaka (Ch --- Choba, Og --- Ogbogoro, Is --- Isaka).

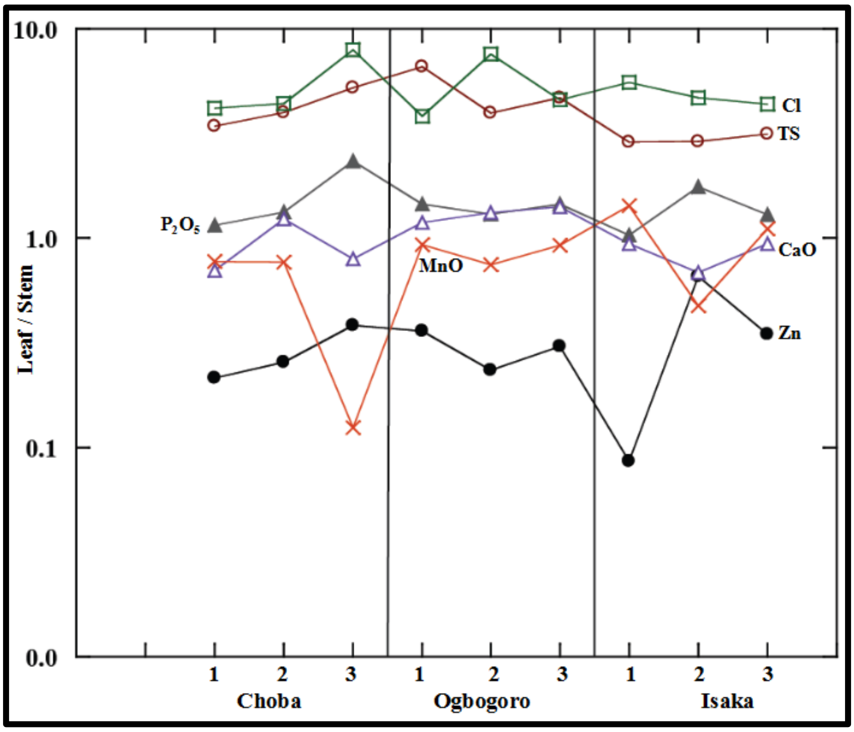

Figure 4.8 Leaf/Stem trace metals and major elements concentration in Choba, Ogbogoro and Isaka.

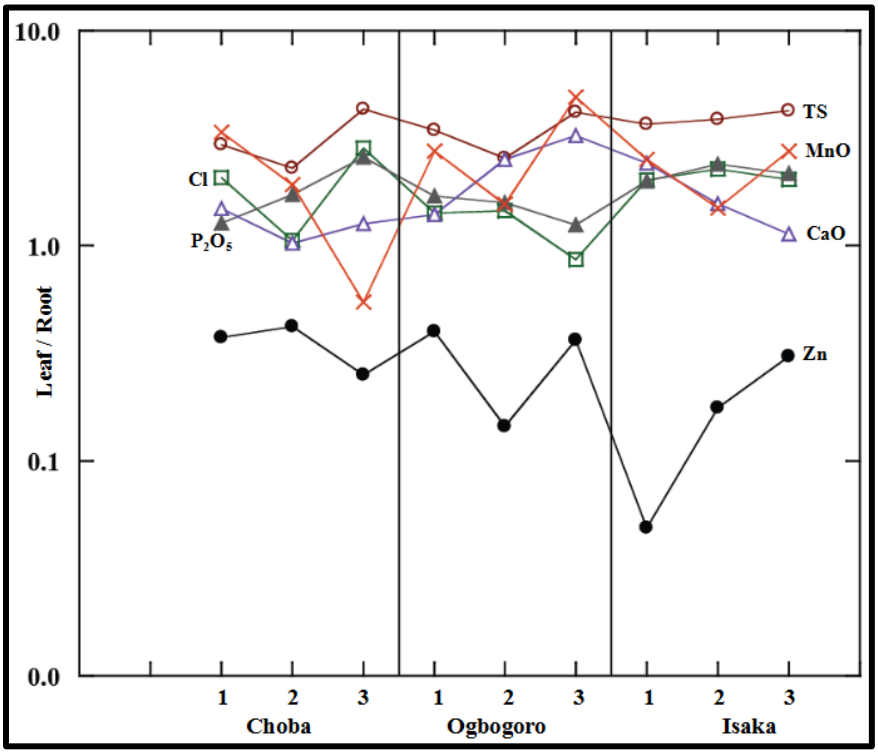

Figure 4.9 Leaf/Root trace metals and major elements concentration in Choba, Ogbogoro and Isaka.

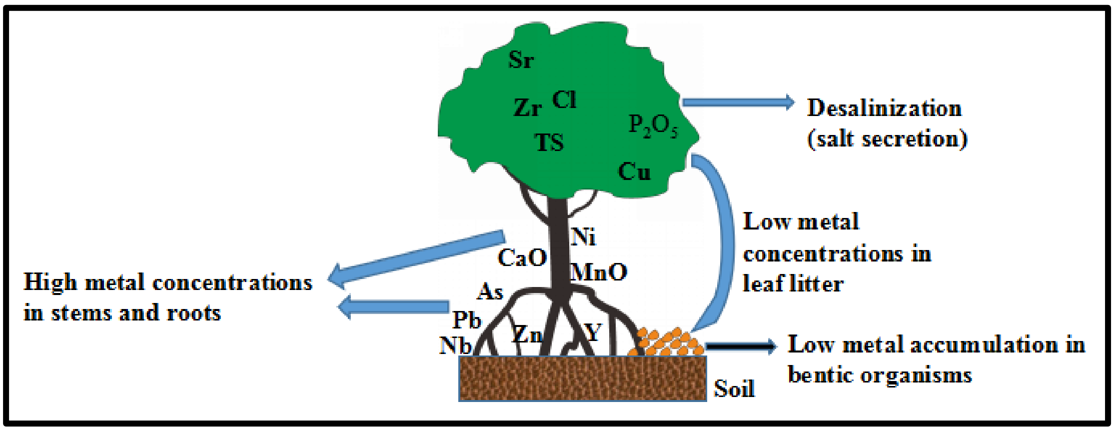

Figure 4.10 Schematics of metals distribution in *R. racemosa* in the mangroves of Niger Delta.

Table 4.2 Concentration of trace and major elements in Niger Delta mangrove *R. racemosa* in Choba, Ogbogoro and Isaka.

Trace Elements	Sample	Choba	Ogbogoro	Isaka
As	Leaves	1.00 ± 0.00	1.00 ± 0.00	1.00 ± 0.00
	Stems	1.14 ± 0.41	1.00 ± 0.00	1.00 ± 0.00
	Roots	2.20 ± 1.32	2.00 ± 0.00	1.54 ± 0.08
Pb	Leaves	4.98 ± 0.60	5.36 ± 0.45	4.19 ± 1.15
	Stems	5.18 ± 0.46	6.39 ± 0.52	6.80 ± 1.29
	Roots	8.62 ± 1.40	7.69 ± 1.22	6.04 ± 2.78
Zn	Leaves	47.13 ± 11.35	41.81 ± 11.71	30.80 ± 19.31
	Stems	170.15 ± 42.25	138.29 ± 10.27	104.65 ± 48.02
	Roots	143.10 ± 57.96	151.84 ± 47.71	187.45 ± 27.84
Cu	Leaves	7.04 ± 0.00	1.00 ± 0.00	2.46 ± 1.17
	Stems	3.14 ± 2.41	3.23 ± 2.16	3.78 ± 2.04
	Roots	3.08 ± 0.47	3.15 ± 1.23	2.53 ± 1.33
Ni	Leaves	14.95 ± 6.06	12.86 ± 1.90	3.99 ± 3.43
	Stems	24.70 ± 1.33	22.97 ± 1.70	16.75 ± 1.48
	Roots	22.08 ± 2.23	16.15 ± 2.36	17.98 ± 2.70
Cr	Leaves	nd	nd	nd
	Stems	nd	nd	nd
	Roots	nd	nd	nd
V	Leaves	nd	nd	nd
	Stems	nd	nd	nd
	Roots	nd	nd	nd
Sr	Leaves	88.61± 27.40	171.54 ± 11.11	261.52 ± 60.33
	Stems	102.00 ± 38.72	131.77 ± 14.30	283.10 ± 79.04
	Roots	53.24 ± 36.61	69.17 ± 38.04	149.39 ± 44.16
Y	Leaves	2.98 ± 0.15	2.53 ± 0.12	2.60 ± 0.11
	Stems	2.47 ± 0.03	2.38 ± 0.04	2.35 ± 0.08
	Roots	3.52 ± 0.20	2.93 ± 0.13	2.45 ± 0.17
Nb	Leaves	2.16 ± 0.14	1.93 ± 0.07	1.65 0.02
	Stems	1.85 ± 0.07	1.97 ± 0.07	1.69 ± 018
	Roots	2.52 ± 0.14	2.24 ± 0.12	2.01 ± 0.20
Zr	Leaves	25.39 ± 4.85	39.59 ± 1.29	50.65 ± 6.40
	Stems	27.73 ± 7.36	32.85 ± 2.30	52.95 ± 8.58
	Roots	22.19 ± 6.27	23.51 ± 7.64	35.97 ± 6.37
Major Elements	Sample	Choba	Ogbogoro	Isaka
TiO_2	Leaves	nd	nd	nd
	Stems	nd	nd	nd
	Roots	nd	nd	nd
MnO	Leaves	0.09 ± 0.07	0.07 ± 0.00	0.17 ± 0.08
	Stems	0.16 ± 0.05	0.08 ± 0.02	0.17 ± 0.03
	Roots	0.05 ± 0.03	0.03 ± 0.02	0.07 ± 0.02
CaO	Leaves	2.27 ± 0.11	4.52 ± 0.40	5.77 ± 0.82
	Stems	2.65 ± 0.77	3.47 ± 0.41	6.86 ± 1.40
	Roots	1.84 ± 0.34	2.14 ± 1.01	3.59 ± 0.85
P_2O_5	Leaves	0.67 ± 0.17	0.56 ± 0.06	0.61 ± 0.07
	Stems	0.44 ± 0.08	0.40 ± 0.07	0.46 ± 0.07
	Roots	0.37 ± 0.08	0.37 ± 0.07	0.28 ± 0.02

4.3.3 Comparison between Heavy Metal Concentrations in Sediments and *R. racemosa*

The comparison of the sediment heavy metal concentration mean values in Table 4.1 and *R. racemosa* heavy metal concentration mean values in Table 4.2 showed variations in concentration. It was found that As, Pb, Cu, Ni, Y, Nb and Zr concentrations were higher in the sediments while Zn, Sr, Cl, TS, MnO, CaO and P_2O_5 had higher concentrations in *R. racemosa* relative to the sediments. However, Cr, V and TiO_2 were not detected in *R. racemosa* despite having sediment concentration values of 136.67, 201 and 1.29 ppm respectively. The graphical comparison of heavy metal concentrations in sediments to concentrations in *R.racemosa* leaves, stems and roots for the sampled locations are shown in figures 4.10, 4.11 and 4.12 for Choba, Ogbogoro and Isaka respectively.

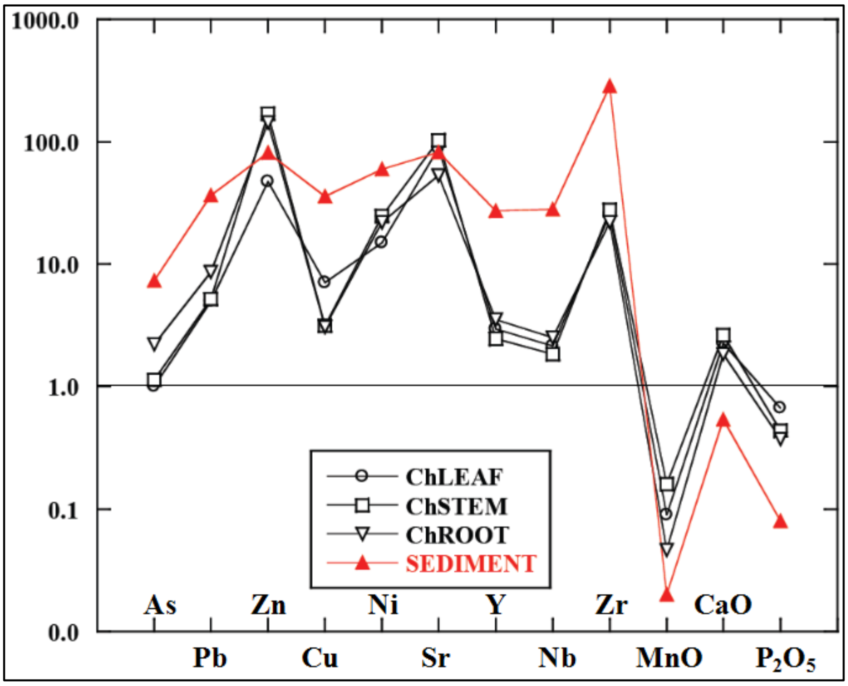

Figure 4.11 Concentration trends of heavy metals in sediments and *R. racemosa* leaves, stems and roots in Choba. (Ch --- Choba)

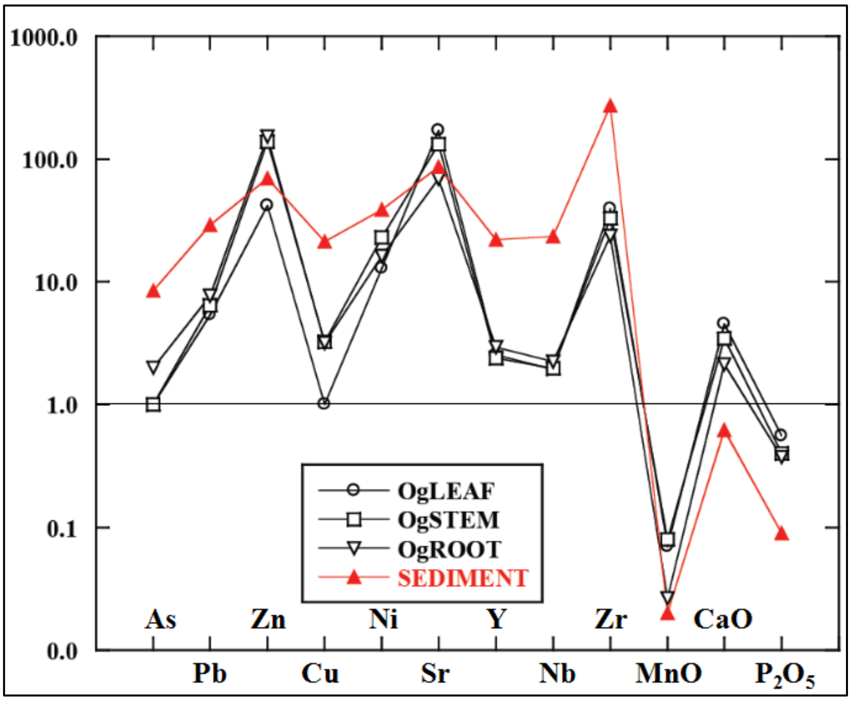

Figure 4.12 Concentration trends of heavy metals in sediments and *R. racemosa* leaves, stems and roots in Ogbogoro. (Og --- Ogbogoro)

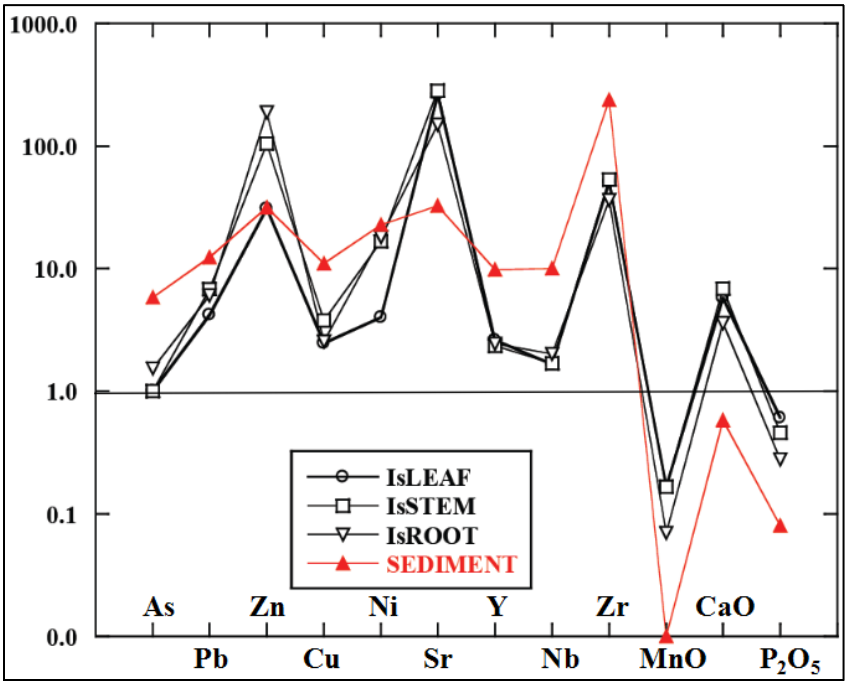

Figure 4.13 Concentration trends of heavy metals in sediments and *R. racemosa* leaves, stems and roots in Isaka. (Is --- Isaka)

4.3.4 Bio-Assessment (BA)

The mangroves of Niger Delta are within the areas of hydrocarbon exploration and exploitation (Nwawuike and Ishiga, 2018b). This area suffers persistent environmental pollution due to industrial and oil related activities. According to Khan *et al* (2013), mangroves are generally considered to have the ability to accumulate metals and tolerate relatively high levels of heavy metal pollution. Also, they participate in bio-chemical remediation of both organic and inorganic pollutants (Mac-Farlane *et al.,* 2007). However, little work has been done on phytoremediation in mangroves around the world (Lacerda, 1997). It therefore becomes imperative to assess the phytoremediation potentials of *R. racemosa* which is the dominant native mangrove specie in Niger Delta. The bio-concentration factor (BCF), bio-accumulation factor (BAF) and bio-translocation factor (BTF) are essential tools used to estimate phytoremediation potentials (Khan *et al.*, 2013; Singh *et al.*, 2017).

4.3.4.1 Bio-Concentration in *R. racemosa*

Table 4.3 presents the results of bio-concentration of heavy metal concentrations in *R. racemosa* roots in Choba, Ogbogoro and Isaka. It was found that As, Pb, Cu, Ni, Y, Nb and Zr have concentration factors lower than 1 in all the locations. The concentration factors of Sr in Choba and Ogbogoro are less than 1 but 4.57 in Isaka. However, Zn, MnO, CaO and P_2O_5 in all the locations have bio-concentration factors greater than (>) 1. It is therefore evident from the findings of this study that *R. racemosa* in Niger Delta mangroves has high concentrations of Zn, MnO, CaO and P_2O_5 in its roots.

Table 4.3 Bio-concentration in *R. racemosa* in Niger Delta mangroves

Trace Elements	ChBCF	OgBCF	IsBCF
As	0.30	0.24	0.26
Pb	0.24	0.27	0.49
Zn	1.76	2.19	5.95
Cu	0.09	0.15	0.23
Ni	0.37	0.42	0.79
Sr	0.65	0.80	4.57
Y	0.13	0.13	0.25
Nb	0.09	0.10	0.20
Zr	0.08	0.09	0.15
Major Elements	**ChBCF**	**OgBCF**	**IsBCF**
MnO	2.33	1.33	7.00
CaO	3.41	3.45	6.20
P_2O_5	4.67	4.15	3.46

ChBCF--- BCF in Choba

OgBCF--- BCF in Ogbogoro

IsBCF--- BCF in Isaka

4.3.4.2 Bio-Accumulation in *R. racemosa*

The results of bio-accumulation of heavy metal concentrations in the leaves and stems of *R. racemosa* in Choba, Ogbogoro and Isaka are shown in Figure 4.4. It was found that As, Pb, Cu, Ni, Y, Nb and Zr have BAF of less than (<) 1 in both leaves and stems in all the locations. Similarly, Zn has BAF of less than (<) 1 in leaves but greater than (>) 1 in the stems in all the locations. The BAF of Sr, MnO, CaO and P_2O_5 in Choba, Ogbogoro and Isaka are greater than (>) 1 in both the leaves and stems.

Table 4.4 Bio-accumulation in *R. racemosa* in Niger Delta mangroves

Trace Elements	$ChBAF_L$	$ChBAF_S$	$OgBAF_L$	$OgBAF_S$	$IsBAF_L$	$IsBAF_S$
As	0.14	0.16	0.12	0.12	0.17	0.17
Pb	0.14	0.14	0.18	0.22	0.34	0.55
Zn	0.58	2.09	0.60	1.99	0.98	3.32
Cu	0.20	0.09	0.05	0.15	0.22	0.34
Ni	0.25	0.41	0.33	0.60	0.18	0.74
Sr	1.08	1.24	1.99	1.53	8.01	8.67
Y	0.11	0.09	0.11	0.11	0.26	0.24
Nb	0.08	0.07	0.08	0.08	0.17	0.17
Zr	0.09	0.10	0.15	0.12	0.21	0.22
Major Elements	$ChBAF_L$	$ChBAF_S$	$OgBAF_L$	$OgBAF_S$	$IsBAF_L$	$IsBAF_S$
MnO	4.50	8.00	3.50	4.00	16.67	16.67
CaO	4.20	4.90	7.28	5.60	9.95	11.83
P_2O_5	8.38	5.46	6.19	4.44	7.58	5.75

$ChBAF_{L\&S}$ ---- Leaves and stems BAF in Choba

$OgBAF_{L\&S}$ ---- Leaves and stems BAF in Ogbogoro

$IsBAF_{L\&S}$ ---- Leaves and stems BAF in Isaka

4.3.4.3 Bio-Translocation in *R. racemosa*

The bio-translocation factor of the *R. racemosa* leaves and stems in Choba, Ogbogoro and Isaka are shown in Table 4.5. The results indicate that As, Y and Nb have translocation factor below 1. Pb and Zn both have translocation factor of 1.13 and 1.19 for *R. racemosa* stem in Isaka and Choba respectively. Also, Ni has a translocation factor of 1.12 and 1.42 respectively for *R. racemosa* in Choba and Ogbogoro. Cu has translocation factor values above 1 in *R. racemosa* leaves and stems in Choba while in Ogbogoro and Isaka, it only had translocation factor value above 1 for the stems. However, Sr, Zr, MnO, CaO and P_2O_5 in all the locations have translocation factor values of more than 1 in both the leaves and stems.

Table 4.5 Bio-translocation in *R. racemosa* in Niger Delta mangroves

Trace Elements	ChTSF$_L$	ChTSF$_S$	OgTSF$_L$	OgTSF$_S$	IsTSF$_L$	IsTSF$_S$
As	0.45	0.52	0.50	0.50	0.65	0.65
Pb	0.58	0.60	0.70	0.83	0.69	1.13
Zn	0.33	1.19	0.28	0.91	0.16	0.56
Cu	2.29	1.02	0.32	1.02	0.97	1.49
Ni	0.68	1.12	0.80	1.42	0.22	0.93
Sr	1.66	1.92	2.48	1.90	1.75	1.89
Y	0.84	0.70	0.86	0.81	1.06	0.96
Nb	0.86	0.73	0.86	0.88	0.82	0.84
Zr	1.14	1.25	1.68	1.40	1.41	1.47
Major Elements	ChTSF$_L$	ChTSF$_S$	OgTSF$_L$	OgTSF$_S$	IsTSF$_L$	IsTSF$_S$
MnO	1.93	3.43	2.63	3.00	2.38	2.38
CaO	1.23	1.44	2.11	1.62	1.61	1.91
P_2O_5	1.79	1.17	1.49	1.07	2.19	1.66

ChTSF$_{L\&S}$ ---- Leaves and stems translocation factor in Choba

OgTSF$_{L\&S}$ ---- Leaves and stems translocation factor in Ogbogoro

IsTSF$_{L\&S}$ ---- Leaves and stems translocation factor in Isaka

4.4 Discussion

Heavy metal accumulation in plants is a multi-step process that includes mobilization from soil into the soil solution, uptake by roots, xylem loading and transport to the shoots (Clemens *et al.*, 2002). This multi-step process is largely determined by pH. Thus, acidity is the most important soil characteristic that determines bioavailability of heavy metals as it affects both the chemical speciation of metals in soil and its binding capacity to the active sites on biota (Weng *et al.*, 2004). This is because a decrease in the rhizosphere's pH increases metal solubility which might enhance uptake by plants (Muhammad, 2011). In an earlier study, Nwawuike and Ishiga (2018a) reported that Choba, Ogbogoro and Isaka sediments have pH range of 5.75 - 6.36, 5.84 - 6.31 and 6.19 - 7.03, respectively. This pH range indicates that the study area sediments are slightly acidic. Hence, the moderate impact on the solubility and bioavailability of the metals analyzed. Comparatively, As, Pb, Zn, Nb and Y concentrated most on the *R. racemosa* roots in Choba, Ogbogoro and Isaka. However, Ni, CaO and MnO as well as Cu, Sr, Zr and P_2O_5 had highest concentrations in stems and leaves, respectively.

Higher As concentration in the *R. racemosa* roots observed in this study is consistent with the findings of Vilhena *et al.* (2013) that As is not readily transported to the aerial plant parts. Though Pb is a non essential metal, its concentration and translocation in plants are determined by salinity. Thus, Pb accumulates mostly in the roots at low salinity while at higher salinity, more proportion of Pb is translocated to the shoots (Weis and Weis, 2004). Zn had higher concentration in shoots compared to Cu. However, the observed high translocation of Zn and Cu particularly from the roots to the stems might be because they are essential for plant growth. The concentration of Zn in the *R. racemosa* leaves corresponds to concentration in sediments. This implies high translocation. Ni concentration was higher in Choba and Ogbogoro relative to Isaka. According to Yusuf *et al.* (2011), Ni uptake in plants usually declines at high soil solution pH values due to the formation of less soluble complexes. Cr, V and TiO_2 had comparatively high concentrations in the mangrove sediments but were not detected in the *R. racemosa* roots, stems and leaves. Though the metals were available in the sediments, they were unavailable for uptake. This might be due to phytoexclusion. However, it has been argued by Quemerais *et al.* (1998) and Dong *et al.* (2000) that unavailability of metals for plant uptake might be due to adsorption onto the surface of minerals like clay, iron or manganese oxy-hydroxides. The observed Sr concentration in the *R. racemosa* tissue far exceeded their concentration in the sediments. This indicates active translocation and is suggestive that *R. racemosa* might be a good phytoextractor or accumulator of Sr. Y, Nb and Zr concentrations in the sediments were much higher compared to concentrations in the *R. racemosa* tissue.

The electrical conductivity (EC) values of the mangrove sediments in Choba, Ogbogoro and Isaka range from -285 to -199 mV, -289 to 93 mV and -229 to -15 mV, respectively (Nwawuike and Ishiga, 2018a). By this, the sediments are in anoxic condition. According to (Barber, 1984), Mn tends to undergo reduction in anoxic environment and as such, its more available for uptake. This is in line with the findings of this study that Mn in oxidized form was found more in *R. racemosa* tissue than in the sediments. Similarly, the uptake of Cl, TS, CaO and P_2O_5 were high. According to Medina *et al.* (2015), *Rhizophora* species have high phosphorous requirement than any other mangrove species. Thus, *R. racemosa* is a good phytoextractor of Cl, TS, MnO, CaO and P_2O_5.

Salts are incorporated into the mangroves from the substrates and eventually transported to the leaves (Ball, 1988). *Rhizophora* species have highly efficient initial salt exclusion and minor salt secretion capacity (Spalding, 2001). However, when the saline conditions are high, the survival rate of the plant is dependent on its ability to effectively regulate internal salt concentrations and as such prevent the ions from becoming toxic (Scholander *et al.,* 1968). Therefore, salt secretion in mangroves is a regulatory mechanism used to control high internal salt concentrations. The secretion of salt is done by the salt glands in the leaves which screen the salinity of the nutrient solution (Nathalie and Ernesto, 2008). Though NaCl is mostly secreted, the secretion solution also contains calcium, sulphur and zinc (Sobrado and Greaves, 2000). High CaO in the leaves helps to increase the rate of salt secretion by the salt glands (Ding *et al.,* 2010) and thus facilitates salt balance. Also, high concentration of P_2O_5 in the leaves play an important role in the enhancement of the food chain quality given that it is critical to ATP (adenosine triphosphate) (Norman and Albert, 1973; Schachtman *et al.,* 1998) and phosphorous cycling in the ecosystem. This is consistent with the findings of this study which indicate high concentrations of Cl, TS, MnO, CaO and P_2O_5 in the *R. racemosa* leaves relative to the stems and roots.

According to Vogel-Mikus *et al* (2005), plants respond to high concentrations of heavy metals by either accumulation or exclusion. The high soil-root and soil-shoot values of Zn, MnO, CaO and P_2O_5 as well as Sr, MnO, CaO and P_2O_5 obtained through BCF and BAF computations indicate that *R. racemosa* is a good accumulator of these metals (Cluis, 2004). However, it tends to exclude As, Pb, Cu, Ni, Y and Nb given that their BCF BAF are less than (<)1. Similarly, Cu, Sr, Zr, MnO, CaO and P_2O_5 have high translocation factors. This implies that these metals are effectively translocated by *R. racemosa* (Baker and Brooks, 1989; Rezvani and Zaefarian, 2011; Fitz and Wenzel, 2002). On the other hand, As, Pb, Zn, Ni, Y and Nb were immobilized given that their TSF values are less than (<) 1.

On the average, it was found that heavy metals were concentrated most on the *R. racemosa* roots and least on the leaves. Given that about 90% of the Niger Delta mangrove forest is dominated by *R. racemosa*; low concentration of metals in its leaves suggests low metal contamination of the detrital food chain. This is because the major components of the detrital food chain is the leaf litter (Edu *et al.*, 2015).

4.5 Conclusion

Variations were observed on the analyzed heavy metal concentrations in both sediment and *R. racemosa* samples. TS and Cl had the highest concentration in sediments while Cl and TS were most concentrated in the *R. racemosa*. However, despite the high concentrations of Cr and V in the sediments, they were not detected in the *R. racemosa* tissue. This might be due to phytoexclusion or adsorption onto the surface of minerals like clay, iron or manganese oxy-hydroxides. *R. racemosa* in Choba, Ogbogoro and Isaka mangroves were found to have similar heavy metal uptake pattern in their leaves, stems and roots. However, the leaf / stem and leaf / root upward transport relationship showed some variations. Heavy metals concentrated most on the roots and least on the leaves. The low concentration of metals on the leaves indicates that the detrital food chain might be uncontaminated. However, there is need for constant monitoring.

CHAPTER FIVE

Comparative Assessment of Heavy Metal Concentrations, Environmental Risks and Phytoremediation Potentials of *R. racemosa* and *A. germinans* in Mangroves of Niger Delta, Nigeria

5.1 Introduction

Mangroves are unique plants that have evolved to thrive in the interface between land and ocean in the humid climate of the tropical and subtropical regions of the world (UNEP, 2007). Precisely, these plants predominate along or close to rivers, intertidal areas, bays, estuaries, lagoons and creeks (Feka, 2015). Temperature and rainfall (Lo *et al.*, 2014) as well as salinity are the major factors regulating their distribution. Mangroves are among the most productive ecosystems of the world. Thus, they are home to many flora and fauna. Also, they produce large amount of detritus that contribute to nutrients in off shore waters and as well, provide conducive breeding ground for many species of fish and other organisms. The complex root system of mangroves enhances shore stability and soil formation by trapping sediments (Nwawuike and Ishiga, 2018c). Hence, the description of the mangrove environment as a sink for not only clastics or sediments but also for CO_2, natural and anthropogenic pollutants.

Defew *et al.* (2005) posit that among the organic and inorganic pollutants within the mangrove environment, heavy metals constitute the major source of poor ecological quality. Put differently, high concentrations of heavy metals in mangrove sediments cause loss of mangroves (Fernandes *et al.,* 2012). The mangroves of Niger Delta, Nigeria are exposed to pollution mostly due to oil related activities. For instance, a total of 6, 817 oil spills occurred in the Niger Delta between 1976 and 2001 (UNDP, 2006). Similarly, some of the estuarine rivers in the area are used for the discharge of both point and non-point wastes as well as means of transportation (Uzoukwu *et al.,* 2014). These and other related human activities increase the pollution load of the mangrove sediments. Thus, polluted sediments within the mangroves could in turn become pollution source (Harbinson, 1986).

Although there are some studies on metal concentrations in mangrove sediments and plant species in Niger Delta (Erakhrumen, 2015; Nwawuike and Ishiga, 2018c), there is dearth of information on the ecological risk of heavy metal accumulation in mangrove plant species. It is against this backdrop that this study seeks to assess the environmental risks of heavy metal concentrations in Niger Delta mangrove sediments in comparison with metal accumulations in *R. racemosa* and *A. germinans*. Specifically, the study focuses on: (a) assessment of metal concentrations in Niger Delta mangrove sediments, (b) assessment of metal concentrations in leaves, stems and roots of *R. racemosa* and *A. germinans* in Niger Delta mangrove, (c) assessment of environmental risks of metal concentrations in *R. racemosa* and *A. germinans* using CF, PLI and (d) assessment of phytoremediation potentials of *R. racemosa* and *A. germinans* using BCF and BTF.

5.2 Materials and Methods

5.2.1 Study Species

R. *racemosa* also known as red mangroves and *A. germinans* (black mangrove) are the mangrove species used for this study. The *R. racemosa* belongs to the family of Rhizophoraceae while *A. germinans* belongs to the acanthus family, Acanthaceae (McKee *et al.,* 1988). *R. racemosa* is the most abundant and pioneer mangrove species in Niger Delta which occupies the wet and more saline areas while *A. germinans* is comparatively less abundant and occupies the drier and less saline upland areas (Chima and Larinde, 2016). However, in some instances, both species inhabit together. Both species are limited to the Atlantic East Pacific (AEP) with largest concentration on the Atlantic coast of West Africa (Lo *et al.*, 2014; Ellison *et al.*, 2010). *R. racemosa* has numerous aerial stilt roots and can grow to a height of 45 m (Chima and Larinde, 2016) while *A. germinans* is smaller and has a pneumatophores. The locals mostly exploit them for firewood and timber. The images of *R. racemosa* obtained from the field are shown in Figures 4.1, 4.2 and 4.3 while the *A. germinans* images are shown in Figures 5.1 and 5.2.

Figure 5.1 *Avicennia germinans* at the bank of New Kalabar River at Ogbogoro, Niger Delta.

Figure 5.2 *Avicennia germinans* at the bank of Bonny River at Isaka, Niger Delta.

5.2.2 Sediment Sampling and Preparation

Sediment core samples were collected from Ogbogoro and Isaka at a depth of 10 cm. Two core samples were collected from each location (n = 2). The cores were taken using a transparent 2-inch diameter PVC pipe. Prior to coring, the PVC pipes were decontaminated using ethanol. The cores were manually driven into the muddy mangrove sediments and carefully retrieved. Homogenization of the retrieved core sediment samples was done after which they were placed in ziplock bags, labeled and transported out and stored at 4°C. The samples were air dried for 48 hours to reduce weight before repackaging and putting them in plastic box for export to the Earth Science Laboratory, Shimane University, Japan.

About 30 g each of the sediment samples were put in decontaminated beakers and covered with aluminum foil and using the ISUZU Muffle Furnace, they were oven dried at 160°C for 48 hours. Sediment grinding was done using the Automatic Agate Mortar and Pestle for 20 minutes. The powdered sediments were made into briquettes by compressing about 5 g each using 200 kN for 60 seconds.

5.2.3 *R. racemosa* and *A. germinans* Sampling and Preparation

The *R. racemosa* samples were equally collected from Ogbogoro and Isaka. The stilt aerial roots, stems and leaves of three *R. racemosa* were sampled in each location (n = 3) while one (n =1) and three (n =3) samples of pneumatophores, stems and leaves of *A. germinans* were collected from Ogbogoro and Isaka respectively. The samples were cut into smaller sizes and placed in plastic ziplock bags and labeled. The samples were immediately taken to the Nigerian Stored Products Research Institute (NSPRI) Port-Harcourt where they were dried at 80^oC for 24 hours. Then, they were repackaged and carefully arranged in plastic boxes, sealed and exported to the Earth Science Laboratory, Shimane University, Japan.

About 20 g of the root, stem and leaf samples each was put in decontaminated beakers, covered with aluminum foil and using the ISUZU Muffle Furnace, they were oven dried at 110^oC for 24 hours and later at 160^oC for 48 hours. They were ground using the Automatic Agate Mortar and Pestle for 20 minutes. Also, the powdered *R. racemosa* samples were made into briquettes by compressing about 5 g each using 200 kN for 60 seconds.

5.2.4 Laboratory Analysis

Eleven trace elements; As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb and Zr as well as four major elements; TiO_2, MnO, CaO and P_2O_5 were analyzed for both sediment and *R. racemosa* samples. Using X-ray fluorescence (XRF) RIX-200 spectrometer. In accordance with Ogasawara (1987), all the XRF analysis were made from pressed powder briquettes with average errors being less than ± 10 %.

5.2.5 Statistical Analysis

The mean concentrations of the trace and major elements in sediment, *R. racemosa* and *A. germinans* samples were done using Microsoft Excel 2013. KaleidaGraph 4.0 was used to plot the graphs.

5.2.6 Environmental Risk Analysis (ERA)

5.2.6.1 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. Tomlinson *et al.* (1980) expressed contamination factor thus:

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

Where:

C_{metal} is the current metal concentration in the plant tissues.

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

In this study, the upper continental crust proposed by Taylor and McLennan (1985) was used as the background metal concentration. The CF is interpreted as follows: $CF < 1$: signifies low contamination; $1 \leq CF < 3$: signifies moderate contamination; $3 = CF \leq 6$: signifies considerable contamination and $CF \geq 6$: signifies very high contamination (Tomlinson *et al.*, 1980).

5.2.6.2 Pollution Load Index (PLI)

To determine the magnitude of heavy metal concentrations in *R. racemosa* and *A. germinans* plant samples, the bio-concentration factor was applied. According to Tomlinson *et al.,* (1980), pollution load index is given as:

$PLI = \sqrt[n]{CF_1 \times CF_2 .... \times CF_n}$

Where:

n is the number of metals and CF is the contamination factor.

PLI value < 1 is unpolluted, PLI = 1 indicates metal load that approximates to the background concentrations while PLI > 1 is polluted (Caberera *et al.*, 1999).

5.2.7 Phytoremediation Potential Analysis (PPA)

5.2.7.1 Bio-Concentration Factor (BCF)

To determine the extent of heavy metal concentrations in the leaves , stems and roots of the *R. racemosa* and *A. germinans* plant samples from the Niger Delta mangroves, the bio-concentration factor was employed. According to Yoon *et al.* (2006), bio-concentration factor is expressed thus:

$BAF\ (leaves) = L_{mc} / S_{mc}$

$BAF\ (stems) = St_{mc} / S_{mc}$

$BCF = R_{mc} / S_{mc}$

Where:

L_{mc}, St_{mc} and R_{mc} are metal concentrations in stems and leaves respectively while

S_{mc} is the soil metal concentration.

BCF > 1 is an indication of hyperaccumulation (Cluis, 2004).

5.2.7.2 Bio-Translocation Factor (BTF)

The rate at which metals concentrated on the *R. racemosa* and *A. germinans* roots were transferred to the stems and leaves was determined using bio-translocation factor (BTF). According to Yanqun *et al.* (2005), bio-translocation factor is given as concentration in shoot divided by concentration in root. In line with this formula, this study formulated bio-translocation factors for leaves and stems as follows:

BTF (leaves) = L_{mc} / R_{mc}

BTF (stem) = St_{mc} / R_{mc}

Where:

L_{mc} and St_{mc} are metal concentrations in leaves and stems respectively while

R_{mc} is the metal concentration in the root.

BTF > 1 indicates effective translocation (Baker and Brooks, 1989; Revani and Zaefarian, 2011).

5.3 Results and Discussion

5.3.1 Heavy Metal Concentrations in Niger Delta Mangrove Sediments

Details of the heavy metal concentrations in Niger Delta mangrove sediments, their distribution (spatially and vertically) and physico-chemical parameters have been reported earlier. See pages 12, 35 and 66.

Table 5.1: Mangrove sediment metal concentrations

Trace Elements	*R. racemosa*	*A. germinans*
	BCF	BCF
As	0.24	0.23
Pb	0.33	0.33
Zn	3.37	2.34
Cu	0.18	0.25
Ni	0.56	0.83
Sr	1.84	0.62
Y	0.17	0.19
Nb	0.13	0.13
Zr	0.12	0.09
Cl	5.87	6.48
TS	0.12	0.57
Major Elements		
MnO	2.5	-
CaO	4.75	2.18
P_2O_5	3.50	2.41

5.3.2 Comparison between Metal Concentrations in *R. racemosa* and *A. germinans*

The mean heavy metal concentrations in the leaves, stems and roots of *R. racemosa* and *A. germinans* are shown in Table 5.2. The table indicates that the heavy metal concentrations differed in different parts of *R. racemosa* and *A. germinans* as well as among heavy metal types analyzed. The sequences of heavy metal concentrations in *R. racemosa* leaves, stems and roots are: Cl>TS>Sr>Zr>Zn>Ni>Pb>Y>Nb>Cu>As; Cl>TS>Sr>Zn>Zr>Ni>Pb>Cu>Y>Nb>As and Cl>TS>Zn>Sr>Zr>Ni>Pb>Cu>Y>Nb>As, respectively. For the major elements, the trends are CaO>MnO>P_2O_5 in leaves and CaO>P_2O_5>MnO in both stems and roots. However, in *A. germinans*, the metal concentration sequences are Cl>TS>Zn>Sr>Zr>Ni>Pb>Cu>Y>Nb>As in the leaves, Cl>TS>Zn>Sr>Zr>Ni>Pb>Cu>Y>Nb>As in the stems and Cl>TS>Zn>Sr>Ni>Zr>Pb>Cu>Y>Nb>As in the roots. The major elements have same concentration pattern in *A. germinans*; CaO>P_2O_5. As (7.15) and MnO (0.02) have the least concentrations of the trace and major elements in the sediments and also are the least concentrated in *R. racemosa* while As and P_2O_5 are the least in *A. germinans*. Though TS (24848.50) and CaO (0.60) are most abundant among the analyzed trace and major elements in the sediments, Cl and CaO were most abundant in *R. racemosa* and *A. germinans*.

Interestingly, Cr,V and TiO_2 were not detected in both *R. racemosa* and *A. germinans* while MnO was detected in *R. racemosa* but not detected in *A. germinans*. The non detection of Cr, V, TiO_2 and MnO despite being available in the sediments might be due to phytoexclusion (Nwawuike and Ishiga, 2018c) or low bioavailability of these metals in the sediments (Usman *et al.*, 2013). Sr, Zr and CaO had higher concentrations in *R. racemosa* relative to *A. germinans* while Zn, Cu, Ni, Nb, Cl and TS are comparatively more concentrated in *A. germinans* than in *R. racemosa*. However, As, Pb, Y and P_2O_5 have similar concentrations in both mangrove species. The observed differences in metal concentrations in *R. racemosa* and *A. germinans* might be due to variations in metal uptake mechanisms of the plants. This according to Clemens *et al*. (2002) includes uptake by roots, xylem loading and transport to shoots. Comparison of metal concentrations in sediments with concentrations in *R. racemosa* and *A. germinans* is shown in Figure 5.3 while the comparison of metal concentration trends in *R. racemosa* and *A. germinans* leaves, stems and roots are presented in Figure 5.4.

Table 5.2: Mean metal concentrations in leaves, stems and roots of *R. racemosa* and *A. germinans*

Trace Elements	Samples	*R.racemosa*	*A. germinans*
As	Leaves	1.00	0.79
	Stems	1.00	1.01
	Roots	1.75	1.62
Pb	Leaves	4.80	5.91
	Stems	6.60	6.33
	Roots	6.85	6.88
Zn	Leaves	36.30	99.90
	Stems	121.50	127.19
	Roots	169.65	117.90
Cu	Leaves	1.75	5.54
	Stems	3.50	3.50
	Roots	2.85	4.07
Ni	Leaves	8.45	11.34
	Stems	19.90	19.73
	Roots	17.10	25.42
Cr	Leaves	nd	nd
	Stems	nd	nd
	Roots	nd	nd
V	Leaves	nd	nd
	Stems	nd	nd
	Roots	nd	nd
Sr	Leaves	216.50	56.49
	Stems	207.45	64.01
	Roots	109.30	37.13
Y	Leaves	2.55	2.90
	Stems	2.40	2.45
	Roots	2.75	3.04
Nb	Leaves	1.80	2.12
	Stems	1.85	1.94
	Roots	2.10	2.20
Zr	Leaves	45.15	23.08
	Stems	42.90	23.51
	Roots	29.75	23.59
Cl	Leaves	66842.25	125399.41
	Stems	14164.65	37276.18
	Roots	43334.15	47829.56
TS	Leaves	14834.80	24136.00
	Stems	3846.30	5385.00
	Roots	3018.75	14045.00
Major Elements	Sample	*R.racemosa*	*A. germinans*
TiO_2	Leaves	nd	nd
	Stems	nd	nd
	Roots	nd	nd
MnO	Leaves	0.15	nd
	Stems	0.15	nd
	Roots	0.05	nd
CaO	Leaves	5.15	1.93
	Stems	5.20	2.26
	Roots	2.58	1.13
P_2O_5	Leaves	0.60	0.75
	Stems	0.45	0.45
	Roots	0.35	0.24

nd ----- not detected

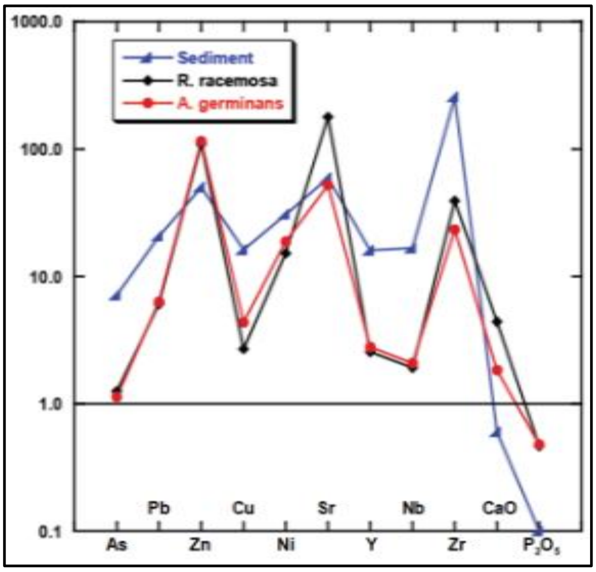

Figure 5.3 Concentrations of metals in sediments in comparison with concentrations in *R. racemosa* and *A. germinans*

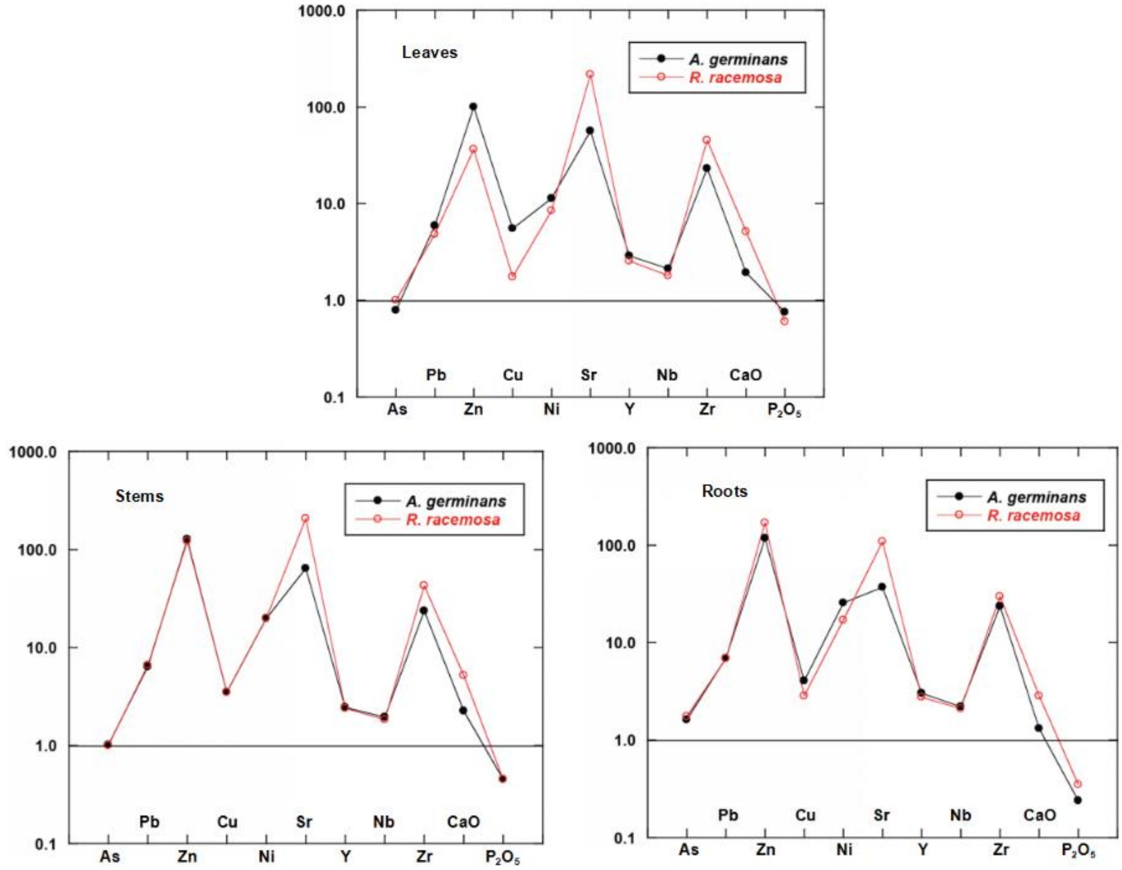

Figure 5.4 Comparison of metal concentration trends in *R. racemosa* and *A. germinans* leaves, stems and roots

5.3.3 Heavy Metal Contamination in *R. racemosa* and *A. germinans*

The extent of heavy metal contamination in *R. racemosa* and *A. germinans* was determined using the contamination factor (CF) with emphasis on biogenic metals and presented in Table 5.3. Though this approach is primarily applied to sediments, however, in this study, an attempt was made to apply it to plants. The interpretation of CF adopted was based on Tomlinson *et al.* (1980). The CF of *R. racemosa* and *A. germinans* are shown in Table 3. The results indicate that As in the leaves and stems of *R. racemosa* and *A. germinans* has a CF of 0.5 while for the roots, it is 0.89 and 1.92 respectively. Pb, Zn, Cu and Ni all have varying CFs for the leaves, stems and roots. In *R. racemosa*, stems and roots have Zn contamination factor of 1.71 and 2.39 while Ni has a contamination factor of 1.00 in the stems. Thus, Zn is moderately contaminated in *R. racemosa* stems and roots while in the stems, Ni has a moderate contamination. Similarly, in *A. germinans*, Zn is moderately contaminated in the leaves (1.41), stems (1.80) and roots (1.93) while As (1.92) and Ni (1.26) are moderately contaminated in the roots.

Table 5.3: Contamination Factors of *R. racemosa* and *A. germinans* in Niger Delta

		CF of Metals				
R. racemosa		As	Pb	Zn	Cu	Ni
	Leaves	0.5	0.24	0.51	0.07	0.42
	Stems	0.50	0.33	1.71*	0.14	1.00*
	Roots	0.89	0.34	2.39 *	0.12	0.86
A. germinans						
	Leaves	0.50	0.29	1.41*	0.22	0.58
	Stems	0.50	0.33	1.80*	0.14	0.99
	Roots	1.92*	0.46	1.93*	0.17	1.26*

**moderately contaminated*

5.3.4 Pollution Load Index of *R. racemosa* and *A. germinans*

The pollution load index (PLI) was used to highlight the pollution severity of metal concentrations in *R. racemosa* and *A. germinans*. Normally, it is used to indicate the the number of times by which the metal concentrations in sediments are more than the background concentrations (Nweke and Ukpai, 2016). However, in this study, it was applied to indicate the extent by which metal concentrations in *R. racemosa* and *A. germinans* are higher than the background metal concentrations in the sediments. The calculated PLI values are presented in Table 5.4 and Figure 5.5. The results show that *R. racemosa* has PLI of 0.27 (leaves), 0.52 (stems) and 0.59 (roots) while in *A. germinans*, the PLI of leaves, stems and roots are 0.47, 0.61 and 0.81 respectively. According to Caberera *et al.* (1999), PLI < 1 is unpolluted, PLI = 1 indicates metal load that approximates to the background concentrations while PLI > 1 is polluted. Thus, the PLI status of the *R. racemosa* and *A. germinans* in Niger Delta mangrove is unpolluted. This finding is consistent with the submission of Nwawuike and Ishiga (2018c) that low metal concentrations of metals in *R. racemosa* leaves show that the detrital food chain might be uncontaminated.

Table 5.4: PLI of *R. racemosa* and *A. germinans* in Niger Delta

Mangrove species	PLI			Status
	Leaves	Stems	Roots	
R. racemosa	0.27	0.52	0.59	Unpolluted
A. germinans	0.47	0.61	0.81	Unpolluted

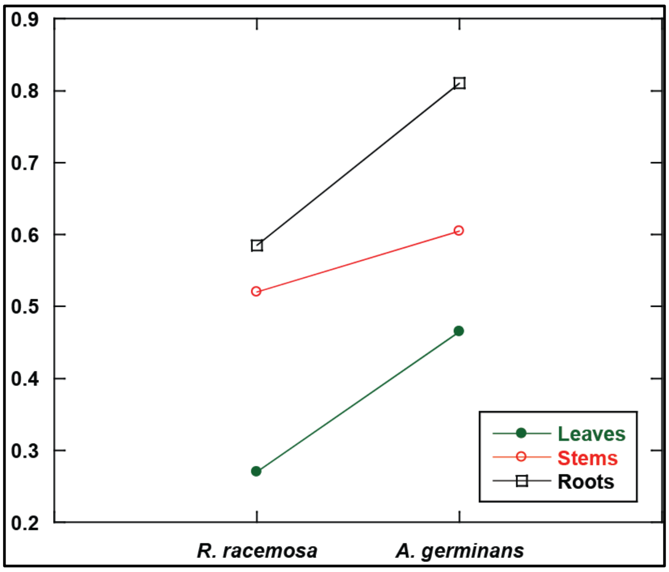

Figure 5.5: Pollution load in *R. racemosa* and *A. germinans*

5.3.5 Phytoremediation Potentials of *R. racemosa* and *A. germinans*

The mangroves of Niger Delta are within the areas of hydrocarbon exploration and exploitation (Nwawuike and Ishiga, 2018b). This area suffers persistent environmental pollution due to industrial and oil related activities. According to Khan *et al.* (2013), mangroves are generally considered to have the ability to accumulate metals and tolerate relatively high levels of heavy metal pollution. Also, they participate in bio-chemical remediation of both organic and inorganic pollutants (Mac-Farlane *et al.,* 2007). However, little work has been done on phytoremediation in mangroves around the world (Lacerda, 1997). It therefore becomes imperative to assess the phytoremediation potentials of *R. racemosa* and *A. germinans* which are dominant native mangrove species in Niger Delta. The bio-concentration factor (BCF) and bio-translocation factor (BTF) are essential tools used to estimate phytoremediation potentials (Khan *et al.,* 2013; Singh *et al.,* 2017). Specifically, BCF highlights the extent to which metal concentrations in tissue relate to concentrations in sediments (Qiu *et al.,* 2011). Also, metal accumulating plants have the capability of having bioconcentration levels of the pollutants in their tissues above that of the contaminated media (Erakhrumen, 2014). BTF is used to indicate the rate of metal concentrations in the shoot relative to the root (Usman *et al.,* 2012).

5.3.5.1 Bio-concentration Factor in *R. racemosa* and *A. germinans* in Niger Delta Mangroves

The results of the bio-concentration factors of heavy metals in leaves, stems and roots of *R. racemosa* and *A. germinans* in Niger Delta are shown in Table 5.5. It was found that the BCF of Sr, Cl, MnO, CaO and P_2O_5 in the leaves; Zn, Sr, Cl, MnO, CaO and P_2O_5 in the stems and roots of *R. racemosa* are greater than 1. This indicates that *R. racemosa* has high efficiency in bio-accumulation of these metals. However, As, Pb, Zn, Cu, Ni, Y, Nb, Zr and TS in the leaves;

As, Pb, Cu, Ni, Y, Nb, Zr and TS in the stems and roots of *R. racemosa* have BCF of less than 1 indicating inefficiency in the bio-accumulation of these elements. In *A. germinans*, the BCF of Zn, Cl, CaO and P_2O_5 in the leaves and roots; Zn, Sr, Cl, CaO and P_2O_5 in the stems are above 1 and thus indicates that these metals are efficiently bio-accumulated. On the contrary, the BCF of As, Pb, Cu, Ni, Sr, Y, Nb, Zr and TS in leaves and roots; As, Pb, Cu, Ni, Y, Nb, Zr and TS in the stems of *A. germinans* are less than 1 and therefore not efficiently bio-accumulated. MnO was not detected in *A.germinans* and as such has no BCF.

Table 5.5: Bio-concentrations in *R. racemosa* and *A. germinans*

Trace Elements	***R. racemosa***			***A. germinans***		
	BCF_L	**BCF_S**	**BCF_R**	**BCF_L**	**BCF_S**	**BCF_R**
As	**0.14**	**0.14**	**0.24**	**0.11**	**0.14**	**0.23**
Pb	**0.23**	**0.32**	**0.33**	**0.29**	**0.31**	**0.33**
Zn	**0.72**	**2.41**	**3.37**	**1.98**	**2.52**	**2.34**
Cu	**0.11**	**0.22**	**0.18**	**0.34**	**0.22**	**0.25**
Ni	**0.28**	**0.65**	**0.56**	**0.37**	**0.64**	**0.83**
Sr	**3.64**	**3.49**	**1.84**	**0.95**	**1.08**	**0.62**
Y	**0.16**	**0.15**	**0.17**	**0.18**	**0.15**	**0.19**
Nb	**0.11**	**0.11**	**0.13**	**0.13**	**0.12**	**0.13**
Zr	**0.18**	**0.17**	**0.12**	**0.09**	**0.09**	**0.09**
Cl	**9.06**	**1.92**	**5.87**	**16.99**	**5.05**	**6.48**
TS	**0.60**	**0.15**	**0.12**	**0.97**	**0.22**	**0.57**
Major Elements						
MnO	**7.50**	**7.50**	**2.5**	**-**	**-**	**-**
CaO	**8.58**	**8.67**	**4.75**	**3.21**	**3.76**	**2.18**
P_2O_5	**6.00**	**4.50**	**3.50**	**7.51**	**4.50**	**2.41**

5.3.5.2 Bio-translocation Factor in *R. racemosa* and *A. germinans* in Niger Delta Mangroves

The BTF of the *R. racemosa* and *A. germinans* leaves and stems in Niger Delta Mangroves are presented in Table 5.6. The results indicate that As, Pb, Zn, Cu, Ni, Y and Nb in *R. racemosa* and As, Pb, Zn, Ni, Y, Nb and Zr in *A. germinans* have BTF of below 1 which is an indication of ineffective translocation of these metals in the leaves. However, Sr, Zr, Cl, TS, MnO, CaO and P_2O_5 in *R. racemosa* and Cu, Sr, Cl, TS, CaO and P_2O_5 in *A. germinans* have BTF greater than 1 in their leaves and this indicates phytoextraction of these metals. In the stems, As, Pb, Zn, Y, Nb and Cl in *R. racemosa* and As, Pb, Cu, Ni, Y, Nb, Cl and TS in *A. germinans* have

BTF less than 1 and implies that these metals are inefficiently translocated in the stems of these mangrove plants. But, Cu, Ni, Sr, Zr, TS MnO, CaO and P_2O_5 in *R. racemosa* and Zn, Sr, Zr, CaO and P_2O_5 in *A. germinans* have BTF greater than 1. As such, these metals are efficiently translocated in the roots.

Table 5.6. Heavy metal bio-translocation factors in *R. racemosa* and *A. germinans*

Trace Elements	***R. racemosa***		***A. germinans***	
	BTF_L	**BTF_S**	**BTF_L**	**BTF_S**
As	0.57	0.57	0.49	0.63
Pb	0.70	0.96	0.86	0.92
Zn	0.21	0.72	0.85	1.08
Cu	0.61	1.23	1.36	0.86
Ni	0.49	1.16	0.45	0.78
Sr	1.98	1.90	1.52	1.72
Y	0.93	0.87	0.95	0.81
Nb	0.86	0.88	0.96	0.88
Zr	1.52	1.44	0.98	1.00
Cl	1.54	0.33	2.62	0.78
TS	4.91	1.27	1.72	0.38
Major Elements				
MnO	**3.00**	**3.00**	-	-
CaO	1.81	1.82	1.47	1.72
P_2O_5	1.71	1.29	3.12	1.87

5.4 Conclusion

Variations were observed on metal concentrations in R. racemosa and A. germinans. Sr, Zr and CaO had higher concentrations in *R. racemosa* relative to *A. germinans* while Zn, Cu, Ni, Nb, Cl and TS are comparatively more concentrated in *A. germinans* than in *R. racemosa*. However, As, Pb, Y and P_2O_5 have similar concentrations in both mangrove species. The observed differences in metal concentrations in *R. racemosa* and *A. germinans* might be due to variations in metal uptake mechanisms of the plants. However, Cr,V and TiO_2 were not detected in both *R. racemosa* and *A. germinans* while MnO was detected in *R. racemosa* but not detected in *A.*

germinans. The non detection of C, V, TiO_2 and MnO despite being available in the sediments might be due to phytoexclusion.

In *R. racemosa*, stems and roots have Zn contamination factor of 1.71 and 2.39 while Ni has a contamination factor of 1.00 in the stems. Thus, Zn is moderately contaminated in *R. racemosa* stems and roots while in the stems, Ni has a moderate contamination. Similarly, in *A. germinans*, Zn is moderately contaminated in the leaves (1.41), stems (1.80) and roots (1.93) while As (1.92) and Ni (1.26) are moderately contaminated in the roots. PLI status of the *R. racemosa* and *A. germinans* in Niger Delta mangrove is unpolluted. *R. racemosa* has high efficiency in bio-accumulation of Sr, Cl, MnO, CaO and P_2O_5 in the leaves; Zn, Sr, Cl, MnO, CaO and P_2O_5 in the stems and roots while *A. germinans* is efficient in bio-accumulating Zn, Cl, CaO and P_2O_5 in the leaves and roots; Zn, Sr, Cl, CaO and P_2O_5 in the stems. It was found that *R. racemosa* and *A. germinans* has phytoremediation capacities in Cu, Ni, Sr, Zr, Cl, TS, MnO, CaO, P_2O_5 and Zn, Cu, Sr, Zr, CaO, P_2O_5 respectively.

CHAPTER SIX

General Conclusion

This study examined the geochemical status of the Niger Delta mangrove surface and core sediments. It also evaluated the elemental concentrations and distribution in *R. racemosa*, the predominant mangrove plant species in the study area. A total of twenty three elements were used for the study (18 trace elements and 5 major elements). In line with the objectives of this study, the major findings are highlighted below.

6.1 Geochemical Concentrations of the Niger Delta Mangrove Surface Sediments

The mangrove surface sediment samples showed different geochemical concentrations. However, mean concentrations indicate that Cl had the highest concentration with a value of 2, 754.2 ppm while As had the least concentration with a value of 5.5 ppm. The sequence of geochemical concentrations in Niger Delta mangrove surface sediments is Cl>Zr>V>Cr>F>Sr>Zn>Ni>I>Br>Pb>Nb>Y>Cu>Sc>Th>As. Fe_2O_3 had the highest concentration among the major elements analyzed with an average value of 5.8 wt% while MnO had the least with a value of 0.02 wt%. The concentration trend of the major elements is $Fe_2O_3>TiO_2>CaO>P_2O_5>MnO$.

6.2 Geochemical Concentrations of the Niger Delta Mangrove Core Sediments

The geochemical concentrations in the core sediments of the Niger Delta mangroves varied with depth. At 0 - 2 cm, the mean concentrations of trace elements indicate that V had the highest concentration with a value of 169.8 ppm while As had the lowest value of 7.4 ppm. Trace elements concentration trend is V>Cr>Sr>Zn>Ni>Pb>Nb>Cu>Th>As. The same trend was observed at depths 8 - 10 cm and 15 - 20 cm. However, V had 149.28 and 151.35 while As had 7.02 and 7.27 ppm, respectively. At 4 - 6 cm, V had the highest concentration value of 145.87 while As had the least value at 6.93 ppm. At this depth, the concentration trend is V>Cr>Zn>Sr>Ni>Cu>Pb>Nb>Th>As. Also, V was the most abundant element at 25 - 30 cm depth with a mean value of 178.83 while As was had the least abundance with the value of 7.47 ppm. Based on the major elements analysed, Fe_2O_3 had the highest mean concentrations of 6.21, 6.12, 6.06, 6.75 and 6.78 while MnO had the lowest mean concentrations of 0.01, 0.01, 0.02, 0.02 and 0.02 ppm respectively for depths 0 - 2, 4 - 6, 8 - 10, 15 - 20 and 25 - 30 cm.

As, Ni, Cr, V, Sr, Nb, Th, TiO_2, Fe_2O_3, MnO and CaO had higher concentrations at 25 - 30 cm and lower concentrations at 0 - 2 cm. However, Pb, Zn, Cu and P_2O_5 had higher concentrations at 0 - 2 cm and lower concentrations at 25 - 30 cm. The concentrations of TS decreased consistently from depths of 25 - 30 cm to 0 - 2 cm while the concentrations of P_2O_5 increased from 25 - 30 cm to 0 - 2 cm.

6.3 Ecological Risk Assessment of Niger Delta Mangrove Sediment Geochemical Concentrations

The ecological risk assessment of heavy metals in the mangrove sediments was done using contamination and enrichment factors, pollution load index and geo-accumulation index to determine the extent of environmental risk posed by the present concentrations of As, Pb, Zn, Cu, Ni, Cr and V at different depths. Contamination factor indicated that Zn and Cu had low contamination across depths except at 4 - 6 cm where Cu had a moderate contamination. The present concentrations of Pb, Ni and V are of moderate contamination. However, As and Cr concentrations are of considerable contamination. The enrichment factor showed that the enrichment of As, Ni, Cr and V across depths are anthropogenic while Pb, Zn and Cu concentrations are geogenic. The concentrations of As, Cr and V across depths are of moderate enrichment except at 4 - 6 cm where Cr concentration is significantly enriched. The concentrations of Pb, Zn, Cu and Ni are of minimal enrichment except at 4 - 6 cm where Ni concentration is of moderate enrichment. The pollution load indicated that the core sediments are polluted across depths and locations. Similarly, the Igeo of As and Cr informed that they are moderately polluted across depths and locations. Ni and V are moderately polluted in Choba and Ogbogoro but are unpolluted in Isaka. Also, the Igeo of Pb, Zn and Cu are in the class of 0 and thus, unpolluted.

Based on the SQGs, As concentrations across depths are more than the LEL and ISQG but below SEL and PEL. This implies that the present concentrations of As have moderate impact on the environment. The Pb and Zn concentrations do not impact appreciably on the environment given that both are below LEL and ISQG. Cu concentrations have low impact given that it is slightly above and below LEL and ISQG. The Ni concentrations impact moderately because it is below SEL. However, Cr concentrations may impact severely on the Niger Delta mangrove environment given that the concentrations across depths are greater than LEL, ISQG and SEL but below PEL.

6.4 Elemental Concentrations and Distribution in *R. racemosa* and *A. germinans*

The evaluation of the elemental concentrations in *R. racemosa* and *A. germinans* indicated varied concentrations in different parts of the plant. Among the trace elements investigated, Cl had the highest mean concentrations of 65,885.80 and 125,399.41 ppm, while As had the least value of 1.00 and 0.79 ppm, respectively for both plants in the leaves. In the stem, Cl was the most concentrated with a mean value of 13, 306.43 and 37,276.18 ppm, while As had the lowest at 1.03 and 1.01 ppm, respectively for both plants. In the roots, Cl also had the highest average concentration value of 39, 764.53 and 47,829.56 ppm, while As had 1.90 and 1.62 ppm, respectively for both plants. Based on the major elements investigated, CaO had the highest mean concentrations in the leaves, stems and roots (4.20, 4.37 and 2.50) for *R. racemosa* and (1.93, 2.26 and 1.13) for *A. germinans.* MnO had the lowest mean concentrations of 0.13, 0.16, 0.10 and 0.75, 0.45, 0.24 ppm, respectively for both plants. However, Cr, V and TiO_2 were not detected in the *R. racemosa* tissues sampled while Cr, V, TiO2 and MnO were not found in *A. germinans* tissues sampled.

6.5 Heavy Metals Uptake Pattern in *R. racemosa* and *A. germinans*

There were variations on the concentrations of heavy metals in *R. racemosa* and *A. germinans* samples from different locations in Niger Delta. However, the concentrations of heavy metals in the leaves, stems and roots of different R. racemosa and *A. germinans* samples revealed similarity in uptake pattern.

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Appendix 1

Mean Metal Concentrations in Niger Delta Mangrove Surface Sediments

Trace Elements	**Values (ppm)**
As	5.53
Pb	23.67
Zn	49.57
Cu	14.87
Ni	34.07
Cr	116.33
V	132.71
Sr	51.79
Y	15.73
Nb	17.33
Zr	265.27
Th	10.93
Sc	13.93
TS	9602.14
F	101.83
Br	24.67
I	29.33
Cl	2913.67
Major Elements	
TiO_2	0.81
Fe_2O_3	4.81
MnO	0.02
CaO	0.50
P_2O_5	0.05

Appendix 2

Mean Metal Concentrations in Niger Delta Mangrove Core Sediments

Trace Elements	**Core Depth (cm)**				
	0 - 2	**4 - 6**	**8 - 10**	**15 - 20**	**25 - 30**
As	7.50	7.17	7.00	7.33	7.50
Pb	29.67	24.50	23.83	22.67	23.17
Zn	58.17	70.33	53.67	51.67	55.83
Cu	20.00	31.00	17.00	15.00	16.83
Ni	42.17	42.33	36.67	38.17	48.00
Cr	125.83	124.17	110.33	108.67	130.33
V	169.83	146.00	149.50	151.33	179.00
Sr	69.50	65.50	66.17	65.67	78.33
Y	20.33	19.67	19.17	19.50	21.67
Nb	21.83	20.17	19.50	19.50	23.33
Zr	286.83	255.17	254.33	225.33	255.33
Th	13.67	12.33	12.67	12.33	14.67
Sc	13.83	12.67	12.50	12.83	15.33
TS	10743.17	19646.67	25081.17	28450.83	30072.33
F	142.67	104.67	129.00	155.50	157.60
Br	41.83	33.67	35.00	29.17	28.50
I	27.83	20.50	24.50	21.20	18.50
Cl	6060.83	4422.17	4962.50	4021.00	6059.75
Major Elements					
TiO_2	1.06	0.96	0.97	0.95	1.18
Fe_2O_3	6.21	6.12	6.06	6.75	6.78
MnO	0.02	0.02	0.02	0.02	0.02
CaO	0.58	0.57	0.59	0.57	0.59
P_2O_5	0.10	0.07	0.07	0.07	0.06

Appendix 3

Mean Metal Concentrations in Niger Delta Mangrove *R. racemosa*

Trace Elements	**Leaf**	**Stem**	**Root**
As	0.89	1.06	1.34
Pb	4.84	6.12	7.45
Zn	39.91	137.70	160.79
Cu	3.12	3.41	2.90
Ni	10.60	21.47	18.74
Cr	nd	nd	nd
V	nd	nd	nd
Sr	173.89	172.29	90.60
Y	2.70	2.40	2.96
Nb	1.91	1.84	2.26
Zr	38.54	37.85	27.22
Th	nd	nd	nd
Sc	nd	nd	nd
TS	14816.38	3731.26	4341.85
F	125.43	163.50	120.56
Br	189.66	38.04	104.44
I	nd	nd	nd
Cl	64422.13	13306.48	39764.53
Major Elements			
TiO_2	nd	nd	nd
Fe_2O_3	nd	nd	0.30
MnO	0.11	0.14	0.05
CaO	4.19	4.33	2.52
P_2O_5	0.61	0.43	0.34

nd…. not detected

Appendix 4

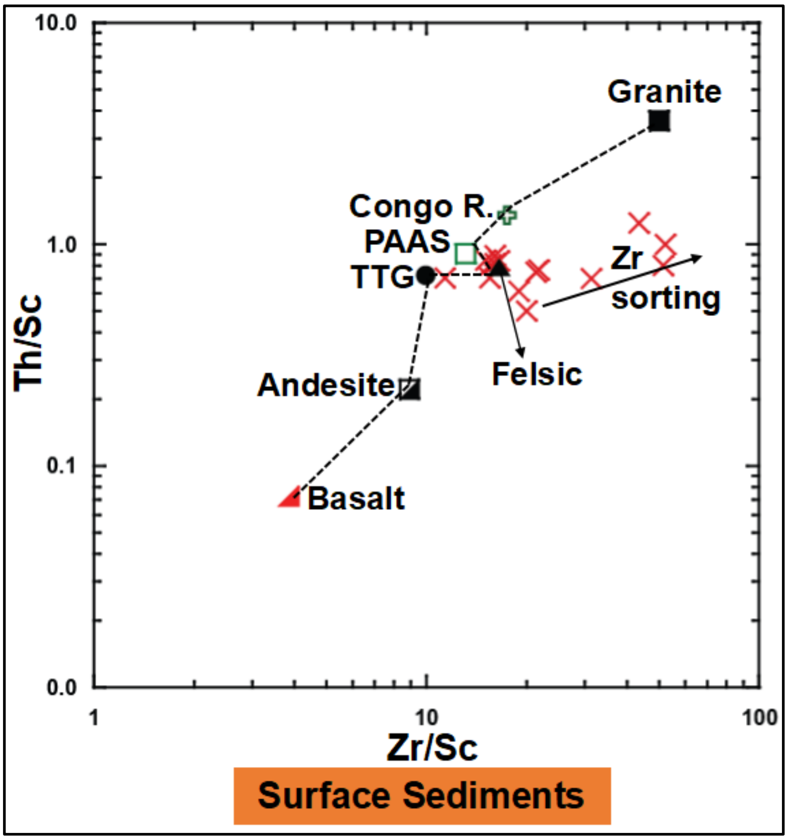
Mean Metal Concentrations in Niger Delta Mangrove *A. germinans*

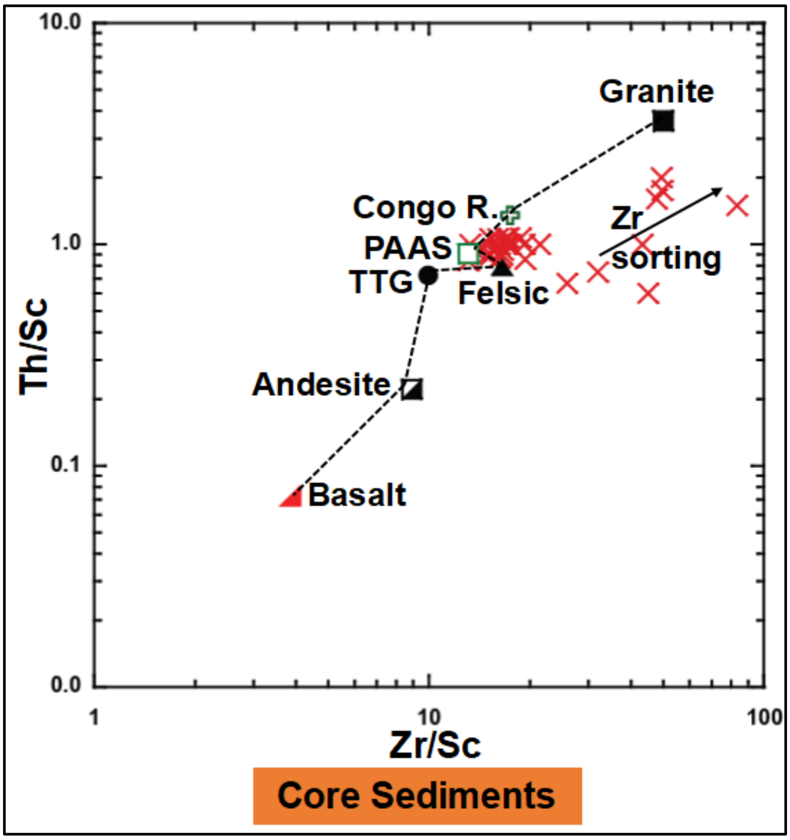
Trace Elements	**Leaf**	**Stem**	**Root**
As	0.91	0.80	3.05
Pb	5.92	6.67	8.09
Zn	90.65	150.96	119.83
Cu	6.31	3.25	3.89
Ni	10.55	18.15	25.41
Cr	nd	nd	12.04
V	nd	nd	23.11
Sr	69.48	88.57	40.87
Y	2.91	2.48	3.59
Nb	2.07	1.89	2.39
Zr	26.24	29.44	27.90
Th	nd	nd	0.80
Sc	nd	nd	nd
TS	12805.09	3065.15	8539.16
F	100.75	27.00	73.00
Br	249.44	51.37	89.36
I	nd	nd	
Cl	64974.36	20589.28	29695.42
Major Elements			
TiO_2	nd	nd	0.13
Fe_2O_3	nd	nd	1.52
MnO	nd	nd	nd
CaO	2.13	2.97	1.28
P_2O_5	0.72	0.38	0.27

nd….not detected

Appendix 5

Source Rock Composition of Niger Delta Mangrove Surface and Core Sediments

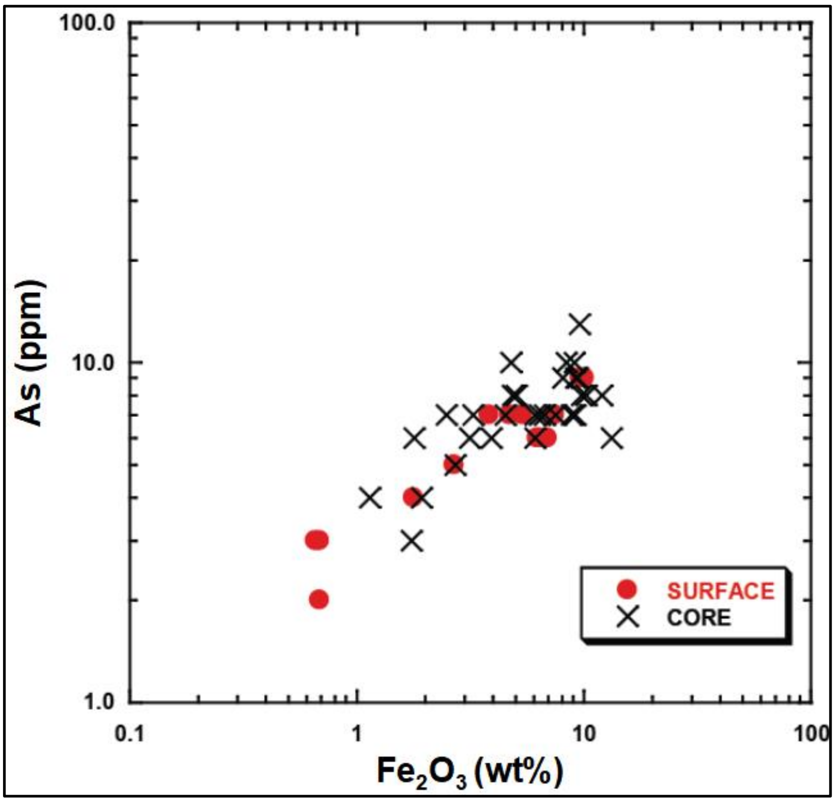


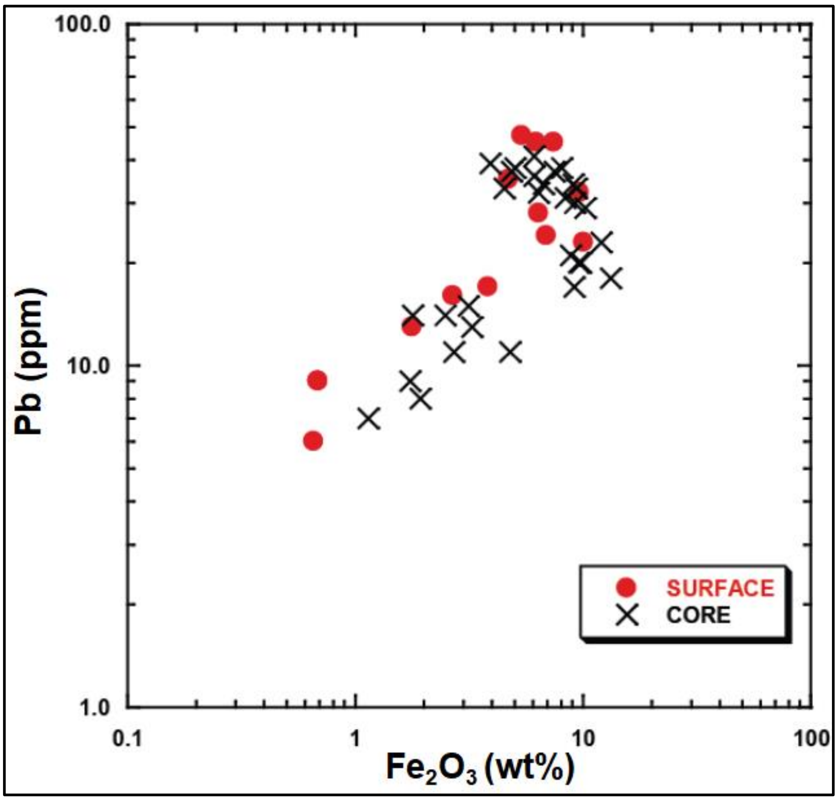


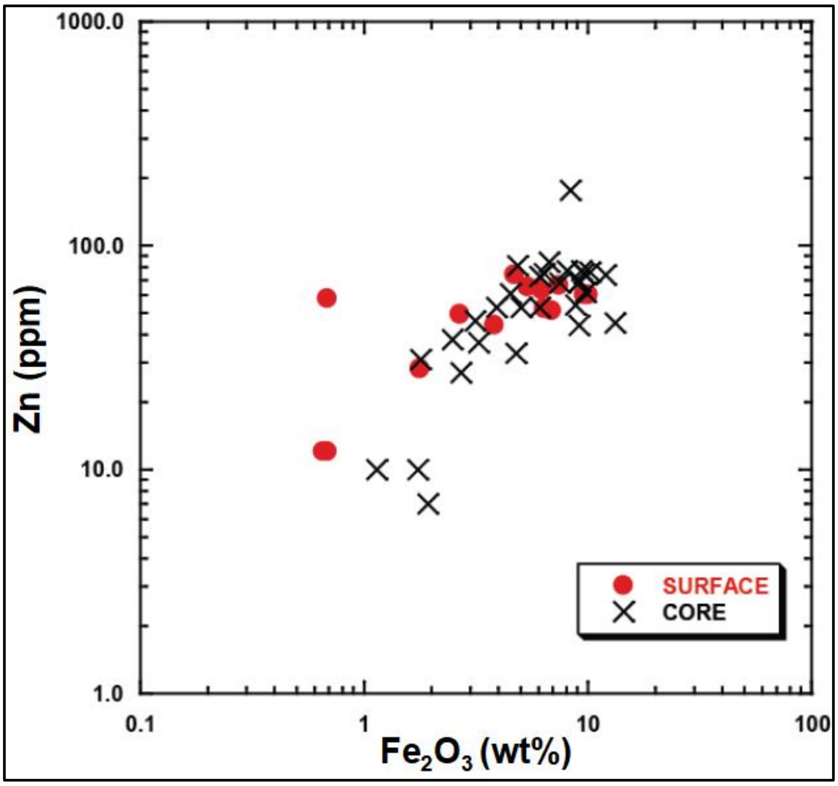
Data for granite, PAAS, TTG, felsic, andesite and basalt were sourced from Condie, K. C. (1992)

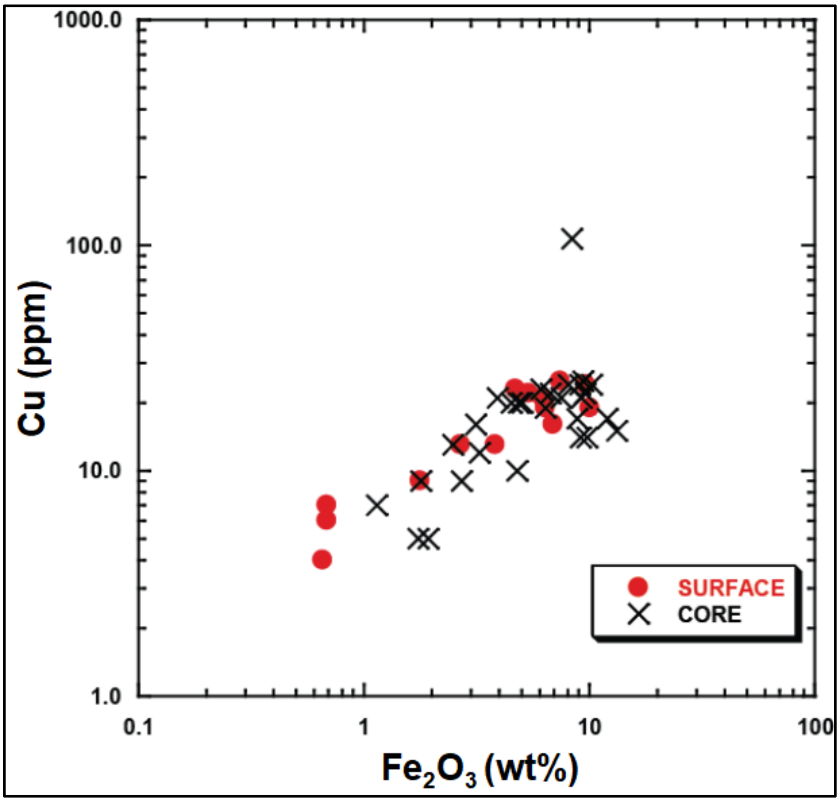
Appendix 6

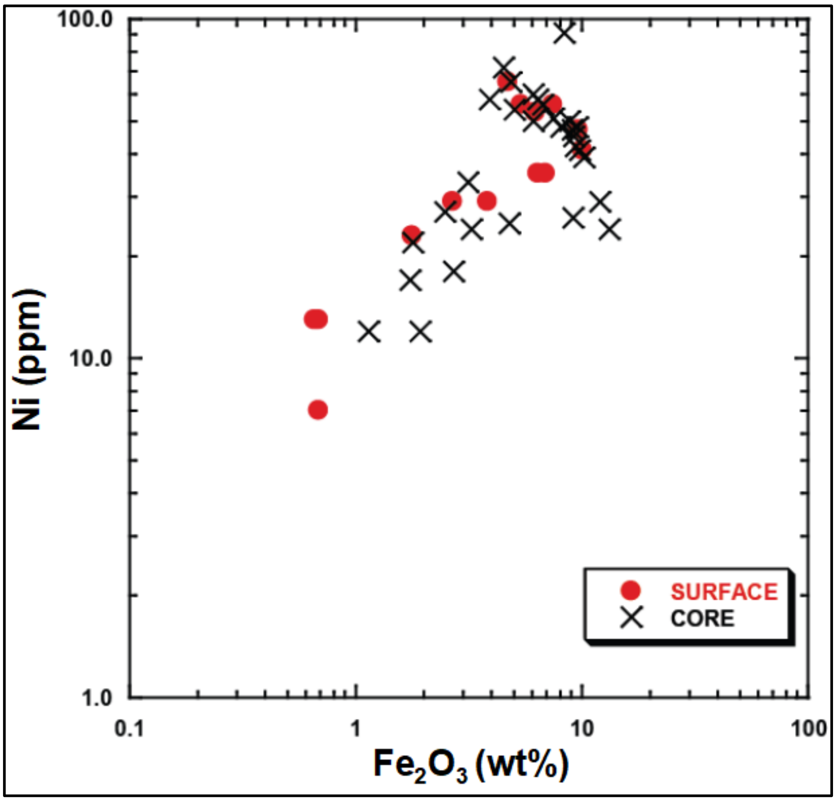
Correlations between Some Biogenic Metals and Fe_2O_3 in Niger Delta Mangrove Surface and Core Sediments

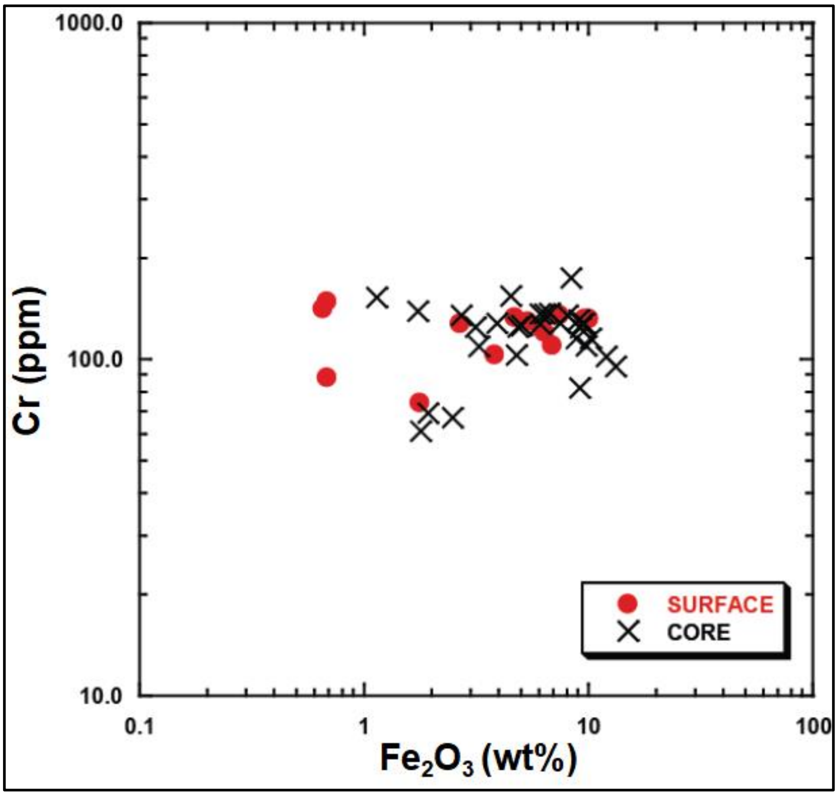





1000.0
100.0
10.0
1.0
Zn (ppm)
0.1
1
10
100
Fe_2O_3 (wt%)
● SURFACE
× CORE

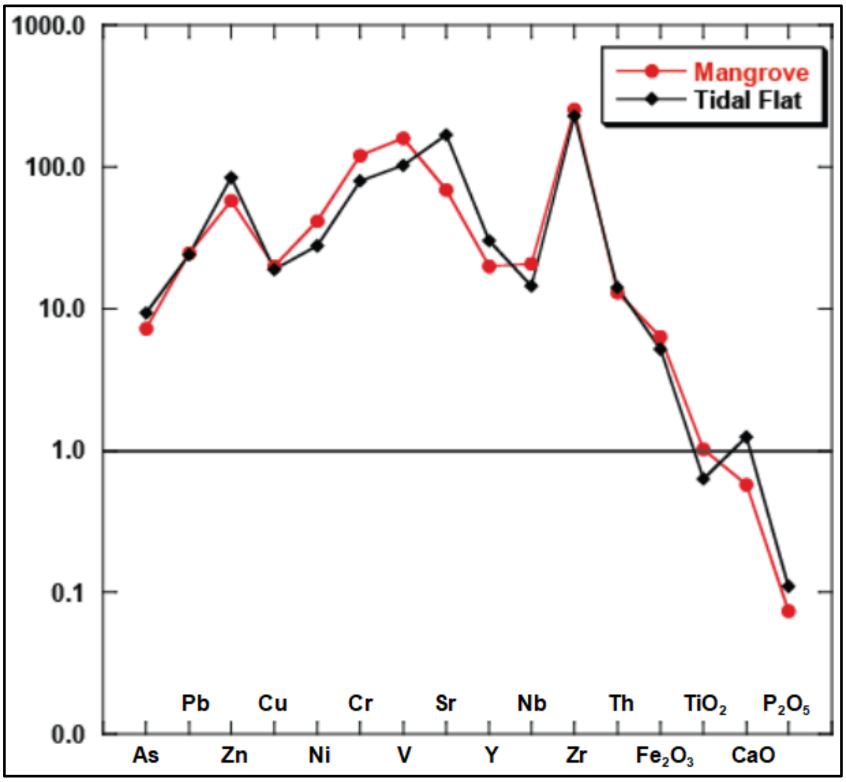

1000.0
100.0
10.0
1.0
Cu (ppm)
0.1
1
10
100
Fe_2O_3 (wt%)
● SURFACE
× CORE

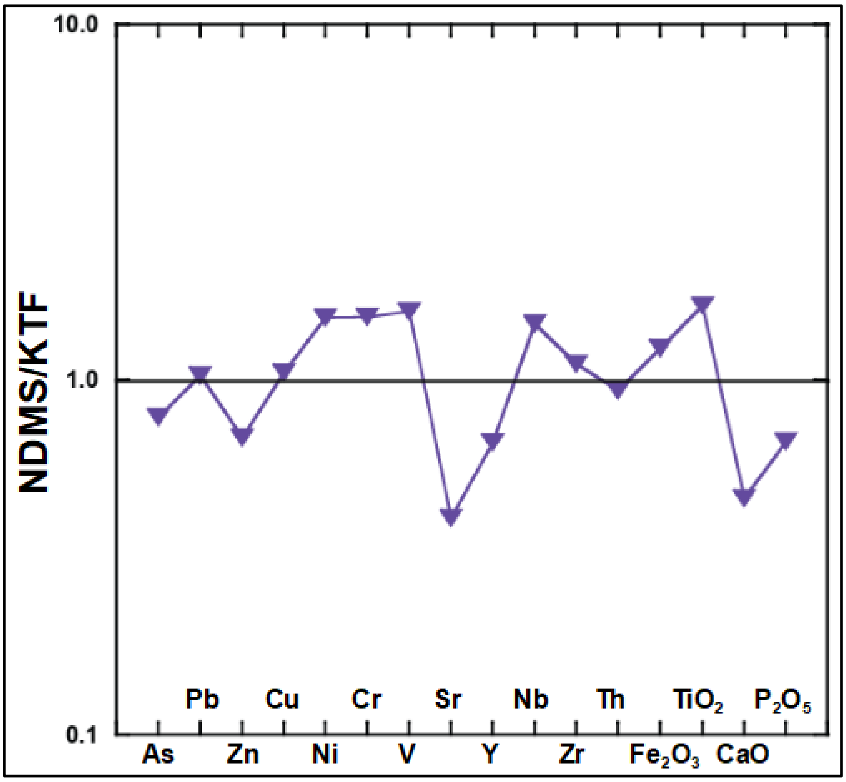

100.0
10.0
1.0
Ni (ppm)
0.1
1
10
100
Fe_2O_3 (wt%)
SURFACE
CORE


1000.0
100.0
10.0
Cr (ppm)
0.1
1
10
100
Fe_2O_3 (wt%)
SURFACE
CORE

Appendix 7

Niger Delta Mangrove / Korean Tidal Flat Metal Concentrations





Source of KTF data:

Ishiga and Dozen (2013)

- NDMS...Niger Delta Mangrove Sediments
- KTF...Korean Tidal Flat