EVALUATION OF TRACE ELEMENTS IN THE SEDIMENTS OF INTERTIDAL ZONE AROUND MAHIN-UGBO AREA, SOUTHWESTERN NIGERIA

Asowata, I. T.*, Bamisaiye, O. A. and Akinwale, J.

Department of Applied Geology, Federal University of Technology, Akure, Nigeria. Corresponding Author's Email: itasowata@futa.edu.ng (Received: 28th February, 2023; Accepted: 29th July, 2023)

ABSTRACT

This study assessed the spatial distribution of Trace Elements (TE) in the muddy sediments of the Mahin-Ugbo coastal area of Southwestern Nigeria, using Inductively Coupled Plasma-mass spectrometry, (ICP-MS). The physicochemical parameters (pH, EC and TDS) of the sediments were also determined. Results showed that the mean values for pH, E.C and TDS were 5.09, 153.6 μ s/cm and 76.8 mg/L, respectively. Further, there was a varying distribution pattern of TE concentrations: Mn> Zn > Ba > Cr > V > Sr > Pb > La > Cu > Ni > Co > As > Th > Sc > Ga. The As, Pb, and Zn concentrations in the sediment with mean values of 11.2, 40.4 and 122.1 ppm, respectively, were significantly higher than the average concentrations of As (10 ppm), Pb (20 ppm) and Zn (90 ppm) in natural shale, suggesting anthropogenic TE enrichment in the study area. To corroborate this, the TE source apportionments in the sediments using correlation coefficient, bi-variant plots and principal component analyses showed that the TE enrichment may have been anthropogenically induced. Pollution status assessments using I-geo, contamination factors and pollution load index indicated that the study area's sediments is slightly to moderately polluted. These findings suggest that although the area is not heavily polluted, increasing human activities, from inland rivers to the coastal area, in the study area will in no time be a cause for concern.

Keywords: Muddy sediments, Pollution, Intertidal, Coastal, Contaminant.

INTRODUCTION

Intertidal sediments that build up over time in the coastal areas are interesting geomaterials that promote the growth of flora and fauna in the coastal and marine ecosystems. The understanding of the enrichment level, distribution pattern, and source of trace elements in this important environment is, no doubt, very important. Globally, trace elements are considered the foremost anthropogenic contaminant in coastal/intertidal and marine environments (Naser, 2013). Trace elements pose a serious threat to human health and aquatic animals because of their toxicity, bioaccumulation, and persistent behaviour, when they get enriched in the environment beyond the tolerable limit (De Forest et al., 2007; Fu and Wang, 2011; Ozkan and Buyukisik, 2012). Over the years, coastal environment has received significant human population growth, as well as its attendant impacts in terms of erosion, flooding and pollution, especially in Nigeria (Dada et al., 2015, 2018, 2019; Nubi et al., 2022). In many coastal areas, the assessment of impacts associated with development around the coast has not been carried out in an orderly manner that rhymes with the relative dynamics of this important environment (Martínez *et al.*, 2017; Hagenlocher *et al.*, 2018).

Anthropogenic inputs that result from human population growth have been found to alter the natural physical and chemical characteristics of the coastal environment (Yi *et al.*, 2018; Dada *et al.*, 2019; Liu *et al.*, 2019). Added to these effects is the connectedness of the coastal areas with the terrestrial and marine environment whereby changes in both or either the terrestrial and/or the marine environment will affect the state of the coastal environment (Martínez *et al.*, 2017; Nubi *et al.*, 2022).

With these obvious dynamisms resulting from human population growth on the land and coast as well as in the marine setting, the need to understand the relative chemical changes in the sediments in this area become very important.

Globally, several studies have established the high enrichment level of some harmful and toxic elements in coastal areas, (Ashiru and Ogundare, 2018; Dada *et al.*, 2019, 2020). This is because this area serves as a sink and repository of the influx of hinterland-contaminated sediments, which are a resultant effect of the increased human population, industrial, among others (Ajani *et al.*, 2015; Dada *et al.*, 2020). This is further complicated by the effect of climate change on human activities in the coastal environment (Ashiru and Ogundare, 2019; Asowata and Akinwumiju, 2020; Osinowo and Popoola, 2021).

The Ugbo-mahin coastal area in southwest Nigeria is essentially built-up by sediments from the hinterland with varying chemical characteristics that may have been influenced by anthropogenic activities (Ashiru and Ogundare, 2018; Dada et al., 2019, 2020). This area is characterized by all-year-round marine transportation and agricultural activities which makes it a vital ecosystem that needs constant geochemical monitoring. Farmers are attracted to this area because water and organic nutrient in the estuary help increase the yield of their crops as well as their fish farming and other livestock farming activities. However, because of poor urban environmental best practices, the river system receives a considerable amount of waste, both industrial and domestic as well as mine tailings from the hinterland, which make the area becomes susceptible to trace element enrichment (Martínez et al., 2017). Some of the sources of these trace elements include waste from automobile by-products, and vehicular activities, which include the use of leaded gasoline, fertilizer application, animal faeces, domestic waste, such as sewage sludge as well as uncontrolled artisanal mining activities. All these wastes, drain from the land through the river body and get deposited in the area, (Odukoya and Akande, 2015; Olatunji and Ajayi, 2016; Adesina and Ogunseiju, 2017; Asowata and Olatunji, 2018; Rasiq et al., 2018).

Trace elements such as Pb, As, Zn, La, V, Ni, Cu, and Th, among others, can be transported and mobilized by the influence of weathering, water transitivity and microbial activities. These elements are largely concentrated in muddy clay fractions, possibly due to high adsorption capacity, redox conditions, pH, weather conditions such as rainfall, and microbes. Also, carrier phases of the clayey sediments can serve as factors that control the mobility and toxic effect of these trace elements in the sediments. Factors such as adsorption on oxides and hydroxides of Fe and Mn and grain sizes of earth materials also control the mobility of trace elements in such geo media (Ajao *et al.*, 1996; Wogu and Okaka, 2011; Etim and Adie, 2012; Ma *et al.* 2015; Yan *et al.*, 2017; Olatunji-Ojo *et al.*, 2019).

Pollution indices statistical tools have been used to evaluate the relative pollution status of most environmental media; these include, cluster analysis, principal component analysis, factor analyses, geo accumulation index, pollution load index and other related methods to infer potential sources of trace elements in muddy sediments and soil. These analyses can assist in knowing the source contribution and compositions of the analyzed geochemical data, whether geogenic or anthropogenic. Several studies have reported the source(s) and relative pollution status of the Nigerian Transgressive Mahin mud coast and suggested useful recommendations to relevant authorities on the need for continuous monitoring of these important parts ecosystem (Odukoya and Akande, 2015; Garba et al., 2015; Popoola et al., 2015 a,b; Udosen et al., 2016; Olatunji and Ajavi, 2016; Abiodun et al., 2017; Sahand et al., 2017; Ibanga et al., 2019; Nubi et al., 2022). Other also focused on diverse published works environmental issues confronting this section of the Nigerian coast (Popoola et al., 2015; Ashiru and Ogundare, 2019; Osinowo and Popoola, 2021, Dada et al., 2021; Adesina et al., 2020, 2022, 2023). The present study seeks to determine the enrichment level of selected trace elements (Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, V, La, Cr, Ba, Ga, and Sc), distribution patterns and possible ecological risks that are associated with these elements in the study area.

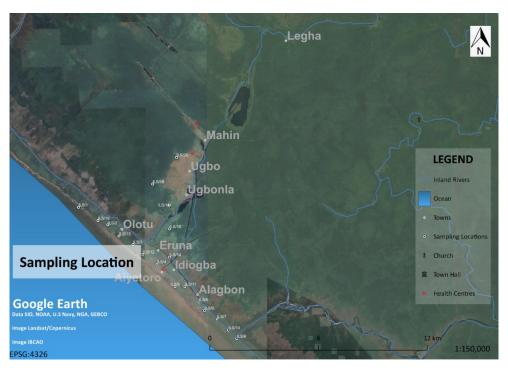


Figure 1: Study location map of the area.

STUDY AREA

The study area lies within the muddy portion of the east end of the southwest segment of the Nigeria coastline. It is generally referred to as the Mahin Transgressive mud coast (Dada et al., 2019; Adesina et al., 2020, 2022, 2023). The area also lies within the Benin flank of the Niger Delta Basin. Some of the settlements in the study area include Ugbo, Alagbo, Ugbeke, Ugbonla, Igbokoda, Ilegboro, among other towns. This area is bounded to the south by the Atlantic Ocean, while several inland rivers empty into the ocean around the study area. The area is characterized by freshwater marshes and swamps, connecting the creek swamps and lacustrine marshes (Ebisemiju, 1987; Mclean et al., 2001; Bale et al., 2007). The area is a morphologically undulating coast plain, rising from about 0.5 to 3 meters in height, above sea level, along the coastline, to between 35 to 55 meters as one moves toward the upland (Fasona et al., 2011; Olorunlana, 2013). The area falls within the tropical rainforest with highly humid conditions, where rainfall occurs between April to October and dry season of between November to March every year (Olorunlana, 2013). During the wet season, there are always strong winds of between 8 - 12 m/s, while mild winds and waves are experienced. Frequent intertidal wave that occur mostly during the rainy season, sometimes over run the area with relatively high tides resulting in flooding in the area (Olorunlana, 2013; Almar et al., 2015; Dada et al., 2018, 2019). In terms of the geology of the area, the study area falls within the Niger Delta Basin of Nigeria (Ebisemju, 1987; Reijers, 2011). However, the area is uniquely known to be overlying the Benin Formation with relatively thick mud that is characteristically transgressive. This mud grows into the Gulf of Guinea as one moves into the Atlantic Ocean (Wright et al., 1985). The general stratigraphy of the study area is uniquely different, from that of the Niger Delta Basin, which is characterized by the Akata, Agbada and Benin formations in stratified sequence. In this study area, the coastal plain sand that is essentially the lithology of the Benin Formation is overlaid with muddy clay of about 60 m in depth (Olorunlana, 2013, Dada et al., 2020).

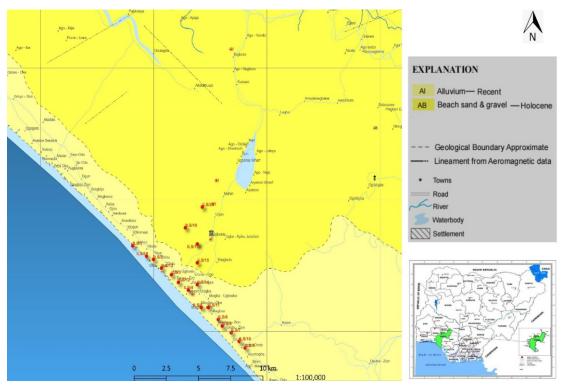


Figure 2: Geological map of the study area (NGSA, 2006).

MATERIALS AND METHODS

A total of 20 muddy sediment samples were collected along the creek river of Igbokoda, Mahin to Ayetoro area, Figure 1. The samples were collected at intervals of 100 m, using stainless steel grabber, from the boat. In every sample location, three (3) sub-samples were collected using the geochemical sampling protocol (Asowata and Olatunji, 2018). This sampling method was chosen to reduce the effect of localized contaminated sample results. The samples were collected both at the center and at the edges of the river channel. All samples were collected in plastic bottles and labeled accordingly. Similarly, all samples were collected with utmost care, in other to avoid sample contamination. After every sample is collected in a location, all materials used are either washed or completely discarded when necessary. The wet samples were allowed to dry over two weeks at a room temperature of 26 °C. The dried samples were sieved using 53 µm and stored in polyethylene sachet bags.

Physico-chemical analysis

A total of twenty (20) sediment samples were subjected to pH, Electrical conductivity (EC) and Total Dissolved Solid (TDS) analyses. Fifty (50) grams of sieved, air-dried samples were measured and transferred into a 250 mL beaker and 100 mL of de-ionized water was added into the samples in the beaker, stirred for some time, using a clean glass rod. After doing this for all the samples, they were allowed to stay for 48 h. This was done to allow for the proper dissolution of the sediment sample in the water. A handheld digital meter was used to measure pH, EC and TDS. Before the use of the meter, proper calibration was carried out on the instrument using the appropriate buffer solution at the geochemistry laboratory of the Department of Marine Science and Technology, the Federal University of Technology, Akure.

Geochemical analyses

A 0.5 g of each of the sediment samples (n = 20) were digested, using aqua regia. The digestion procedure involves gradual input of 5 mL nitric acid (Merck Suprapur 65%), with the addition of 2 mL hydrochloric acid (HCl) (Merck Suprapur 36%) and 10 mL of pure water of 18 m Ω /cm (specific resistivity) in an ultraclean tube. The samples were heated at 95 °C for 2 h, using a microwave oven. The samples were decanted into a 100 mL volumetric flask at the end of heating. The solution was then extracted using a disposable syringe filtered through a 0.45 filter membrane.

The digested samples were analyzed using Inductive Coupled Plasma – Mass Spectrometry (ICP-MS), AVIO200, PerkinElmer, MA USA model, for the trace elements Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, V, La, Cr, Ba, Ga, and Sc.

Quality control and assurance were carried out using reference materials, duplicate and blank samples analyses, as presented in Table 1. The outcome of the duplicate analysis showed very little deviation of between 1.00 - 0.1 ppm, in variation from each other. This suggests that the sensitivity, reproducibility, and precision are okay, reliable and acceptable. Similarly, the results of the standards and blank samples, as presented in Table 1, showed a very low deviation of 0.1 - 0.2. All standards and blank samples were classified and coded, based on the policy of the Bureau Veritas Commodities laboratory, (ACME), Canada.

								STD	STD	STD	STD		
		ILS13	ILS13	ILS5	ILS5	ILS20	ILS20	DS11	OREAS262	DS11	OREAS262	BLK	BLK
		Sed.		Sed.									
TE	MDL	Pulp	REP	Pulp	REP	REP	REP	STD	STD	STD	STD	BLK	BLK
Cu	1	23	23	14	14	19	20	150	122	148	119	<1	<1
Pb	3	22	23	17	18	19	19	139	57	139	55	<3	<3
Zn	1	72	72	74	74	56	55	343	157	337	154	<1	<1
Ni	1	26	26	18	18	22	21	79	65	77	63	<1	<1
Со	1	17	17	13	12	17	17	14	28	13	27	<1	<1
Mn	2	1011	997	225	221	1113	1110	1023	555	1025	547	<2	<2
As	2	15	15	5	5	13	12	45	39	43	38	<2	<2
Th	2	12	12	8	8	12	12	6	8	9	9	<2	<2
Sr	1	51	51	33	30	33	31	65	37	63	36	<1	<1
V	1	70	69	31	30	62	60	48	21	48	21	<1	<1
La	1	45	45	26	27	44	44	16	15	16	14	<1	<1
Cr	1	88	87	47	45	49	51	56	41	56	40	<1	<1
Ba	1	58	58	86	84	55	54	429	269	414	256	<1	<1
Ga	5	10	11	5	5	10	9	<5	<5	<5	<5	<5	<5
Sc	5	10	10	9	9	9	9	<5	<5	<5	<5	<5	<5

Table 1: Quality control data for trace elements of the sediments in the study area.

Abbreviations: BLK = Blank Samples, STD = Standards, REP = Replicate, MDL = Minimum Detection Limit, TE = Trace Elements, ILS = code to the sample numbers representing Ilesha

Assessment of pollution status of trace element in the study area

Pollution Load Index (PLI) and Contamination Factor (CF)

The pollution status of the samples were evaluated by computing the Pollution Load Index (PLI) of the selected trace elements. Before the computation of PLI, the contamination factor (CF) was first computed, by dividing the concentration of the metal in the geologic media by the background values of the metal (Rabee *et al.*, 2011).

Contamination Factor (CF) = Metal concentration in sediments/background values of metal

i.e. $CF = C_{metal} / C_{background} \dots Equation 1$

The CF values were interpreted based on Hakanson classification (1980), thus:

- \blacktriangleright Cf < 1: Low contamination factor,
- >1 ≤ Cf < 3: Moderate contamination factor,</p>
- > $3 \le Cf < 6$: Considerable contamination factor,
- → $-Cf \ge 6$: Very high contamination factor.

The PLI values were obtained, according to Tomilson *et al.* (1980), by applying the formula:

Pollution Load Index (PLI) = $(CF_1^* CF_2^* CF_3 \dots CF_n)^{1/n} \dots$ Equation 2

Where the PLI value is greater than 1 i.e. (PLI > 1), the sample is considered polluted whereas if the

PLI < 1, the sample is unpolluted (Chakravarty and Patgiri, 2009).

Geo-accumulation index (Igeo)

Similarly, the analytical data were further evaluated for pollution status quantification based on the geo-accumulation index (Igeo) (Muller, 1979) using the formula:

Igeo = $\log_2 (Cn / 1.5Bn)$ Equation 3

RESULTS AND DISCUSSION

The result of the physico-chemical properties of the sediments in the study area is presented in Table 2. From the results of the temperature in (°C), it ranges from 25.57 to 26.46 at a mean temperature of 26.20. The average temperature was found to be far lower than the average tropical temperature of > 40 °C as reported by World Health Organization 1997. This suggests that the area at the time of temperature reading had a relatively low temperature. The pH reading ranged from 3.7 - 5.91 at a mean value of 5.095. The relatively slightly acidic pH values suggest the effect of decomposing anthropogenic activities, such as petroleum product discharge, and domestic and industrial wastes (Olatunji and Ajayi, 2016; Asowata and Olatunji, 2018). This pH reading was found to be lower compared to the 6.1 - 9 pH reading reported by Nkwoji et al. (2016). Varying concentration of Electrical conductivity (EC) in μ S/cm was also recorded in the sediments studied, ranging from 23 to 404, with a mean value of 153.6 and a standard deviation of 115.67. The relatively low to moderate EC values may be because of coastal wastes, which may have reduced the decomposing anthropogenic materials. Similarly, the values of the Total Dissolved Solid (TDS) in mg/L ranged from 13 to 202, with a mean value of 76.8 and a standard deviation value of 57.65. Locations with relatively lower TDS suggest low concentrations of dissolved solids, while locations with relatively higher TDS, suggest higher input of dissolved solids which may be caused by the effect of waste disposal run-off, being carried by the inland rivers that drain the area.

Trace elements distributions in the sediments of the study area

The summary of the selected trace element concentrations in the sediments analyzed is presented in Table 3. These elements include Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, V, La, Cr, Ba, Ga, and Sc.

Copper (Cu) in ppm, ranged from 14 to 175, with a mean value of 30.4 and a standard deviation of 34.6. A considerable level of Cu enrichment was found in location ILS/1 (175 ppm) while other locations with relatively low concentrations of Cu include ILS/2 (26 ppm), ILS/5(14 ppm) and ILS/3 (18 ppm). It was generally observed that Cu is significantly lower in over 95% of the sample locations.

Lead (Pb) concentration (in ppm) ranged from 17 to 376, with a mean value of 40.4 and a standard deviation of 77.5. Pb concentration was relatively high in ILS/1 (376.0 ppm). Locations with relatively lower concentration of Pb include ILS/12 (17 ppm), ILS/17 (19 ppm) and ILS/9 (18 ppm) among other locations. It was also observed that the Pb concentration is significantly low in over 90% of the samples analyzed.

Zinc (Zn) concentration (in ppm) ranged from 47 to 782, with a mean value of 122.1 and standard deviation of 159. Locations with relatively high concentration of Zn include ILS/1 (782), ILS/14 (235), ILS/16 (172) and ILS/19 (188). Locations with relatively low concentration of Zn include ILS/3 (47), ILS/12 (56) and ILS/18 (50), among other locations. It was observed that about 65% of the sample locations were relatively low in Zn concentration.

As concentration (in ppm) in the sediments ranged from 3 to 21, with a mean value of 11.2 and a standard deviation of 4.9. Location ILS/4 (21 ppm) recorded the highest concentration of As. Other locations with relatively high concentration of As include ILS/5 (16), ILS/19 (16) ILS/10 (16) and ILS/13 (15). Locations with a relatively low concentration of As include ILS/11 (3), ILS/15 (4), among other locations. It was observed that the As content was considerably high in over 70% of the analyzed samples, and was greater than 10 ppm. This suggests that the sediments of the IlajeUgbo-Mahin area are considerably high in As concentration. The other elements were observed

to vary in concentration from one location to the other as presented in Table 2.

Variables	Mean	Max	Min	STDV
Temp. (°C)	26.20	26.46	25.57	0.28
рН	5.095	5.91	3.7	0.71
Elect. Cond (µs/cm)	153.6	404	23	115.67
TDS (mg/L)	76.8	202	13	57.65

Table 2: Results of the physico-chemical properties of sediments in the study area.

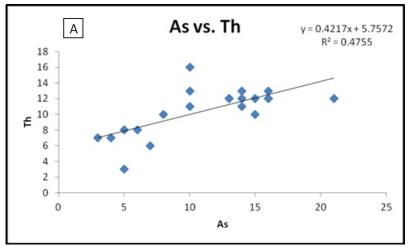
Table 3: Summary results of the trace elements concentration in the sediments of the study are	Table 3: Summar	v results of the	trace elements c	concentration i	in the	sediments	s of the stud	varea.
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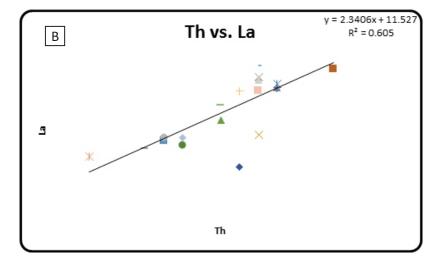
Elements	Min	Max	Mean	Stdv
Cu	14.0	175.0	30.4	34.6
Pb	17.0	376.0	40.4	77.5
Zn	47.0	782.0	122.1	159.0
Ni	14.0	31.0	21.8	4.6
Со	6.0	23.0	14.9	3.7
Mn	142.0	1498.0	682.5	441.6
As	3.0	21.0	11.2	4.9
Th	3.0	16.0	10.5	3.0
Sr	18.0	55.0	40.6	9.7
V	30.0	104.0	56.0	17.9
La	20.0	48.0	36.0	9.0
Cr	35.0	128.0	64.4	20.9
Ba	50.0	278.0	84.9	53.8
Ga	5.0	10.0	7.4	1.5
Sc	5.0	10.0	8.0	1.7

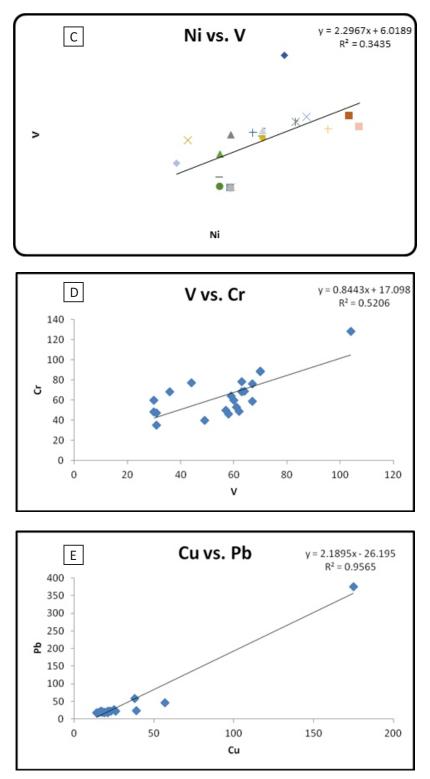
Inter-elemental relationship

The relative elemental association was analyzed using the Pearson correlation coefficient, coefficient of determination and principal component analysis. These were carried out in other to know the possible enrichment source (s) of these elements in the sediments studied. For the Pearson Correlation analysis (\mathbf{R}^2) as shown in Figure 3 (a-f), the bi-variant correlation between As and Th showed a relatively fair correlation ($R^2 =$ 0.4755); Th and La showed a strong correlation $(\mathbf{R}^2 = 0.605)$; Ni and V exhibited weak correlation of ($R^2 = 0.3435$). Similarly, V and Cr were found to have a fair correlation ($R^2 = 0.5206$). However, there was a very strong correlation between Cu and Pb ($R^2 = 0.9565$) as well as between Zn and Pb $(R^2 = 0.9282)$. Elements that showed a fair to very strong correlation relationship suggest that such associated elements may have been enriched in the sediments of similar source (s), whereas elements that showed weak to very weak association apparently imply that these elements are not from similar sources of enrichment. In the case of the correlation coefficient matrix (r), as presented in Table 4, varying degrees of correlation were exhibited by the selected elements being studied. The relative variational correlation ranged from very weak correlations as seen between Co/Cu (-0.17), As/Pb (-0.020), As/Zn (0.08), Th/Cu (0.03) among others, to very strong correlations as seen in Cu/Pb (0.98), Cu/Zn (0.98), Zn/Pb (0.96), Co/Ni, (0.82), Mn/Ni (0.66), among others (Table 4). Elements that exhibited relatively weak to very weak correlations suggest that these elements may not have similar origin, while those elements that showed fair to very strong association or correlations, may have been enriched by similar source (s).

The trace elements were further analysed using Principal Component Analysis, veromax laiser normalisation method. From the results, a total of three (3) factors with an eigenvalue greater than 1, which accounted for over 84% of the data variability were extracted and considered appropriate (Table 5). The first factor is Cu, Pb, Zn Ba, Cr and V, accounting for 34.50%. Cumulative %. These elements may have been enriched by scavenging activities as well as possibly by lithophile-silicate minerals that are transported and deposited from the basement complex, which is about 40 km away. In the second factor, Th, Sc, V, As, La, Mn and Ga, accounted for 31.9% of the variation and 66.40 cumulative %. These elements may have been associated with the clayey mud that underlies the study area. While in the third factor, Mn, Co, Ni, Sr, and Ga, had an eigenvalue of 19.37 and a cumulative of 35.77%. Their association suggests that enrichment in the sediments is from similar sources, apparently from anthropogenic sources.







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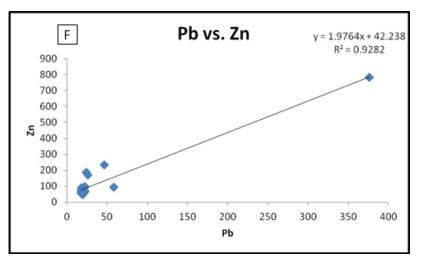


Figure 3 (A-F): Bivariant plots of some selected trace elements in the sediments of the study area.

	Cu	Pb	Zn	Ni	Со	Mn	As	Th	Sr	V	La	Cr	Ba	Ga	Sc
Cu	1														
Pb	0.98	1.00													
Zn	0.98	0.96	1.00												
Ni	0.16	0.09	0.19	1.00											
Со	-0.17	-0.22	-0.15	0.82	1.00										
Mn	0.32	0.33	0.28	0.66	0.62	1.00									
As	-0.01	-0.02	-0.08	0.40	0.29	0.36	1.00								
Th	-0.03	0.02	-0.10	0.56	0.50	0.70	0.69	1.00							
Sr	0.42	0.35	0.46	0.57	0.46	0.39	0.18	-0.04	1.00						
V	0.58	0.60	0.52	0.59	0.30	0.80	0.61	0.73	0.36	1.00					
La	-0.44	-0.44	-0.48	0.59	0.67	0.52	0.60	0.78	0.03	0.41	1.00				
Cr	0.63	0.67	0.63	0.47	0.13	0.58	0.12	0.35	0.43	0.72	0.01	1.00			
Ba	0.89	0.86	0.88	-0.09	-0.27	0.03	-0.34	-0.37	0.36	0.20	-0.71	0.44	1.00		
Ga	-0.23	-0.25	-0.22	0.59	0.53	0.47	0.38	0.41	0.17	0.36	0.72	0.17	-0.48	1.00	
Sc	0.11	0.11	0.05	0.70	0.57	0.78	0.70	0.89	0.22	0.83	0.82	0.43	-0.29	0.61	1.00

Table 4: Correlation coefficients of trace elements in the analysed sediments of the study area.

Elements	1	2	3
Cu	0.99	0.04	0.01
Pb	0.98	0.08	-0.08
Zn	0.98	-0.05	0.08
Ba	0.90	-0.37	-0.04
Cr	0.70	0.36	0.26
Th	-0.05	0.95	0.12
Sc	0.06	0.91	0.35
V	0.56	0.79	0.21
As	-0.06	0.78	0.07
La	-0.49	0.75	0.40
Mn	0.31	0.66	0.49
Со	-0.20	0.33	0.85
Ni	0.12	0.46	0.82
Sr	0.44	-0.08	0.76
Ga	-0.29	0.49	0.54
Total	5.17	4.79	2.91
% of Variance	34.50	31.90	19.37
Cumulative %	34.50	66.40	85.77

 Table 5: Principal component analysis of the studied sediments.

The results of the mean concentration of the determined trace elements in this study were further compared with the mean concentration of trace elements in selected studies in Nigeria and beyond.

From the results, the mean concentration of Cu in this study (30.4 ppm) was found to be higher than the mean results from Southwest River Basin (17.2 ppm; Lapworth, 2012) and Lagos Coastal Stream Sediments (9.99 ppm; Odukoya and Akande, 2015). However, the mean elemental concentration of the present study was significantly lower than the mean from the Ndemili River (64.42 ppm; Asowata, 2017) by two folds as well as the average shale concentration of Cu (50.0ppm; Turekian and Wedepohl, 1961), and for others presented in Table 6.

The mean concentration of Pb in this study (40.4 ppm) was found to be higher than the mean concentration of Lagos Coastal Stream Sediments (9.73 ppm; Odukoya and Akande, 2015), Lagos lagoon Sediments (20.27 ppm; Olatunji and Abimbola, 2010), Average Share Concentration, (Turekian and Wedepohl, 1961) at (20.0 ppm) and Southwest River Basin sediments (36.3 ppm; Lapworth *et al.*, 2012). But the mean concentration of Pb in this study was significantly lower than the mean result of Ndemili stream sediment (106.95 ppm; Asowata and Olatunji, 2018) Nkisi stream sediment (50.0 ppm; Asowata and Olatunji, 2018) and Akure (Ala) Stream sediments (56.67 ppm; Asowata *et al.*, 2015).

As shown in Table 6, there was a relatively higher mean concentration of As in the sediments of this study (11.2 ppm) compared to the mean value for Average Share Concentration (10.0 ppm; Turekian and Wedepohl, 1961) and the other works used for comparison, except for Nkisi River, (11.4 ppm; Asowata and Olatunji, 2018). Similar variations in the mean concentration of the other selected trace elements compare to the published works were presented in Table 6. The fact that some of the trace elements in sediments of the present study showed significant mean concentration enrichment higher than those of previous studies in major cities of Nigeria suggests that of the present study area has received significant loads of trace element enrichment to a level of concern, suggesting that the effect of anthropogenic activities has to a great extent affected the area.

	This								
Elements	study	А	В	С	D	Е	F	G	Н
Cu	30.4	64.42	37.6	34.75	53	36.04	50	17.2	9.99
Pb	40.4	106.95	50	56.67		20.27	20	36.3	9.73
Zn	122.1	482.15	263.5	257.08	110	72.33	90	65	95.21
Ni	21.8	18.73	10.7	14.45	130	12.66	80	19	3.3
Со	14.9	7.19	3.9	26.18	70	9.52	20	15	2.93
Mn	682.5	282.2	443.6	1221.31	70	494.98	850	779	126.1
As	11.2	5.02	11.4	0.6		2.99	10	1.61	0.99
Th	10.5	24.55	14.7	12.06	25.5	3.29	12	65.6	2.16
Sr	40.6			46.9	183	31.43	400	150	11.94
V	56.0	84.6	111.8	79.77	128	33.64	130	86.1	10.98
La	36.0	24.55	14.7	48.63	70.8	26.97	40	171	5.91
Cr	64.4	54.62	53.6	41.77	310	31.52	100	72.9	12.55
Ba	84.9				777	37.81	600	773	25.29
Ga	7.4	12	13.56		27	6.8	25	14.9	1.32
Sc	8.0	6.93	9.49			4.7	15		1.63

Table 6: Comparison of the determined trace elements in this study with those in previous studies.

A- NdeMili River (Asowata, 2017)

B- Nkisi River (Asowata, 2017)

C- Akure stream sediments (Asowata et al., 2015)

D- Geregu River sediments (Adiotomre, et al. 2017)

E- Lagos lagoon (Olatunji and Abimbola, 2010)

F- Average Share Concentration (Turekian and Wedepohl, 1961)

G- Southwest River Basin Sediments (Lapworth, et al., 2012)

H- Lagos Coaster Stream Sediments (Odukoya and Akande, 2015)

The results of the trace elements were further analyzed, using the contamination factor equation as presented in Equation 1 in the methodology session. From the results, it was observed that a significant amount of the elements falls under low contamination status (Table 7 and Figure 4). More than 70% of the trace elements result indicated low contamination factor, while about 27% were moderately contaminated and less than 1% highly contaminated. Only a location showed considerable contamination factor for Cu (Figure 4). Similarly, Pollution Load Index (PLI) indicated unpolluted since they were <1. According to Chakravarty and Patgiri (2009), when the PLI is <1, it suggests that the area is apparently unpolluted.

The results of the geo accumulation index (I-geo), as presented in Figure 5, showed that most of the elements exhibited uncontaminated to moderately contaminated. From the results, Cu Igeo showed that 85% of the samples analyzed ranged from practically uncontaminated to moderately contaminated. While about 15% of the samples

fell under moderately contaminated to strongly contaminated.

For Pb, about 70% of the sample locations revealed uncontaminated to moderately contaminated, while about 25% showed moderately to strongly contaminated. Only at 1 location, 5% of the samples locations fell under strongly contaminated. This suggests that this area is not seriously contaminated with Pb, apart from that very location.

For Zn, the Igeo result showed that only 5% (1 location) strongly exhibited contamination as against the remaining 95% of the locations that fell between uncontaminated to moderately contaminated. This suggests that, apparently, this study area is not strongly contaminated with Zn elements. The other selected elements also showed varying Igeo values, as presented in Figure 5. Generally, the results of Igeo for most of the selected trace elements were essentially moderately contaminated.

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Table 7: Contamination factor and pollution load index results of trace elements in the sediments of the study area.

Cu	Pb	Zn	Ni	Со	Mn	As	Th	Sr	V	La	Cr	Ba	Ga	Sc	PLI
3.50	18.80	8.69	0.30	0.60	1.65	1.00	0.92	0.14	0.80	0.50	1.28	0.46	0.24	0.60	0.97
0.52	1.10	0.72	0.38	1.15	1.76	1.00	1.33	0.10	0.54	1.18	0.89	0.15	0.32	0.67	0.97
0.36	0.95	0.52	0.24	0.55	0.68	1.00	1.08	0.07	0.46	1.05	0.60	0.08	0.24	0.60	0.97
0.76	2.90	1.04	0.19	0.45	0.18	2.10	1.00	0.08	0.44	0.73	0.50	0.17	0.20	0.47	0.95
0.42	1.10	0.79	0.31	0.85	1.09	1.60	1.08	0.13	0.52	1.08	0.76	0.09	0.28	0.60	0.97
0.28	0.85	0.82	0.23	0.65	0.26	0.50	0.67	0.08	0.24	0.65	0.47	0.14	0.20	0.40	0.94
0.38	0.95	0.66	0.26	0.90	1.40	1.40	1.08	0.09	0.47	1.05	0.53	0.09	0.28	0.60	0.97
0.44	1.10	0.80	0.31	0.80	0.95	1.40	1.00	0.12	0.52	1.10	0.59	0.10	0.36	0.60	0.97
0.42	0.90	1.02	0.23	0.70	0.25	0.70	0.50	0.13	0.28	0.63	0.68	0.19	0.24	0.50	0.95
0.38	0.90	0.66	0.28	0.80	0.24	1.60	1.00	0.07	0.45	1.10	0.46	0.09	0.32	0.60	0.97
0.34	1.10	1.09	0.24	0.70	0.27	0.30	0.58	0.10	0.23	0.68	0.60	0.18	0.24	0.33	0.93
0.30	0.85	0.62	0.23	0.65	0.84	0.80	0.83	0.08	0.38	0.83	0.40	0.09	0.28	0.47	0.95
0.46	1.10	0.80	0.33	0.85	1.19	1.50	1.00	0.13	0.54	1.13	0.88	0.10	0.40	0.67	0.97
1.14	2.30	2.61	0.24	0.65	0.17	0.50	0.25	0.12	0.24	0.58	0.35	0.29	0.24	0.33	0.93
0.34	1.10	1.10	0.24	0.70	0.25	0.40	0.58	0.10	0.23	0.70	0.48	0.18	0.28	0.33	0.93
0.50	1.30	1.91	0.35	0.90	0.83	1.40	0.92	0.12	0.48	1.03	0.78	0.10	0.36	0.60	0.97
0.42	1.05	0.73	0.28	0.85	1.13	1.30	1.00	0.12	0.48	1.20	0.68	0.09	0.36	0.67	0.97
0.34	0.95	0.64	0.28	0.80	1.20	1.50	0.83	0.12	0.45	0.93	0.64	0.10	0.32	0.53	0.96
0.32	1.00	0.56	0.18	0.30	0.26	0.60	0.67	0.05	0.34	0.70	0.77	0.11	0.32	0.40	0.94
0.78	1.20	2.09	0.39	0.90	0.94	1.60	1.00	0.12	0.49	1.03	0.69	0.10	0.36	0.60	0.97
0.38	0.95	0.62	0.28	0.85	1.31	1.30	1.00	0.08	0.48	1.10	0.49	0.09	0.40	0.60	0.97
-0.81	0.51	7.08	-1.28	0.35	0.97	0.96	0.58	-3.01	-0.48	0.72	-0.44	-2.86	-0.74	-0.15	-0.88

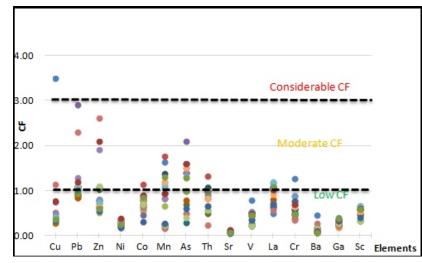


Figure 4: Contamination factor results of trace elements in the study area.

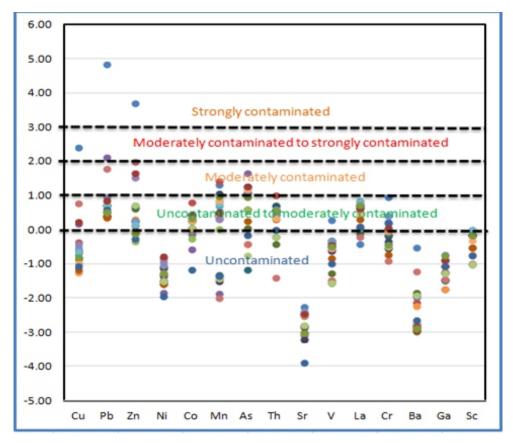


Figure 5: Geo accumulation index results of trace elements in the studied sediments

CONCLUSION

The muddy Mahin- Ugbo transgressive coastal area has been studied for trace elements concentration. These elements include Cu, Pb, Zn, Ni, Co, Mn, As, Th, Sr, V, La, Cr, Ba, Ga, and Sc. The TE concentrations decreased in this order: Mn > Zn > Ba > Cr > V > V > Sr > Pb > La > Cu> Ni > Co > As > Th > Sc Ga. Elements such as As, Ba, Pb and Zn were found to be relatively high, while the other trace elements were relatively low. It was observed that s As, Zn, Cr and Sc, among others, were significantly higher in the sediments being studied than most of the mean concentration used for comparison. The relatively higher mean concentrations of these elements compared to the referenced samples suggests that the study area has received significant quantities of these elements to a level of environmental concern. While other elements such as Pb, Mn, Th and La, among others showed relatively low concentration in their mean level, their presence in significant quantities also calls for concern. Since the enrichment of these elements take place over time, with time, their concentration might reach a level of harmful status in the environment.

Results from correlation analyses, using Pearson correlation, coefficient of determination and PCA showed varying elemental associations that suggest that some of the elements analyzed are analogous, that is from the same sources of enrichment, essentially as a result of human induced activities. While some other elements showed geogenic sources. The level of enrichment of these selected elements from Igeo, CF and PLI showed that some of the elements in this study area are slightly to moderately contaminated, while some of the elements have not in any way reached contamination level of concerns.

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