

Trace Metal Concentrations, Site Variations and Partitioning Pattern in Water and Bottom Sediments from Coastal Area: A Case Study of Ondo Coast, Nigeria

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Abstract: The observed trend in the investigation of the fate of trace metals in the water and bottom sediments of the Ondo coastal area revealed how domestic waste disposal, oil exploration and agricultural activities can create potential hazard to the ecosystem. Samples of water and bottom sediments collected and analysed for 12 metals: As, Cd, Cr, Co, Fe, Ni, Mn, Mo, Pb, V, Sn and Zn, showed elevated concentration of these metals in the environment while, the enrichment factors calculated showed Fe as the most enriched metal. There were significant relationship between these metals and organic matter concentration in sediment samples. Site SW01, SW02 and SW06 had the highest enrichment of metals indicating pollution from anthropogenic sources and trans-boundary movement. The Principal Component Analysis (PCA) showed that Mn and Fe found to be abundant in both water and sediment were clearly from the geological structure of the area with minimal anthropogenic contributions. The partitioning and the Pollution Load Index (PLI) of the metals favour the accumulation of metals in the sediment phase. The observed relationships of the metals with organic carbon caused the association of the metals concentration with the sediment column but increased salinity and storm action are aiding increasing concentration of bioavailable metals in the water column creating potential hazard for the coast.

Key words: Trace metals, water, bottom sediment, principal component analysis, pollution load index and Ondo coast

INTRODUCTION

Trace metals and other highly toxic, persistent substances which, bioaccumulate in the food web (Maddock and Taylor, 1977) biotransform to toxic forms (Chau and Wong, 1977) and create health problems for man (Lewis, 1991), are increasing in the coastal water system due to deposit of human wastes in the coastal area (Fang *et al.*, 2006). The environmental situation of coastal area globally is therefore, increasingly deteriorating with these depositions of contaminants from anthropogenic sources which thus, elevate the concentration of nutrients, organic pollutants and trace metals (Kennish, 1997; Bothner *et al.*, 2002). There are increasing global concerns over this because of the possibility of trans-boundary movement of these contaminants across coasts; increased water scarcity and competition for clean water; loss of biodiversity and adverse effects on the ecosystem and man. Hence, there is the need for efficient, equitable and sustainable water resource management, planning and policies for the coastal waters.

The coastal area of Ondo state, located in the Niger Delta area of Nigeria is not free from this global problem.

It has over 50 settlements dispersed within 2 local government areas close to the coast and there is none existence of any waste treatment plant or any pollution monitoring programme in the area. All domestic wastes are directly discharged untreated into the water. Pollutants are also introduced into the coastal area by agricultural practises, atmospheric precipitation, roof and urban runoffs, soil leaching, seawater intrusion, water transportation means and oil exploration.

Areas with such discharge of wastes into the coastal system around the world have been reported to have high concentration of trace metals and other persistent contaminants of high risk to the ecosystem and human health (Bothner *et al.*, 1998, 2002; Dhage *et al.*, 2006; Langston, 1990; Long *et al.*, 1995; Chapman *et al.*, 1996; Pearson, 1987; Rodger *et al.*, 1991). There is therefore, a high possibility that the area under this study is polluted with trace metals and other pollutants since there is none existence of any pollution control or remediation programme in the area. However, the toxicity of such contaminants is largely dependent on the water chemistry and the sediment composition of such system.

To the best of our knowledge, limited works have been reported on the water chemistry and biogeochemical reactions effects metal constituents of coastal area particularly in developing world. An earlier research (Asaolu *et al.*, 1997) did only investigate concentration of few metals in some river tributaries of this study area. Hence, there are no data, which could have served as baseline for the determination of Enrichment Factor (EF) in the normalisation of the contaminants against background concentration. However, the EF will be calculated relative to the metal concentration at a selected background control site (Liu *et al.*, 2005; Fang *et al.*, 2006). This study therefore, serves as a baseline study of metals in the water and sediments from the estuarine points of Ondo Coastal area as an indication of the pollution status of the area.

Therefore, this study is aimed at investigating the effects of the anthropogenic activities, biogeochemical reactions and geological structure on the concentrations, site variations and the partitioning (i.e., environmental fate) of trace metals in the water and sediments across the different sites in the coast to understand the nature and extent of pollution; the health risk that arise from such parameters on coastal areas.

MATERIALS AND METHODS

Study area: The coastal region of Ondo State, Lat. 5°50'-6°20'N and Long. 4°40'-5°05'E (Fig. 1) at the Ilaje Local Government area of the South-western part of Nigeria, was the study area. The surveyed catchments have a total area of over 500 km² and a watershed of over 2,500 km transverse by river tributaries (Ondo State Surveys, 1998). The population of the state is about 3 million people and a population growth rate of about 2.2% (NPC, 1991). The mean annual temperature of the area is 26.8°C. The economic activities in the area include agricultural practises, oil prospecting and commercial activities carried out by motorboat transportation. The coast is close to the Bright of Benin in the Atlantic Ocean and is in-between Lagos coast and Delta Coast, which are highly industrialised and heavily populated.

This study selected 9 sampling sites as test sites and a background site (Fig. 1) for the survey. The choice of sampling points was based on the economic activities and nearness to possible sources of pollutant like oil exploration, agricultural activities, settlements and the exchange point into the Atlantic Ocean etc. Sampling site SW01 (Lat. 5°50'N, Long 5°04'E) is a crude oil prospecting area and site SW10 (Lat. 6°06'N, Long 4°48'E) is background site far from the estuary discharge point and industrial or domestic activities. Close to site SW10

however, are fishing activities. Sites SW02 is the discharge point of the coastal water into the Atlantic Ocean while, sites SW03-SW09 are near to settlements. The vegetation of the area is mainly mangrove forest with light scrubs and marshy areas. The salinity of the water (mean value 28.51) indicates intrusion of sea water into the coastal area due to tidal current and possibility of trans-boundary movement of pollutants between coasts.

Field sampling and preservation: Sampling facilities were washed with metal free detergent and tap water. Then, they were soaked in 0.1M HNO₃ for 24 h and rinsed in demineralised distilled water, covered and stored in polyethylene bags prior to use. All samplings were done by discrete grab method through a commercial motorboat and preserved at 4°C in an ice chest for transportation to the laboratory (about 300 km apart). Analyses of these samples were done immediately on returning to the laboratory. Samples of a litre each per sampling point were collected for determination of metals in water using High Density Polyethylene (HDPE) bottles and were preserved with 2 mL of conc. HNO₃/L to reduce the pH to below 2 and prevent precipitation of the metals. Samples used for the determination of Chemical Oxygen Demand (COD) were collected in separate HDPE bottles and kept below 4°C in an ice chest to arrest microbial activities. Sediments sampling were done, after water sampling, by the use of Van veen grab sampler and samples kept in aluminium foil. The period between sampling and analysis were however, kept between the recommended time by standard method for examination of water and wastewater (APHA, 1995).

Analytical method: The acid preserved water samples were agitated and digested to get the total metals. The digestions were done with addition of 5 mL -16 M HNO₃ (J.T. Baker) to the water sample with few boiling chips and evaporating to 20 mL. The light coloured, clear solutions were transferred into 100 mL volumetric flasks and made to mark with deionised water.

Sediment samples were air-dried naturally, ground and sieved to particle size <200 µm diameter. Known weights (about 1 g) were digested with mixture of 16 M HNO₃ (J.T. Baker) and 11.5 M HCl (Fisher trace metal grade) in a ratio 2:1. The resulting digests (filtrate) were made-up in 100 mL volumetric flasks with deionised water. The metals obtained were regarded and analysed as pseudo-total metal because not all the silicate phase present in the sediments were dissolved but filtered out with an acid washed filters (45 µm pore size). The digests used for Pb determination were obtained by the same process without including HCl in the digestion.



Fig. 1: Map of the coastal area of Ondo State and the sampling points

The analyses of As, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sn and Zn in the digested samples were done using Flame Atomic Absorption Spectrometer (AAS) buck scientific 205 model with direct air-acetylene flame method. Analysis of V and Mo were done with the same instrument but by direct nitrous oxide-acetylene flame method. Cr in both water and sediment samples was determined as Cr^{6+} .

All vessels used were acid washed while, blanks were analysed for all the processes. The blank concentrations were used for the correction of the contributions of metals from reagents or vessels used in the analyses. Also, reference materials from USA National Institute of Standards and Technology (NIST) Standards were subjected to same digestion and analytical procedures to measure accuracy, precision and ensure good quality control of the methods. Recovery of water samples was done by spiking standard solutions of the metals into some chosen samples. Blank analyses were all below 3% of the metals investigated while, the analysis of reference materials gave a recovery between 71-96% indicating further that the metals obtained in sediment digestion by our method were pseudo-total. The recoveries of the water sample analysis were between 92-104%. The analyses were done in triplicate to measure reproducibility of methods. Mean values are presented and the Standard Error of Mean (SEM) estimated at 95% confidence limit.

The determination of organic carbon (C_{org}) was done in the sediments using wet oxidation according to

Standard Methods (APHA, 1995). Chemical oxygen demand was used to measure organic matter in water samples. Potassium dichromate oxidation in open reflux method was used. Silver sulphate in conc. H_2SO_4 catalysed the reaction and mercuric sulphate was used to mask chloride in the reaction matrix. All reagent used were analytical grade and analysis done in triplicate.

Data analyses: The concentration data obtained were compared with standards while, concentration and site variations were established with statistical analysis using ANOVA. Likewise, Dunnett-Equivalent Parametric Multiple Comparison (Dunnett, 1955; Steel, 1959) was used to establish the relationships of the metals with measures of organic matter (COD and C_{org}) and salinity indicating their influence on partitioning of metals, the trend of the water biogeochemistry and the anthropogenic contributions of metal contaminants. Further, Principal Component Analysis (PCA); a multivariate ordination technique was used to extract information on patterns and clusters of data (Flores and Navar, 2002). This helped us to appreciate association between these metals and to understand the possibility of them being contributed by the same source (s). The data analyses were performed using the KvPlot and SPSS softwares.

Partitioning of the each metal between the sediment and the water was determined by the modification of the equation proposed by Ball (1988, 1989):

$$K_d = \frac{\text{Conc. metal in sediment (mg kg}^{-1}\text{)}}{\text{Conc. metal in water (mg L}^{-1}\text{)}}$$

where:

K_d = The partitioning coefficient of the individual metal in each of the sites

Moreover, the concentration of the metals were normalised against the background level by the estimation of Enrichment Factor (EF) calculated by the comparison of each tested metal concentration with that of a reference metals using modification of an equation reported in literatures (Fang *et al.*, 2006; Loring and Rantala, 1992; Luoma, 1990; Liu *et al.*, 2005).

$$E.F. = \frac{\frac{C_n(\text{sample})}{C_{ref}(\text{sample})}}{\frac{B_n(\text{background})}{B_{ref}(\text{background})}}$$

where:

$C_n(\text{sample})$ = The metal's concentration in sample
 $C_{ref}(\text{sample})$ = The reference metal's concentration in sample
 $B_n(\text{background})$ = The metal's concentration in reference (background) environment
 $B_{ref}(\text{background})$ = The reference metal's concentration in reference (background) environment

The commonly used reference metals are Mn, Al, Ti, Sc and Fe (Liu *et al.*, 2005; Reinmann *et al.*, 2000; Fang *et al.*, 2006; Quevauviller *et al.*, 1989; Schiff and Weisberg, 1999). Thus, Mn was used as the reference metal in this study because it was found most abundant in the sediments and natural to the environment. The background environment is taken away from the coast perceived to be less polluted.

Finally, the pollution severity and its variation along the sites were determined with the use of an expression defined by Tomlison *et al.* (1980) as Pollution Load Index (PLI). It is thus, formulated:

$$PLI = \left(\prod_i^n (C_{fi}) \right)^{1/n}$$

where:

C_{fi} = The metal concentration factor obtained by dividing concentration of each metal in water or sediment samples by that of the metal in baseline samples
 π = The multiplication operator
 n = The number of metals investigated
 i = Each metal

PLI value close to one indicates less trace metal pollution in the test site, while, values above one indicate pollution of the water or sediment with metals.

RESULTS AND DISCUSSION

Concentration variation of trace metals: The results of concentration ranges, the means and the spreads (SEM) of the 12 metals investigated in the water and sediments of the study area and their comparison with standards are presented on Table 1. The concentrations of Fe and Zn were found to be most abundant in water samples (mean concentration -67.35 and 12.90 mg L⁻¹, respectively) while, Mn and Fe predominate in the sediment samples (mean concentration -1875.70 and 1171.51 mg kg⁻¹, respectively). Generally, the results of the metals determined in the water column from the coastal system were found to be high indicating stress on the environment and risk to lives. However, comparison of the metals concentrations in the sediments with sediments from other polluted marine environment around the world (Table 2) shows that the concentrations at this coast were relatively moderate. The observed concentration of metals in the water column of this study could be best explained by a number of reasons. First, the metals investigated were determined as total metal since samplings were done at relatively high tide (0.78 m tidal height). This made the water system turbid with the suspension of sediment particles into the water column and depicts the effect of storm and wave current on the concentration of metals in the water column. Second, Connell and Miller (1984) and Elder (1988) reported that sudden increase in salinity, which occurs in estuaries and coastal waters, like our study area with mean salinity value of 28.51, are due to the elevated salt concentration because of the fluctuation in flow between the fresh river water and the sea water. This, they reported, increases the competition between cations and metals for binding sites in particulates. Cations being more prominent drive the heavy metals into the overlying water column and increasing their concentrations. Third, the nature of organic carbon prevalent in a site affects the concentration of the metals in the different phases (Elder, 1988; Ouyang *et al.*, 2006). Dissolved Organic Carbon (DOC) favours metals in the water column by the formation of chelates with such metals making it water soluble. However, Particulate Organic Carbon (POC) favours metals in the sediments. Therefore, the high concentrations observed in this study depict the effect of stress on the coastal environment by anthropogenic activities, storm action, which resuspend metals

Table 1: Descriptive statistics of concentration of metals, organic matter and salinity in water and sediment samples

Metals	Sample	Statistics				Standards	
		Mini	Max	Mean	SEM	World mean (mg kg ⁻¹) ^d	(mg L ⁻¹)
As	Water (mg L ⁻¹)	0.02	0.04	0.07*	0.08	nd	0.01 ^a
	Sediment (mg kg ⁻¹)	0.38	0.80	0.66**	0.08		0.05 ^b 0.05 ^c
Cd	Water (mg L ⁻¹)	0.35	0.48	0.41*	0.03	0.50	0.003 ^a
	Sediment (mg kg ⁻¹)	5.37	9.39	8.07**	0.96		0.008 ^b
Cr	Water (mg L ⁻¹)	0.30	0.56	0.40*	0.05	100-300	0.05 ^a
	Sediment (mg kg ⁻¹)	6.61	14.92	12.09*	1.70		0.05 ^b 0.05 ^c
Co	Water (mg L ⁻¹)	0.87	1.19	1.04*	0.06	nd	Nd
	Sediment (mg kg ⁻¹)	9.97	62.99	22.50**	9.34		
Ni	Water (mg L ⁻¹)	0.67	1.09	0.94*	0.10	nd	0.02 ^a
	Sediment (mg kg ⁻¹)	9.75	21.28	17.70**	2.40		0.07 ^b
Mo	Water (mg L ⁻¹)	0.36	0.46	0.40*	0.01	nd	0.07 ^a
	Sediment (mg kg ⁻¹)	4.13	9.44	7.45**	1.07		
Pb	Water (mg L ⁻¹)	1.48	2.29	1.85*	0.19	15-25	0.01 ^a
	Sediment (mg kg ⁻¹)	20.32	48.85	36.94*	4.85		0.058 ^b 0.05 ^c
V	Water (mg L ⁻¹)	0.66	0.85	0.72*	0.04	nd	nd
	Sediment (mg kg ⁻¹)	6.80	16.34	12.68*	1.89		
Sn	Water (mg L ⁻¹)	0.20	0.33	0.24*	0.02	nd	nd
	Sediment (mg kg ⁻¹)	2.51	6.00	4.53**	0.71		
Fe	Water (mg L ⁻¹)	5.68	193.52	67.35*	48.31	nd	nd
	Sediment (mg kg ⁻¹)	662.05	1,463.10	1,171.50**	165.64		
Mn	Water (mg L ⁻¹)	0.24	5.68	1.71*	1.27	nd	0.40 ^a
	Sediment (mg kg ⁻¹)	982.57	2,527.10	1,875.70**	349.78		
Zn	Water (mg L ⁻¹)	9.64	24.28	12.90*	2.70	50-100	4.00 ^a
	Sediment (mg kg ⁻¹)	76.47	193.49	124.08**	22.64		0.08 ^b 5.00 ^c
Organic matter	Water COD (mg L ⁻¹)	150.40	1034.00	456.80*	178.90	nd	nd
	Sediment TOC (%)	1.89	6.96	4.96*	1.14		
Salinity	Water	23.73	31.51	28.51	1.34	nd	nd

^aWHO standard for drinking water, ^bUSEPA standard for coastal aquatic life, ^cFEPA standard nd- no data, ^dLiu *et al.* (2005); Metals with different number of asterisk (*) are significantly different, at 95% confidence limit, between the 2 tested media

Table 2: Comparison of metal concentration with other coastal waters and sediments

Metals/location	Sample type (mg kg ⁻¹)	As	Cd	Cr	Co	Fe	Mn
Santa Monica Bay ^a	Sediments	6.30-23.60	0.90-73.40	58-761	nd	nd	nd
Vancouver Island ^b	Sediments	nd	<0.10-0.70	31.8-59.4	nd	nd	nd
Arabian Gulf ^c	Sediments	nd	0.73-31.59	2.69-23.18	0.72-11.32	708-117.866	11.73-196.06
Havana Bay ^d	Sediments	nd	Nd	49-124	nd	0.30-7.77	68-279
Izmit Bay ^e	Sediments	13.5-28.2	2.5-9.5	38.9-112.4	10.5-28.0	25.000-47.500	305-690
Tanshui Coast ^f	Particulates	nd	0.03-1.11	4.75-16.39	nd	0.27-1.36	320-667
Thane Creek ^g	Sediments	nd	1.7-6.1	29-69	nd	nd	nd
Mejillones Bay ^h	Sediments	nd	3-38	nd	nd	nd	20-138
Ondo Coast ⁱ	Sediments	0.38-0.80	5.37-9.39	6.61-14.92	9.97-62.99	662.05-1463.06	982.57-2527.10

Metals/location	Sample type (mg kg ⁻¹)	Mo	Ni	Pb	Sn	V	Zn
Santa Monica Bay ^a	Sediments	nd	18-146	19-303	nd	nd	58-1447
Vancouver Island ^b	Sediments	nd	nd	8.20-129	nd	nd	7.70-197.70
Arabian Gulf ^c	Sediments	nd	3.30-37.15	4.72-46.33	nd	4.73-60.56	2.13-33.64
Havana Bay ^d	Sediments	nd	nd	321-768	nd	nd	294-980
Izmit Bay ^e	Sediments	nd	20.05-55.50	55.2-172	100-296.5	nd	440-1900
Tanshui Coast ^f	Particulates	nd	nd	10.23-35.80	nd	nd	18-116
Thane Creek ^g	Sediments	nd	91-130	34-143	nd	nd	114-273
Mejillones Bay ^h	Sediments	10-118	2-36	nd	nd	<1-97	10-62
Ondo Coast ⁱ	Sediments	4.13-9.44	9.75-21.28	20.32-48.85	251-6.00	6.80-16.34	76.47-193.49

Nd: No data, ^aBay *et al.* (2003), ^bChapman *et al.* (1996), ^cSadiq (2002), ^dGonzalez *et al.* (1999), ^ePekey (2006), ^fFang *et al.* (2006), ^gSahu and Bhosale (1991), ^hValdes *et al.* (2005), ⁱThis study

precipitated in, or adsorbed on, sediments, the biogeochemical reactions (vis-à-vis reactions between metals and organic carbons or changes in redox potential)

within the environment and the effect of intrusion of seawater into the coast, which increases salinity and drives out the metals into the water column.

Metals concentrations in sediments were found to be many magnitudes (about 25 times) higher than that of the water column (Table 1). Sediments, generally regarded as sinks, could accumulate metals and give a better indication of stress on the environment and pollution over time. Likewise, the metal concentration in sediments is attributable to the fact that metals generally have strong affinities for iron and manganese oxyhydroxides particulates thus, they adsorb on such particles, which are commonly found in sediments. They also precipitate, at high pH, form particles themselves or accumulate in biological particles found in sediments. The bioavailable metals are principally from the soluble phase but partitioned into the sediment phase by their accumulation in the biological particles.

A comparison of the concentrations with regulated standards of WHO (2004) and USEPA (1993), Nigerian FEPA indicates that most of the metals were beyond maximum regulated standard for drinking water and the standard for coastal aquatic lives (Table 1). There is therefore, an indication of high health risk to humans and other lives in this environment by the observed concentration of these metals.

The concentration of Cd and Pb in the water are of much concern because of their tendency to accumulate in fish and other aquatic lives present in the food web. It has been reported that Pb has caused anaemia, brain damage, anorexia, renal failure, mental deficiency, vomiting and even death in human (Low *et al.*, 2000; Bulut and Baysal, 2006) even at trace levels lower than the observed concentration in this study. Cd also has been reported to cause bone disease, agonistic and antagonistic effects on hormones and enzymes leading to lots of malformations (Manahan, 1992). Renal damage resulting in proteinuria has been caused by Cd through its adverse effect on the enzyme responsible for the re-adsorption of protein in the kidney tubules (Donalson, 1980). These 2 metals have affinity for -SH groups in proteins, haemoglobin, enzymes/hormones thus, affecting their activities (Manahan, 1992).

Ni and V concentration observed in the water system is attributable to the oil exploration in the area. There are also indications of trans-boundary movement of these metal pollutants from heavy oil prospecting areas like Delta State Coast and heavy populated, industrialised and commercial coastal state like Lagos Coast being on the same coastal line.

The observed concentration of Sn could have an association with Tributyltin (TBT) and Triphenyltin (TPT) extensively used as fungicides, acaricides, disinfectants and antifouling boat paints since the early 1970s. TBT is used in preservation of woods, papers and textiles, which

end up being discharged into the environment as domestic wastes. It can easily be absorbed through the skin to cause skin rashes; binds with protein and interferes with mitochondrial functions (Lau, 1991; Clark *et al.*, 1988). Both TBT and TPT had been shown to be hazardous to aquatic life (Hoch, 2001) even at low aqueous concentrations ($1-2 \text{ ng L}^{-1}$). They are ionizable, organometallic compounds, which can complex with various ligands present in the abiotic and biotic environment to cause hazardous effects (Arnold *et al.*, 1997; Buck *et al.*, 2003). TBT causes chronic and acute toxic effects in small and most sensitive aquatic organisms, such as zoo and phytoplankton, algae, mollusks, even the larval stage of some fishes (Gibbs and Bryan, 1996). Thus, these metals must be further investigated and regulated in this coast.

Site variations of trace metals: The knowledge of site distribution of contaminants helps appreciate the spatial fate of such and enables identification of sites with higher hazardous concentration for immediate action. Hence, the concentration of the investigated metals in water column and sediments across the sites in the coastal area are presented in Fig. 2 and 3. The test sites were significantly different from the control except sites SW08 and SW09 for water sample analysed. Exceptional situation was witnessed in the concentration distribution of Cobalt in site SW03 in sediment. Further, the PLI graph as presented in Fig. 4 indicates that metal pollution is more severe in sediment than water samples. Water samples from the oil prospecting area (SW01) had the highest PLI of 1.85 and the values reduce progressively as we move away from the site with slight deviation in site SW04. It thus implies that the oil exploration is contributing negatively to the environment. Likewise, the PLI of the water sample reduces with increasing distance from the estuary discharge point at SW02 due to reduction in salinity. This confirms the earlier view that salinity aids the release of metal into the water column.

Moreover, the results of the Principal Component Analysis (PCA) represented in Fig. 5a for the water samples relative to metals help us appreciate the clusters of the metal pollution. The cluster of the metals in water correlated perfectly except Fe and Zn. Thus, the pollution sources of these metals are related anthropogenic activities while, Fe and Zn are possibly natural to the geological structure of the environment. The likely sources of the pollutant metals investigated vary widely and are subjected to a number of activities engaged in coastal sites vis-à-vis domestic and industrial waste products, urban (i.e. roof and road) runoff, runoff from agricultural activities, contributions from soil and

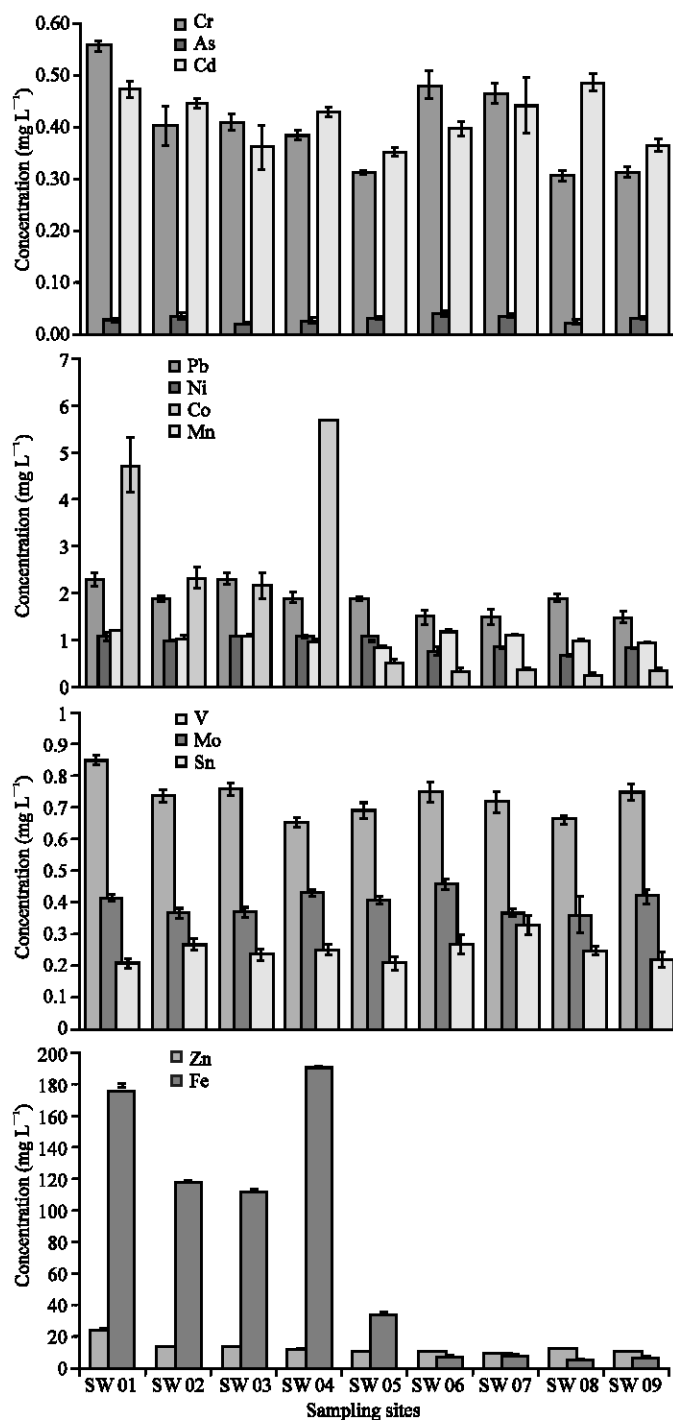


Fig. 2: Concentration variation of metals' in water samples from the 9 test sites. The error bars are the Standard Error of Mean (SEM) obtained from the triplicate analysis of samples collected from the same site

geological structure of the area and trans-boundary movement. Likewise, atmospheric precipitation or dry deposition introduces some metals into the aquatic environment (Legret and Pagotto, 1999) and affects the distribution of such metals relative to sites and time.

However, an established major source in this coast is the oil exploration activity and the domestic waste disposal in the area. The consideration of the PCA of metals in water in relation to site variation presented in Fig. 5b further confirms that site SW01-SW05 were impair by pollutant

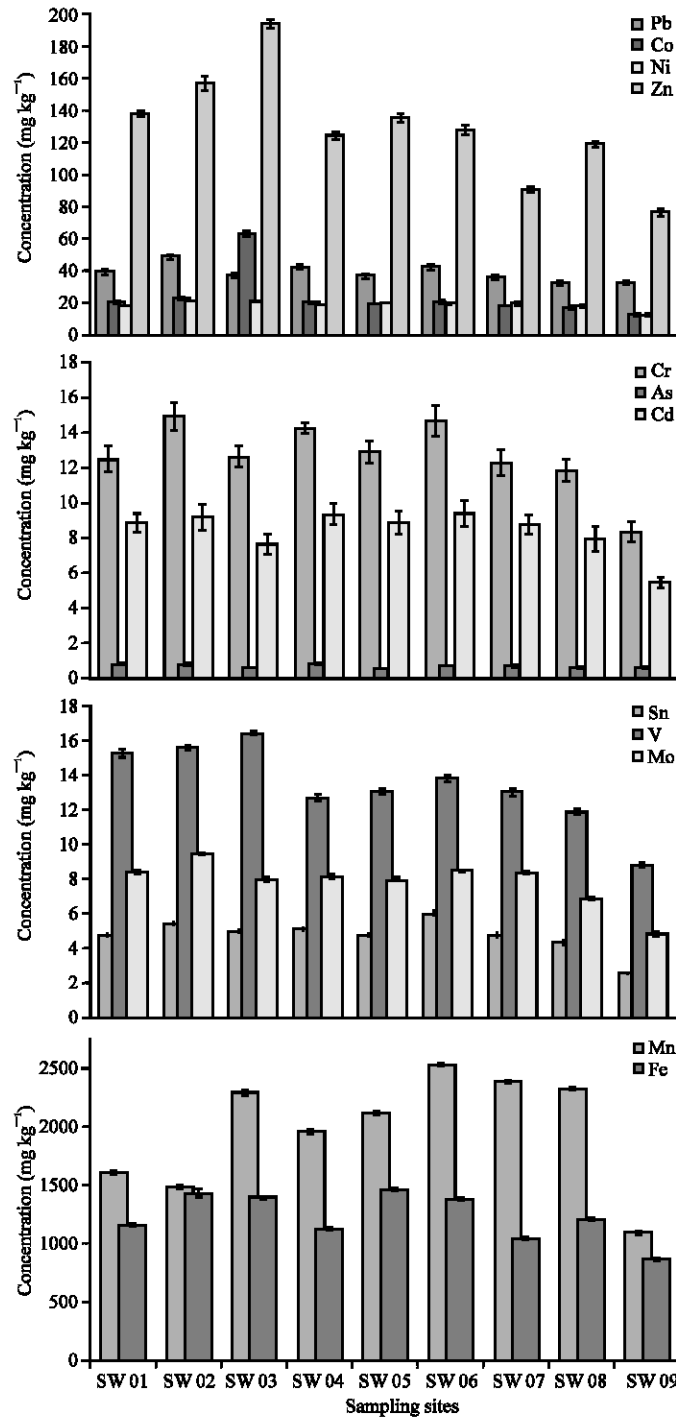


Fig. 3: Concentration variation of metals' in sediment samples from the 9 test sites. The error bars are the Standard Error of Mean (SEM) obtained from the triplicate analysis of samples collected from the same site

form same source (oil exploration) while, SW06-SW09 received pollutant from domestic discharges. Also, the PCA of sediments relative to metals and sites presented in Fig. 6a and b, respectively show a close clustering of all sites indicating even sinking of the

pollutants into the sediments while, Mn and Zn stand out clearly among the metal clusters. It thus strongly implies that Mn, Fe and Zn are contributed significantly from the geological structure that from anthropogenic activities.

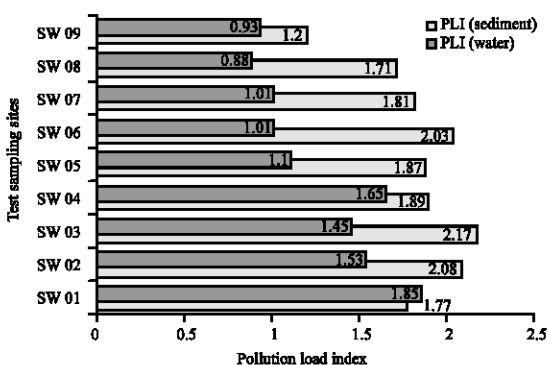


Fig. 4: Comparative graph of pollution load index of sediment and water samples in the 9 test sites

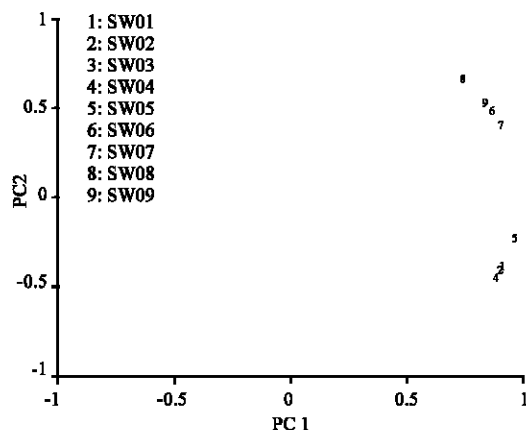


Fig. 5b: Principal component analysis of cluster for trace metals pollution in water samples for site

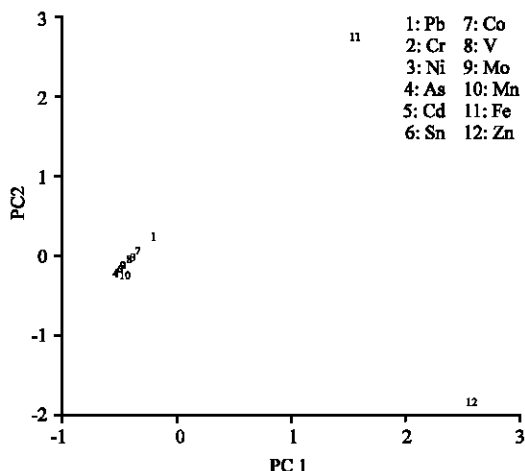


Fig. 5a: Principal component analysis of cluster for trace metals pollution in water samples for metals

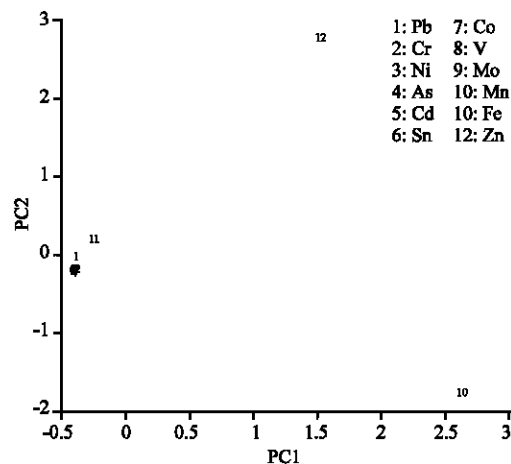


Fig. 6a: Principal component analysis of cluster for trace metals pollution in sediment samples for metals

Possible and priority features, that need control, responsible for the observed distribution of the metal contaminant in coastal areas, beside natural contribution by their geological structure are: Cd-deposition of electroplated metals used to prevent corrosion, pigments, plastics and Cd-based batteries; Pb-residues from insecticides and herbicides (lead acid arsenate), Pb-based batteries, anti-knocking in gasoline, atmospheric precipitation, clutch facing, disc brakes of speedboats, water pipes with Pb solder, ceramic products, alkyd paints, rubber and marches; V-effluents from oil exploration, alloy of steel and as common air contaminant; Ni-effluents from oil exploration, Ni catalysed products, Ni plating and as common air contaminant; Mo-runoff of agricultural fertilizers and coal firing; Sn-marine antifouling paints and paper preservatives; Mn-fungicides, dry deposition; Zn-fungicides, antiseptics, rodenticide and dry deposition.

Finally, the normalizations of the observed concentrations done by the evaluation of the Enrichment Factor (EF) showed the extent of enrichment of an area with metals above background concentration natural for the area and indicate the effect of anthropogenic activities on the sites. The results of mean EF for metals and all the test sites are presented in Fig. 7a and b. Fe was the most enriched metal in the sediments while, Cobalt had the highest in water samples. Sites SW02, 01 had the most enriched sediments with contaminant metals in decreasing order while, site SW06 was the most enriched water column. Therefore, its is clear that seawater intrusion in SW02 (being near to the Atlantic Ocean) is contributing trans-boundary contamination into the coastal area while, waste from the oil exploration in SW01 and domestic wastes from site SW06 are negatively impacting the environment and needs to be urgently curtailed.

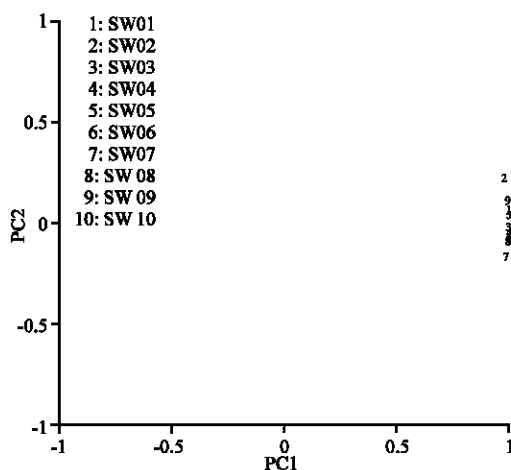


Fig. 6b: Principal component analysis of cluster for trace metals pollution in sediment samples for sites labelled as

Partitioning of trace metals in water and sediments:

Metals in the coastal system are partitioned between the sediments, suspended particulate matters and the soluble phase (James, 2002). Metals partitioning between phases are caused by different reactions like complexation, precipitation, adsorption and biological accumulation. Partition coefficient (K_d) was used to evaluate the partitioning of metals between the sediments and the water column and the results presented in Fig. 8.

These values vary with metals, sites and time because of the complex nature of the water chemistry that affect the coefficient and the partitioning of metals (James, 2002). Of all the reactions that affect partitioning; adsorption predominates because of metals' affinity for particulates, organic matters and to some extent clay (Elder, 1988). However, other factors like pH, concentration of organic carbon, types of organic carbon (DOC or POC) and redox potential have been reported to affect metal partitioning between these phases (Connell and Miller, 1984; Ouyang *et al.*, 2006). At low pH (acidic state); solubility of metal carbonates and hydroxides increases, adsorption capacity decreases and H^+ ion competition with metals for binding site in organic complex increases thereby favouring the partitioning of metals into the dissolved phase. A reduction in redox potential, witnessed in a hypoxic (low dissolve oxygen) condition, changes the composition of metals complexes and releases the metals into the dissolved state (Elder, 1988; Connell and Miller, 1984). Also, affecting metal partitioning is the type of particles involved. Biological particles (planktons) have varying affinities for metals (James, 2002). High organic carbon aids the weathering of the geological base structure of the water

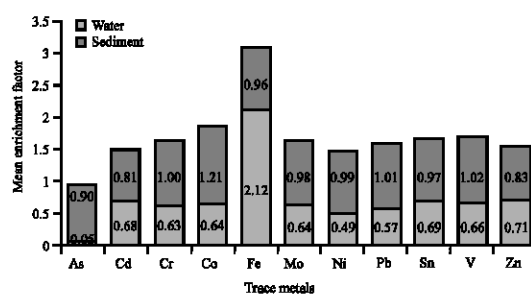


Fig. 7a: Comparative graph of mean enrichment factor of metals in the water and sediment samples

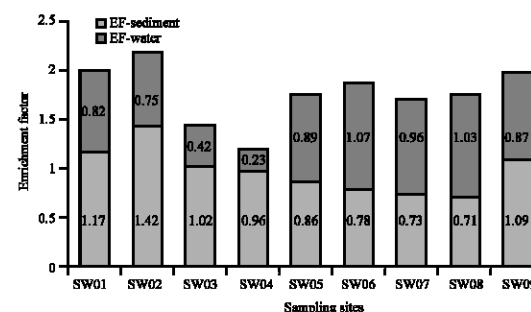


Fig. 7b: Comparative graph of mean enrichment factor of metals in the test sites for water and sediment samples

system and its type affects the partitioning of metals. Therefore, Dunnett Parametric Multiple Comparison of organic matter with metals in water and sediment presented in Table 3a and b, respectively was used to establish the link between pollutant metals and organic matter. The results for the sediment samples show that there were no significant differences between the organic matter and trace metals except metals that have been indicated as natural to the environment (Fe and Mn) while, all the metals in water sample were significantly different from the measure of organic matter. It therefore, means that the organic matter in this coast area aids the partitioning of metals into the sediment phase and not the water column. This also implies that the biological particles do accumulate the metals and settles down as bottom sediments aiding the increase concentration of metals in the sediment.

Thus, the observed trend of the partitioning of the metals between the water column and the sediments (Fig. 8) are affected by the organic matter present and other factors, which made them vary across sites and metals. However, about 75% of the K_d was between 15-35 with few lower or higher. The metals definitely were more in the sediment phase than the water column. The partitioning coefficients of the natural metals to this site (Mn and Fe) were exceptionally. They were therefore, not

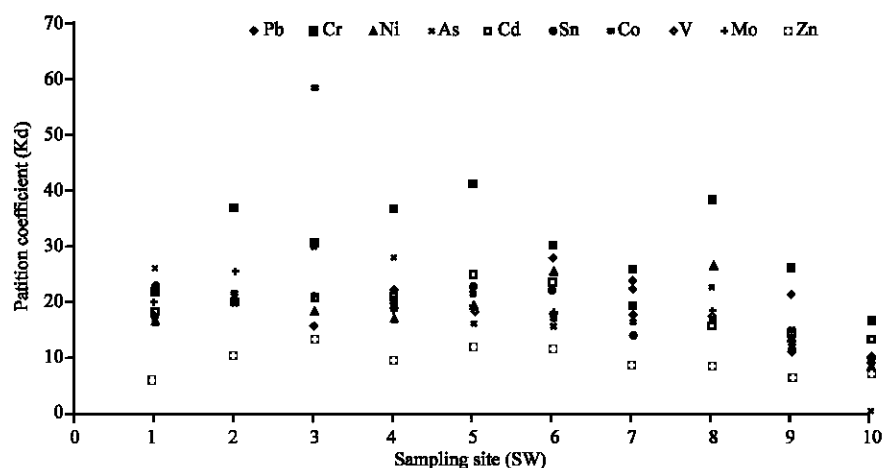


Fig. 8: Graph of partition coefficient of the metals between water and sediment

Table 3a: Table of dunnett parametric multiple comparison of trace metals in water samples with chemical oxygen demand

Metal	t1j	p-value	Upper probability (Multivariate t-distribution)
Pb	-12.516	$\leq 0.001^{***}$	1.41E-06
Cr	-12.556	$\leq 0.001^{***}$	1.41E-06
Ni	-12.541	$\leq 0.001^{***}$	1.41E-06
As	-12.565	$\leq 0.001^{***}$	1.41E-06
Cd	-12.556	$\leq 0.001^{***}$	1.41E-06
Sn	-12.560	$\leq 0.001^{***}$	1.41E-06
Co	-12.538	$\leq 0.001^{***}$	1.41E-06
V	-12.547	$\leq 0.001^{***}$	1.41E-06
Mo	-12.556	$\leq 0.001^{***}$	1.41E-06
Mn	-12.520	$\leq 0.001^{***}$	1.41E-06
Zn	-12.212	$\leq 0.001^{***}$	1.41E-06
Fe	-10.714	$\leq 0.001^{***}$	1.41E-06

Table 3b: Table of dunnett parametric multiple comparison of trace metals in sediment samples with total organic carbon

Metals	t1j	p-value	Upper probability (Multivariate t-distribution)
Pb	0.420	$> 0.05ns$	1.00
Cr	0.094	$> 0.05ns$	1.00
Ni	0.168	$> 0.05ns$	1.00
As	-0.057	$> 0.05ns$	1.00
Cd	0.041	$> 0.05ns$	1.00
Sn	-0.006	$> 0.05ns$	1.00
Co	0.231	$> 0.05ns$	1.00
V	0.102	$> 0.05ns$	1.00
Mo	0.033	$> 0.05ns$	1.00
Mn	24.595	$\leq 0.001^{***}$	0.00
Zn	1.566	$> 0.05ns$	0.60
Fe	15.337	$\leq 0.001^{***}$	0.00

presented in the Fig. 8. There are clear indications that the soil around the watershed contributes significant concentration of Fe and Mn and the biogeochemical conditions favour their precipitation into the sediments. Zn had the lowest K_d in most of the sites meaning that it is more partitioned into the water column relative to other metals. Cr had the highest K_d in 70% of the site among the metals presented indicating it as the metal with the

highest preference for sediment phase beside the 2 metals not presented. Therefore, the general partitioning trends of all the metals revealed an accumulation of metal contaminants in the sediments over time coupled with biological accumulation and contributions from geological structure of the area. Hence, caution must be taken to control anthropogenic contributions, which do elevate the concentrations of the metals so as to preserve the ecosystem.

Finally, the organic matter is believed to support the weathering of Fe, Zn and Mn from the geological structure and their partitioning into the water column making them the most abundant set of metals in the water while, the partitioning of Pb, Cr, Ni, As, V into the water column are weakly supported by organic matter concentration. Ouyang *et al.* (2006) have reported that Dissolved Organic Carbon (DOC) forms strong complexes with metals like Cu, Fe, Zn, Mn and Al thus supporting their dissolution in water. It also, increases the weathering rate of minerals in rock, which increases metals solubility and mobility, aiding their release into the water column from sediments or the geological structure of the area. Thus, the relationships of organic matter in water and sediments with all the metals observed (Table 3a and b) in this research aid the partitioning of the metals into the sediment column and indicate that the organic matters contain more of POC, which supports partitioning of metals into particulate state (Moore, 1989; Elder, 1988; Ouyang *et al.*, 2006). This finding explains the earlier observed high concentration of metals and the PLI in the sediment column. Moreover, the salinity of the coastal water was not significantly different from the metals (Table 4) in both the water and sediment sample except Fe and Mn, which have been confirmed to be from the geological structure. This trend means that salinity plays

Table 4: Table of dunnett parametric multiple comparison of trace metals in water and sediment samples with salinity

Metals	t _{ij}	p-value	Upper probability (Multivariate t-distribution)
Pb (water)	-0.482000	>0.05ns	1.00
Cr (water)	-0.508000	>0.05ns	1.00
Ni (water)	-0.499000	>0.05ns	1.00
As (water)	-0.514000	>0.05ns	1.00
Cd (water)	-0.508000	>0.05ns	1.00
Sn (water)	-0.511000	>0.05ns	1.00
Co (water)	-0.497000	>0.05ns	1.00
V (water)	-0.503000	>0.05ns	1.00
Mo (water)	-0.509000	>0.05ns	1.00
Mn (water)	-0.485000	>0.05ns	1.00
Zn (water)	-0.282000	>0.05ns	1.00
Fe (water)	0.703000	>0.05ns	1.00
Pb (sediment)	0.152493	>0.05ns	1.00
Cr (sediment)	-0.297100	>0.05ns	1.00
Ni (sediment)	-0.195480	>0.05ns	1.00
As (sediment)	-0.504520	>0.05ns	1.00
Cd (sediment)	-0.369660	>0.05ns	1.00
Sn (sediment)	-0.433760	>0.05ns	1.00
Co (sediment)	-0.108660	>0.05ns	1.00
V (sediment)	-0.286350	>0.05ns	1.00
Mo (sediment)	-0.380900	>0.05ns	1.00
Mn (sediment)	33.418470	≤0.001***	1.43e-06
Zn (sediment)	1.729133	>0.05ns	0.64
Fe (sediment)	20.678730	≤0.001***	1.43e-06

an important role in the partitioning and distribution of metals in coastal areas. It is then established that there is a mark impact of organic matter and salinity on the biogeochemical reactions that govern the concentration, site variation and partitioning of metals into the difference phases of the coastal zone.

CONCLUSION

The concentrations of metal contaminate observed in the water and sediment column indicate potential hazard on the environment by adverse anthropogenic activities that needs to be curtailed. The metals have accumulated in the biological matter and sediments and are being released into the water column from where it can get into the food web by bioaccumulation. The partitioning of the metals into the sediment column and the weathering of the geological structure is being aided by salinity and the organic carbon present in the sediments and are contributing significantly to the pollution of the coast. The resuspension by storm action, pH variation and the change in salinity of the coastal water does favour the increase of metals in water samples. Fe and Mn follow a trend that indicate they have the same source, which is the geological structure of the area but with indication of minimal contributions from human activities. Zn was seen as a borderline metals between natural and anthropogenic sources. The PLI, PCA and the enrichment factor of the metals and sites across the coast show that site SW01, 02

and 06 are much impacted than the others and need immediate attention. Caution must be taken to regulate the effects of oil exploration in site SW01 and domestic waste discharge across the coast while, Pb, Cd and Sn should be metal of priority control interest in this coast.

ACKNOWLEDGEMENT

We acknowledge Mr. Ohaegbulem of the Analytical Service lab of International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria for the operation of the AAS for metal analysis.

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