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Geochemical Evaluation of Surface Sediments in Niger Delta Mangrove, Nigeria

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Abstract

Mangrove surface sediments from Choba, Ogbogoro and Isaka along the New Calabar and Bonny rivers respectively in Niger Delta, Nigeria were sampled and analyzed 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 plot of the elements show contrasting concentrations in different sampling locations. Compared to the upper continental crust (UCC), As and Ni are higher in Choba, Ogbogoro and Isaka. The abundance of Pb was found to be higher in Choba and Ogbogoro. Though Th and Sc are 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.

Keywords: Mangrove sediments, Geochemistry, Heavy metals, Sediment quality, Niger delta

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 favors the retention of water-borne heavy metals. In the aquatic ecosystem, trace metals are among the most persistent pollutants (Arnason &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 & Fletcher 2003).

The mangrove of Niger Delta in Nigeria is the largest in Africa with estimated area coverage of 7,386km^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 & 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 Calabar and Bonny rivers in eastern Niger Delta was undertaken to evaluate its 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. Materials and methods

2.1 Study Area

Niger Delta seats directly on the Gulf of Guinea on the Atlantic Ocean in southern Nigeria. It lies between longitudes 5°E to 8°E and latitudes 4°N to 6°N (Opafunso 2007; Dada *et al*. 2015). It is situated in the equatorial climatic region. The mean annual rainfall decreases from about 4,500mm within the coastal margins to about 2,000mm around its northern fringe while the relative humidity decreases from 85% within the coastal margins to 80% around its northern fringe (Adejuwon 2012). The temperature ranges from 18°C to 33°C (UNDP 2012). The Niger Delta has twenty-one tidal inlets (Dada *et al*. 2015). It is home to Global 200 Eco-region and harbors many locally and globally endangered species as well as about 60 - 80% of all plant and animal species found in Nigeria (Myers *et al*. 2000; UNDP 2012; Okonkwo *et al*. 2015). Also, it has been the focus of hydrocarbon exploration and exploitation since 1937 and at present, it is the Africa's leading oil province (Reijers 2011). However, environmental degradation is high in many parts of Niger Delta due to pollution from oil related activities and industrial effluents.

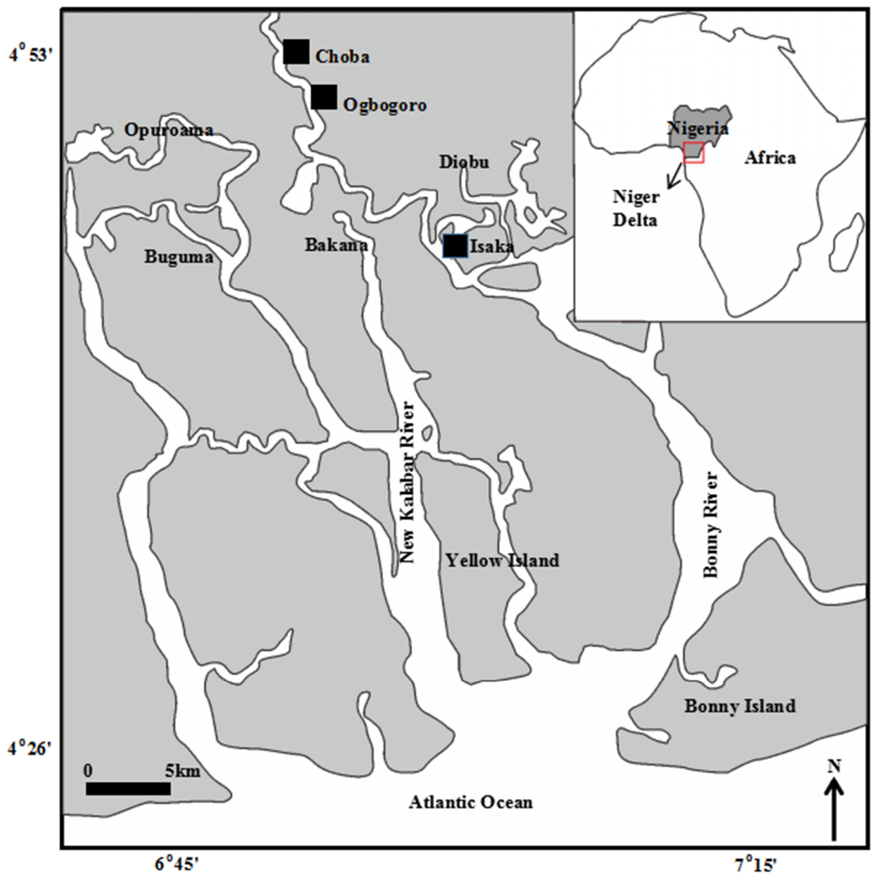

Figure 1. Map of study area showing sampling locations

2.2 Geological and Hydrological Settings

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 & 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 ranges in age from tertiary to recent (Short & Stauble 1967; Burke *et al*. 1971; Reijers 2011; Emujakporue & Ngwueke 2013; Ola & Alao 2013; Dada *et al*. 2015; Didei &Akana 2016). The lithostratigraphic units are the Benin Formation, Agbada Formation and Akata Formation. 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). The Agbada Formation underlies the Benin Formation. It is made up of an alternation of sand (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). 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 sand and small amounts of silt and clay with an estimated thickness of 7,000 meters (Tuttle *et al*. 1999; Asadu *et al*. 2015).

The Niger River basin emptied into the Atlantic Ocean through the Niger Delta. With a length of 4,200km, drainage area of 2.27 million square kilometers and discharge rate of 9,570m^3 /s, the Niger river is the third longest river in Africa and its basin is the ninth largest in the world (Oyebande &Odunuga 2010; Dada *et al*. 2015). The basin is shared among ten countries (Oyebande & Odunuga 2010). Through its multiple distributaries, the Niger River discharges its sediment load at the Niger Delta (Abam 1999; Abam 2001).

3. Analytical Procedures

3.1 Sediment Sample Collection and Preparation

Surface sediment samples were collected in the mangrove areas along the New Calabar 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.Sampling points in Choba mangroves

Source: Google Earth (2018).

Figure 3.Sampling points in Ogbogoro mangroves

Source: Google Earth (2018).

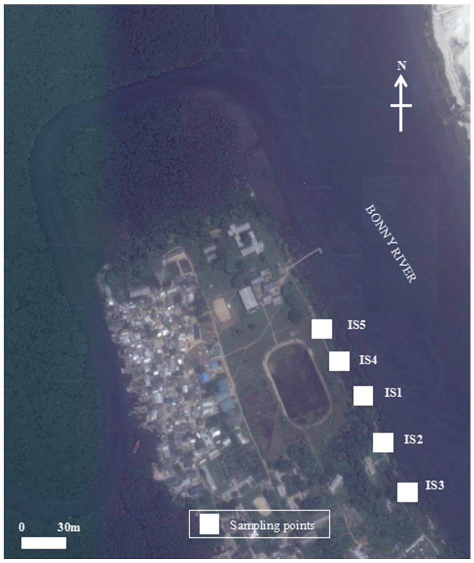

Figure 4.Sampling points in Isaka mangroves.

Source: Google Earth (2018).

The surface sediment samples were collected using bucket auger. Sediment samples weighing about 200g were packaged in plastic bags in the field and stored in a cooler at 4^{o}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 Geoscience laboratory, Shimane University, Japan for analysis.About 50g of each sediment sample was oven dried at 160^{o}c for 48 hours. The dried samples were ground for 20 minutes using automatic agate mortar and pestle grinder. Then, about 5g of each of the powdered sediment samples were compressed into briquettes using a force of 200kN for 60s.

3.2 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%.

3.3 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^{o}C for 4 hours. Net weight loss was used to calculate the gravimetric LOI.

3.4 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.

4. Results and Discussion

4.1 Sediment Characteristics

The surface sediment samples (0-2cm) 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 - 199mV for Choba; - 289 to 93mV for Ogbogoro and - 229 to - 15mV 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).

4.2 Concentrations of Elements in the Sediments

Trace element compositions of the surface sediments in New Calabar and Bonny rivers sampled at Choba, Ogbogoro and Isaka respectively are presented on Table1 in comparison with the UCC from Taylor & McLennan (1985). These elements had contrasting concentrations at different sampling locations as indicated by the box plot in Figure 5.

Table 1. Trace element geochemical compositions of surface sediments of New Calabar River at Choba; Ogbogoro and Bonny river at Isaka in Niger Delta, Nigeria

Area		Trace Elements (ppm)																		
		As	Pb	Zn	Cu	Ni	Cr	V	Sr	Y	Nb	Zr	Th	Sc	TS	F	Br	I	Cl	LOI (wt%)
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

The average concentrations of the trace elements obtained from the mangrove sediments in Choba shows 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 is TS>Cl>Zr>V>Cr>F>Sr>Zn>Ni>Br>Pb>I>Nb>Y >Sc>Cu>Th>As while the trend in Isaka is 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 are comparatively higher in Choba along the New Calabar 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 & 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 & 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 are higher in Choba, Ogbogoro and Isaka. The abundance of Pb was found to be higher in Choba and Ogbogoro. Though Th and Sc are 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 1).

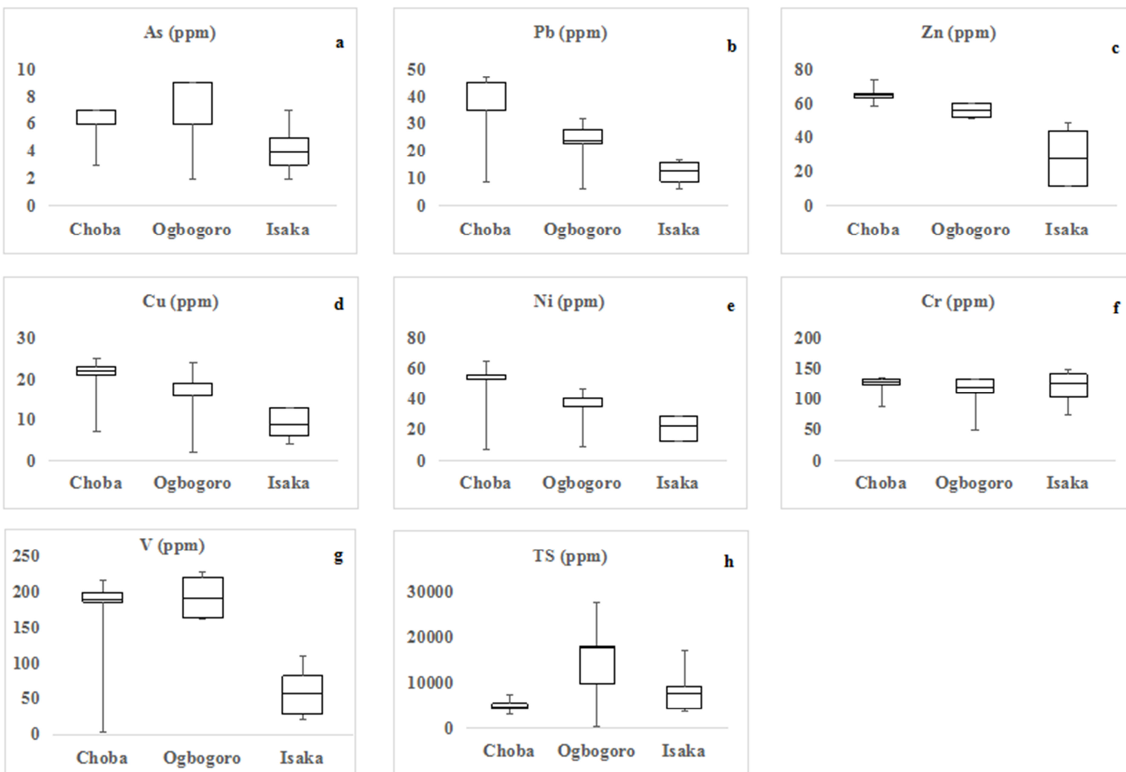

Figure 5**a-h**. Box plot summary of trace metal concentrations in surface sediments in New Calabar River at Choba; Ogbogoro and Bonny River at Isaka. Vertical lines of the plots indicate the range while boxes enclose 50% of data and illustrates the 25% quartile, median (horizontal bar) and 75% quartile

Table 2. Major element geochemical compositions of surface sediments of New Calabar 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	5.00	0.08	4.20	0.16

Table 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 6).

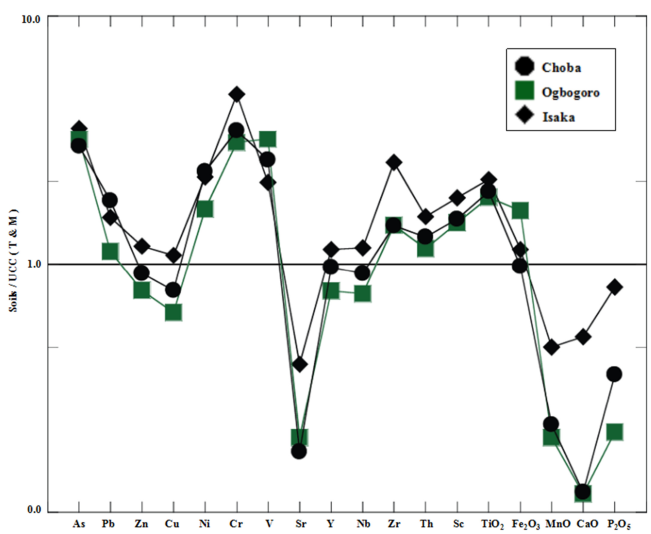

Figure 6. Comparison of concentrations of trace and major elements in Choba, Ogbogoro and Isaka. All values were normalized to the UCC values of Taylor & McLennan (1985).

4.3 Inter-element Relationship

Table 3. Correlations between elements in mangrove sediments in Choba, Ogbogoro and Isaka

	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

	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

	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

Table 3 shows the correlation matrix for elements in the Choba, Ogbogoro and Isaka mangrove sediments. 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_3diagrams (Figure 7) show the behaviour of element correlations with Fe_2O_3in 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/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 & 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.

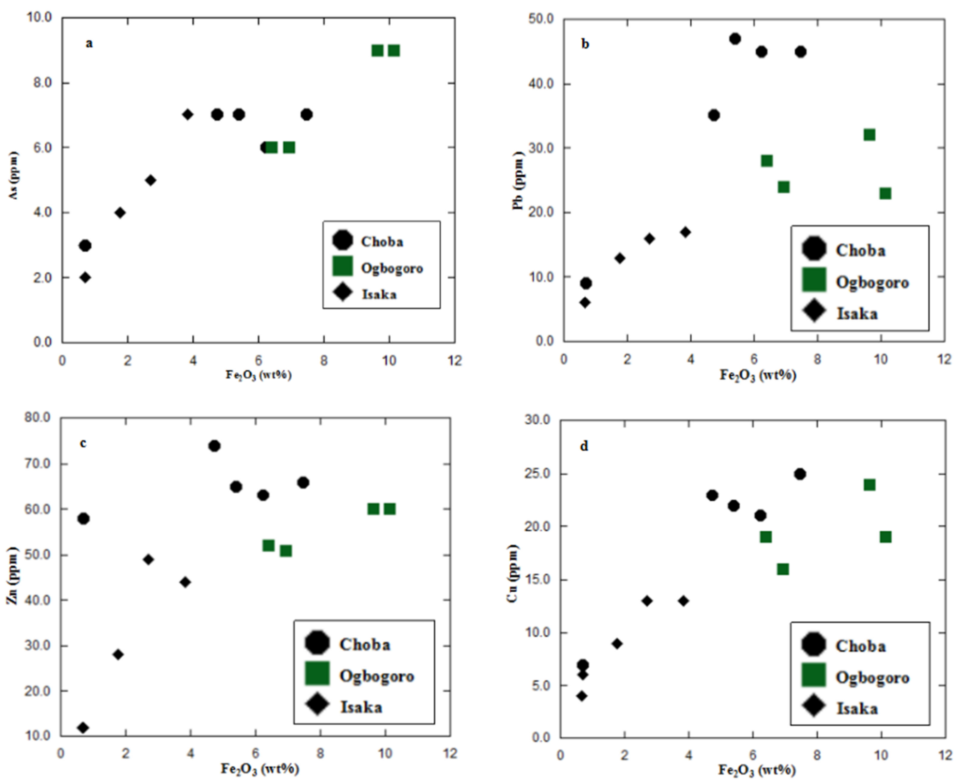

Figure 7 **a-d**. Correlations between Fe_2O_3 and As, Pb, Zn and Cu in Choba, Ogbogoro and Isaka

4.4 Comparison of Metal Concentrations with Sediment Quality Guidelines

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 4. 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;NYSDEC1999)

[2]Severe effect level (SEL;NYSDEC1999)

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

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

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 suggests 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.

5. Conclusions

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.

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