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Ecological risk assessment of heavy metals in soil developed on coastal marine sediment along coastal area in Anantigha, Calabar, Nigeria

E. E. Aki* and **I. A. Isong**

Department of Soil Science, University of Calabar, Nigeria

*E-mail address: eneakita@gmail.com

ABSTRACT

Coastal areas in Anantigha are utilized as dumpsite for industrial and domestic wastes including effluent from local industries and inhabitants of the area despite their usage for crop cultivation. Thus, the present study was designed to assess the concentration, pollution load and ecological risk of heavy metal in Anantigha coastal area. Standard pollution indices such as contamination factor (C_f), degree of contamination, pollution load index (PLI), enrichment factor (EF), geo-accumulation index (Igeo) and ecological risk index were deployed to assess the level of heavy metals contamination in the area. The results showed that the sediment was acidic under dried conditions and low in conductivity. The mean concentration levels of all the heavy metals were lower than their mean background values except for Al. The orders of dominance for concentration of heavy metals were: Al>Fe>Mn>Cu>Zn (Station 1) and Al>Fe>Mn>Zn>Cu (Stations 2, 3 and 4). Analyzed data showed that the sediments in the area are contaminated with Al with Igeo result showing station 2 and 4 been moderately to heavily contaminated with Al while station 4 was heavily contaminated with aluminium. Station 1 had low degree of contamination, whereas station 2 and 4 had moderate degree of contamination, and station 3 showed considerable degree of contamination. The PLI result indicates unpolluted condition and the area were not enriched by the studied heavy metals as shown by EF values. Hence, the sediment in Anantigha coastal marine area was classified as having low ecological risk factor. However, the levels of these metals are not static; there is tendency for increase as a result of increased human input and activities. Hence, there is a need for regular soil testing.

***Keywords*:** ecological risk factor, geo-accumulation Index, heavy metal, pollution load index marine sediment

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1. INTRODUCTION

Agriculture is the livelihood of the overwhelming majority of Nigerians. It is the source of food and income for those who are engaged in the sector. With the rapidly increasing population of Nigeria, there is now high pressure on land to meet the increasing demand for food, fiber and animal feed. In Cross River State, upland soil been the most important and determinant factors that strongly affect agriculture and on which most of the crop cultivation is heavily dependent is faced with stiff competition for industrial and other uses.

However, most wetland soil which would have serve as an alternative to already scarce and in most cases degrading upland soil for crop cultivation are either pedogenetically high in heavy metals (Akpan and Thompson, 2013; Andem *et al.*, 2015; Udofia *et al.*, 2016) or are direct recipients of industrial and domestic wastes including effluent from local industries and inhabitants of the areas where it is located (Jonah *et al.*, 2014) This can lead to soil pollution including hazard to human health if not properly managed. For example, Arora *et al.* (Arora *et al.*, 2008) has reported that "consumption of heavy metal contaminated food/crop can seriously deplete some essential nutrients in the body causing a decrease in immunological defences, intrauterine growth retardation, impaired psycho-social behaviour, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer." Thus, the continuous identification, quantification and assessment of heavy metals in sediment should be encouraged, given its immense health benefit.

Heavy metals which can be sourced through anthropogenic and geologic sources are stable and persistent environmental contaminants of coastal waters (Akan *et al.*, 2010; Barakat *et al.*, 2012; Ephraim and Ajayi, 2014) and sediments (Akpan and Thompson, 2013; Andem *et al.*, 2015; Moses *et al.*, 2015). According to Akpan and Thompson (2013), sediment is the loose sand, clay, silt and other soil particles that is deposited at the bottom of body of water or accumulated at other depositional sites. Sediments conserve important environmental information (Gumgum and Ozturk, 2001; Eddy and Ukpong, 2005), and are increasingly recognized as both sink and sources of organic and inorganic materials in ecosystems (Morelli and Gasparon, 2014) and can support the growth of funna and flora including terrestrial plant. However, nutrient enrichment and elevated concentrations of heavy metals in most coastal environmental have now capture the attention of agronomist and soil scientist especially now that most fertile soils are scarce due to urbanization and/or population pressure, and unproductive as a result of land and soil degradation.

Several decades ago, Anantigha coastal area was originally covered by tropical rainforest but has now become a beehive of agricultural, forestry and industrial activities. Like other coastal areas (Offiong *et al.*, 2013; Gurumoorthi and Venkatachalapathy, 2016), numerous human activities including farming, logging, fishing, boating, watercraft maintenance, automobile repairs, welding, saw-milling, laundering, bathing, effluent discharge, etc. are carried out within and around this area. Some of these activities in addition to the intrinsic nature of coastal area may result to elevated concentrations of heavy metals in amount several times higher than the permissible limits established for mineral soil environment and may render the soil unfit for crop cultivation.

Studies by Udofia *et al.* (2016) evaluated heavy metal pollution in sediment of Okporku River, Yala, Cross River State. The heavy metals determined in their study were, lead, chromium, iron, copper and cadmium. Their result revealed that the sediment is not heavily polluted with heavy metal.

The PLI estimated was less than 1 for all stations indicating unpolluted condition and the Igeo values for iron fell in class '0' in all the 3 sampling stations, indicating that there is no pollution. Also, Ephraim and Ajayi (2014) investigated the current level and distribution of seven heavy metals (Pb, Zn, Cu, Ni, Cr, Cd, As) collected from surface sediment at 12 stations, located within Mbat-Abbiati and Oberakkai Creeks of the Great Kwa River.

The pollution status was evaluated using Enrichment Factor (EF), Index of Geoaccumulation (Igeo), Contamination Factor (C_f), Degree of Contamination (C_d) and Pollution Load Index (PLI). Their results indicated that the sediments were unpolluted with regards to the measured heavy metals based on geoaccumulation index.

The computed Enrichment Factors (EF) showed that some heavy metals (Pb, Zn, Cr, Cd) have EF values of up to 1, which indicates enrichment through lithogenic and anthropogenic sources. Jonah *et al.* (2014) studied the physicochemical properties and heavy metal status of sediment samples from Ohii Miri river in Abia State, Nigeria. Their results showed that the sediment was acidic and the heavy metals concentrations exceeded the USEPA standard. Values of geo-accumulation factor showed that the sediment is not polluted with the studied heavy metals.

Soils along coastal areas may likely contain toxic metals especially in places where there are numerous industrial activities. These toxic metals can pose dangers to people who utilize the soil within this area for agriculture if vegetables and other food crops cultivated are contaminated. These contaminated foodstuffs become integral component of the body system after consumption and bio-accumulate over a period of time, and may deplete some essential nutrients in the body if in high concentration, thus causing immunological damages in the body (Arora *et al.*, 2008).

It is against this back drop that Mosses *et al*. (2005) conducted a research to determine the levels of trace metals in sediments from Qua Iboe river estuary (QIRE) in Nigeria and assess their extent of contamination. Their results revealed that the levels of trace metals investigated were below the sediment quality guidelines except Fe and the sediments were contaminated with respect to the indices considered in their study. Enrichment factors and geo-accumulation indices indicated anthropogenic sources of pollution for Pb, Cd and V.

Whereas, many researches concerning heavy metals concentrations in the surface sediments in Cross River State and Calabar in particular had been reported (Offiong *et al.*, 2013; Ephraim and Ajayi, 2014; Eddy and Ukpong, 2005), but there is a paucity of information on heavy metals toxicity and ecological risks in Anantigha coastal area. Studies by Edem *et al.* (2008) only considered the concentration of heavy metals.

However, the results of this study will provide environmental database of soils along Anantigha coastal area which is crucial and a prerequisite to meet the numerous challenges being faced by the populace in relation to crop production, water resource management, environmental protection and above all sustainable economic development in the area. Also, the results will provide authorities with data to develop appropriate management strategies to control the contamination of heavy metals in soils.

1. 1. Objective of the study

i. The study was designed to document the current state and distribution of heavy metals in Anantigha coastal sediment; and

ii. Determine the current pollution status and ecological risk of the area.

2. MATERIALS AND METHODS

2. 1. Description of the study Area

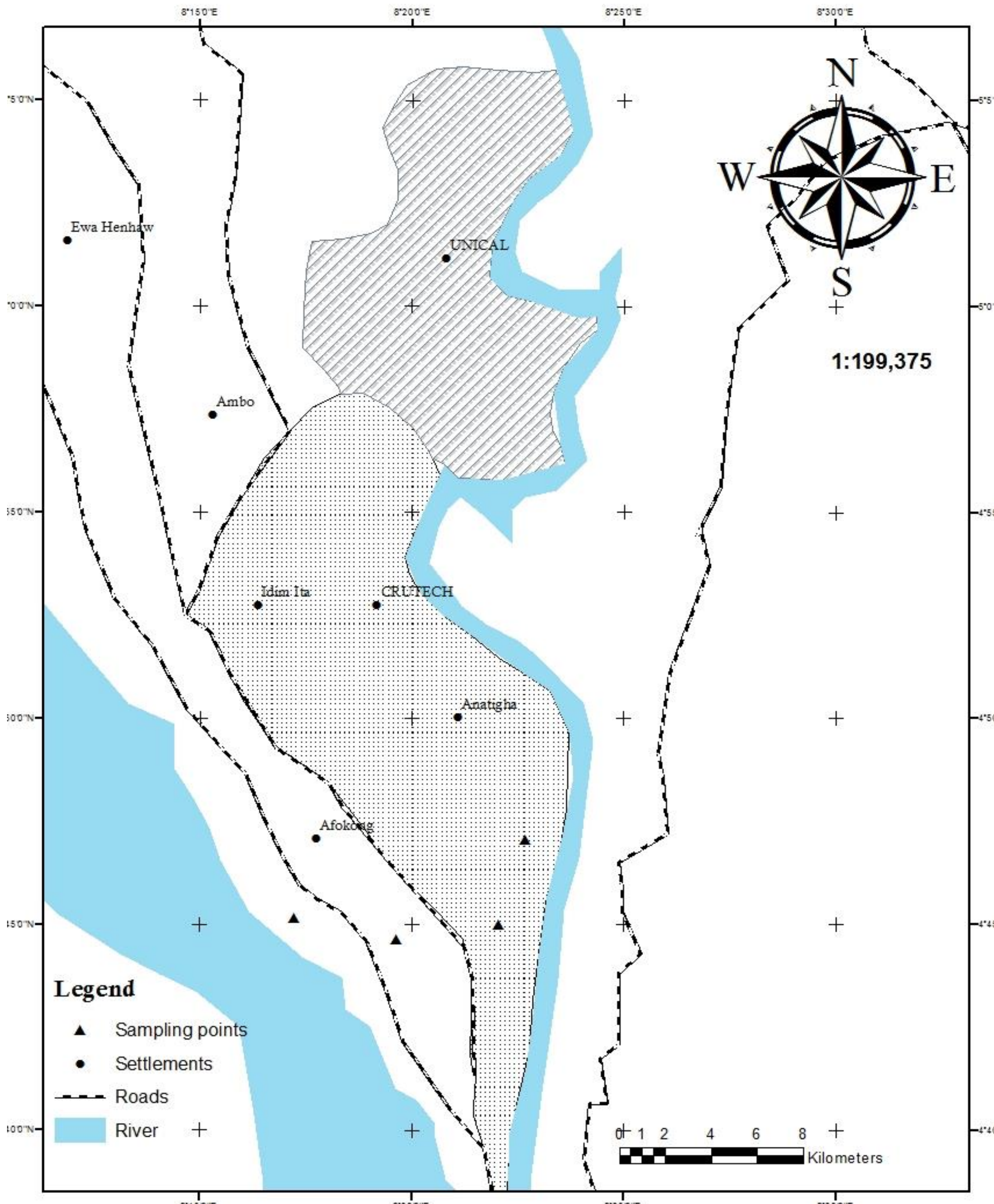

Fig. 1. Map of the study area showing sampling point

The study was carried out in soil developed on coastal marine sediments in Anatigha coastal areas, Calabar. Anatigha coastal area (Fig. 1) is located in Calabar, Cross River State, South-East Nigeria. The exact coordinates of the location where samples were collected are given in Table 1. The area is situated in the rain forest vegetative zone, which experiences humid tropical climate with marked dry season (November-March) and rainy season (April-October). The mean relative humidity of the area varies from 65-90 %, with the estimated annual rainfall range between 2000 and 3000 mm. The annual temperature varies from 27-31 ºC. The geological formation of the area consists of coastal marine sediment derived from fluvio-marine deposits and the soils are acidic and coarse-textured. Some physico-chemical properties of the soils are shown in Table 2. The area is used predominantly for horticultural and arable crop cultivation where crops like maize, pepper, watermelon, fluted pumpkin, cassava and yam are grown. Vegetation and trees are found over the low lying plains and marshes around the creek. The predominant vegetation and trees along the shorelines are made up of woody plants, shrubs, coconut and oil palm trees.

Table 1. Field codes and GPS coordinate in the study sites.

Stations	Site name	Elevation above sea level	Coordinates		Anthropogenic activities
			Northing	Easting	
S1	Anantigha beach	2m	04º54.88’	008º19.16’	Sand mining and domestic/industrial effluents dumpsite.
S2	Annatigha fish pond area	2m	04º54.847’	008º19.232’	Residential sewage and industrial effluents, oil and grease dumpsite.
S3	Anantigha slughter area	1m	04º54.860’	008º19.402’	Slaughter/abattoir house and effluents from the nearby market.
S4	Ibesikpo timber market area	6 m	04º55.759’	008º18.636’	Wood logging, saw milling, saw dust input, sand mining, sewage and industrial effluents, oil and grease dumpsite and automobile repair and related activities.

2. 2. Surface Sediment Sampling and preparation methods

Guided by the geographical map of the study area (Fig. 1), soil samples were collected from four (4) stations in coastal marine sediment within Anantigha coastal area, namely; Anantigha Jamekon beach, Anantigha fish pond area, Anantigha slughter area and Ibesikpo timber area (Table 1). Soil sampling was done at a depth of 0-20 cm within each station. Surface (0-20) sediments samples were collected in triplicates from five different points within a certain area (approximately 1 meter radius) from each sampling site using a sterilized soil auger and placed in separate labeled polyethylene plastic bags and transported to the laboratory. Each sediment samples were air-dried at room temperature depending on moisture content for two about (2) weeks. The dried sediment samples were crushed to powder by using a porcelain mortar and pestle and later sieved vigorously to produce homogeneity, through 2mm mesh sieve, bagged and labeled for soil routine analysis.

2. 2. 1. Digestion of sample

The digestion of sediment samples was done by dissolving 1 g of the dried powdered sediment samples in a clean 100 ml beaker. This was followed by the addition of 20 ml concentrated HCl in small portions, 5 ml of concentrated HNO_3 and 2 ml of HF. The mixture was covered with watch glasses and heated to near boiling for one hour. It was filtered hot and made up to mark with distilled water in 100 ml volumetric flask.

2 .2. 2. Quality assurance

The accuracy and precision of the analytical methodology was assessed by triplicate analyses of certified reference material from the International Atomic Energy Agency (Marine sediment, IAEA 256) at the same time as the sediment samples to control the accuracy and to determine the uncertainty of metal determination. The precision was < 5 % and recoveries were between 88-95 % for the investigated heavy metals, hence, indicating the accuracy of the methodology.

2. 3. Laboratory Analysis

Soil samples were analyzed for physico-chemical properties following a standard procedure: particle size distribution of the soil samples was determined using Hydrometer method (Gee and Or, 2002); Soil pH (H_2O) was determined using a ratio 1:2.5 (soil: solution) by glass electrode pH meter following procedure outlined by Udo *et al.* (2009); soil organic carbon content was determined by the dichromate wet oxidation method of Walkley and Black as outlined in Nelson and Sommers 1982) and converted to organic matter by multiplying by a factor of 1.742 (Van Bemmelen factor); the exchangeable bases (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were extracted by saturating soil with neutral 1*M* NH_4OAc (Thomas, 1982) and Ca and Mg were determined by the EDTA titration method while K and Na were determined by flame photometry; the exchangeable acidity (H^+ and Al^{3+}) was determined by extracting the soil with 0.1*N* KCl solution and titrating the aliquot of the extract with 1*N* NaOH following the procedure outline by Udo *et al*. (2009); electrical conductivity (EC) was determined using conductivity bridge by dipping the electrode into the soil-water suspension; cation exchange capacity (CEC) was determined by saturating the soil with 1*N* NH_4OAc at pH 7.0 (Chapman, 1965); base saturation was calculated as the sum of total exchangeable bases divided by NH_4OAc cation exchange capacity and expressed as a percentage; total concentrations of Fe, Mn, Cu and Zn in sediment samples were carried out following the procedure outlined in IITA Manual (1979) and percentage aluminium saturation was computed using the formula below:

$$\%\ Al \text{ saturation} = \frac{Exchangeable \text{ Aluminium}}{Effective\ Cation\ Exchange\ Capacity} \text{ x } 100$$

2. 4. Statistical Analysis

Mean of the studied soil properties were computed and employed to compare the results with the critical limits for interpreting levels of soil fertility status (Landon, 1991), and background values and permissible limit for heavy metal concentration (Lindsay, 1979; Turekian KK, Wedepohl, 1961). Correlation analysis was computed and used to indicate the relationship between micronutrients, soil pH, soil organic matter and clay. Also, cluster analysis was used to assess common pollution sources between sampling stations. Various indices as presented in equation (1) to (7) below were also computed and used to assess the current pollution status and ecological risk of the area.

2. 4. 1. Contamination Factor (CF)

Contamination factor (CF) was calculated using the equation below:

$$C_f = \frac{C_{metal}}{C_{backgrund}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where:

C_{metal} is the measured concentration of the examined metal (n) in the sediment

$C_{background}$ is the concentration of the examined metal (n) in the reference environment.

Hakanson (1980) express four main classes of contamination factor and is given as:

CF < 1 refers to the low contamination factor,

1 ≤ CF < 3 refers to the moderate contamination factor,

3≤ CF < 6 refers to the considerable contamination factor,

CF ≥ 6 refers to the very high contamination factor.

2. 4. 2. Degree of contamination

The overall contamination of sediment was assessed based on the degree of contamination (Cd). This was computed as the sum of the contamination factors of all elements examined as expressed below:

$$C_d = \sum_{i=1}^{n} C_f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Following Hakanson (1980) and Aksu *et al.* (1998), four classes have been used to define the degree of contamination of each station in the present study and these are:

Cd < 7 = low degree of contamination,

7 ≤ Cd < 14 = moderate degree of contamination,

14 ≤ Cd < 28 = considerable degree of contamination,

Cd ≥ 28 = very high degree of contamination.

2. 4. 3. Geo-accumulation Index (Igeo)

The Geo-accumulation index (Igeo) was calculated following Muller (1969) equation as follows:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 * B_n}\right) \quad (3)$$

where:

Cn = the measured concentration of the examined metal (n) in the sediment,

Bn = the background concentration of the metal (n) in reference environment

Factor 1.5 = the background matrix correction factor due to lithogenic effects.

Muller (1969) proposed seven classes of the geo- accumulation index as:

Class 0 = Igeo < 0 (practically uncontaminated)

Class 1= 0 < Igeo < 1 (uncontaminated to moderately contaminated)

Class 2 = 1 < Igeo < 2 (moderately contaminated)

Class 3 = 2 < Igeo < 3 (moderately to heavily contaminated)

Class 4 = 3 < Igeo < 4 (heavily contaminated)

Class 5 = 4 < Igeo < 5 (heavily to extremely contaminated)

Class 6 = Igeo > 5 (extremely contaminated)

2. 4. 4. Enrichment factor (EF)

Enrichment factor (EF) was used in this study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soils. Enrichment Factors (EF) were computed as follows:

$$EF = \frac{(C_M / C_{Al})_{sample}}{(C_M / C_{Al})_{earth\ crust}} \quad (4)$$

where:

$(C_M / C_{Al})_{sample}$ is the ratio of metal concentration (mg kg^{-1}) in relation to Al (mg kg^{-1}) in sediment samples.

$(C_M / C_{Al})_{earth\ crust}$ is the ratio of metal concentration (mg kg-1) in relation to Al (mg kg^{-1}) in earth crust.

Aluminium was used as a reference metal because of been major constituent of clay mineral (Reimann and de Caritat, 2000) and also because of its conservative nature (Schropp *et al.*, 1990; van der Weijden, 2002). It has been used as a reference element to assess the status of heavy metals pollution by Ephraim and Ajayi (2014) in surface sediments from some Creeks of the Great Kwa River, Calabar.

Following Sakan (2009), seven contamination categories are recognized and interpreted on the basis of the enrichment factor as follows:

EF < 1 indicates no enrichment,

EF = 1-3 is minor enrichment,

EF = 3 - 5 is moderate enrichment,

EF = 5 - 10 is moderately severe enrichment,

EF = 10 - 25 is severe enrichment,

EF = 25 -50 is very severe enrichment and

EF > 50 is extremely severe enrichment.

The contributions of the anthropogenic origins increases as the EF values increase.

2. 4. 5. Pollution load index (PLI)

The Pollution load index (PLI) represents the number of times by which the metal content in the soil exceeds the average natural background concentration (Ololade, 2014), and this gives an assessment of the overall toxicity status for a sample. The pollution load index (PLI) proposed by Tomlinson *et al.* (1980) was used in this study and is expressed as:

$$PLI = \left(CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x ... x } CF_n\right)^{1/n} \quad \text{(5)}$$

where:

CF is the contamination factor

The PLI value >1 indicates a polluted condition and PLI < 1 indicates no metal polluted existing (Tomlinson *et al.*, 1980).

In the computations from equation (1-5), average concentration of Fe (46,700 mg/kg), Zn (95 mg/kg), Cu (45 mg/kg), Mn (850 mg/kg) and Al (47, 200 mg/kg) reported for shale (Turekia and Wedepohl, 1961) were considered as the background values.

2. 4. 6. Ecological risk factor

The ecological risk index was first proposed by Hakanson (1980) to assess the risk of aquatic pollution in sediments by the effect of trace metals. However, ecological risk of single metal in this study can be expressed as:

$$E_r = T_r \text{ x } \frac{C_{metal}}{C_{backgrund}} \quad \text{(6)}$$

$$E_r = T_r \text{ x } C_f \quad \text{(7)}$$

where:

T_r = metal toxic response factor for metals and were given by Hakanson (1980) and Theoneste *et al.* (2013) as (Mn = 1; Cu =5; Zn =1) and Fe does not have value for Tr.

According to Hakanson (1980) the following tiers are used for the E_r value:

$E_r < 40$ (low risk)

$40 \leq E_r < 80$ (moderate risk)

$80 \leq E_r < 160$ (considerable risk)

$160 \leq E_r < 320$ (high risk)

$E_r \geq 320$ (very high risk)

Similarly, the ecological risk of environment was computed using the equation expressed below:

$$RI = \sum_{i=1}^{n} E_r \quad (8)$$

The terminology used to categorize the RI values suggested by Hakanson (1980) and also used by many authors are:

IR< 150 (low risk)

150 ≤ IR < 300 (moderate risk)

300 ≤ IR < 600 (considerable risk)

IR ≥ 600 (very high risk)

3. RESULTS AND DISCUSSION

3. 1. Physical and chemical properties of the sediment

The result in Table 2 showed the physical and chemical characteristics of the sediments from the various sediment stations along Anantigha coastal area. As shown in table, there are considerable differences in soil particle size distribution under the four stations within Anantigha coastal marine sediment. Soil texture showed variability in percent sand, silt and clay contents in all the stations with sand fraction been the dominant texture except in station 3 where silt (837 g/kg) was the dominant particle fraction. However, the texture observed in station 1, 2 and 4 could be favourable for crop cultivation. Most field crops could grow well in soils having sandy loam and sandy clay loam textural class as these soils have a potentially well-balanced capacity to retain water, form a stable structure and provide adequate aeration (Aytenew, 2015).

The result of pH under wet and dry soil conditions is presented in Table 2. Soil samples from all the stations had pH values which were slightly below neutral in the wet state, but on air-drying, the pH decreased to less than 4.0 in all stations (Table 2). This decrease in pH may indicate the presence of sulfidic materials in the soils which could release appreciable amount of acid on exposure (Dublin-Green and Ojanuga, 1988). Dublin-Green and Ojanuga (1988) have reported that potential acid sulfate soils are identified by simple pH measurement; where pH of these soils usually drops from near neutral in the moist state to less than 4 after oxidation by air drying for several weeks. The result of this study is in line with this report.

Electrical conductivity of the saturation extract was low; < 4 dsm^{-1} in soils under the four stations within Anatigha coastal marine sediment. This result indicates non saline nature of the studied sediment which according to Shrivastava and Kumar (2005) is one in which the electrical conductivity (EC) of the saturation extract (ECe) in the root zone (0-20 cm) is below 4 dsm^{-1}.

The soils have a substantial amount of organic carbon contents (Table 2). These values translate into mean organic matter contents of 6.53, 2.89, 6.22 and 12.29 % respectively, for surface soil sediment. The exchange complex of the sediment samples were predominantly occupied by Ca and Mg. Except for station 1 and 2, the result obtained for the sediment samples agreed with the decreasing cation magnitude, that is $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$.

The exchangeable aluminium values (Al^{+3}) for station S1, S2, S3 and S4 within Anantigha coastal marine sediment were 32.8, 8.8, 37.0 and 20.0 cmol/kg respectively. Percent Al saturation value > 30% may affect sensitive crops [40], while, over 60% could bring about Al toxicity (Kyuma, 2004). Chapman (1966) reported absolute levels of 2-3 cmol kg^{-1} exchangeable Al as excessive for some crops. The value of exchangeable Al and Al saturation obtained for this study could result to Al toxicity to crop and may interfere with crop growth and nutrient availability. Similarly, exchangeable H^{+} concentration in the surface soil where plant root usually concentrate in the four stations except for station 2 could be detrimental to crop growth.

The CEC obtained for the four stations were above the value of 15-20 cmol kg^{-1} (Landon, 1991) stipulated as moderate values in the top soil (0-20 cm) for satisfactory crop production under rain-fed condition. The high CEC may be attributed to the strong association between organic matter and CEC. As per base saturation all the stations except station 1 were rated low in BS as they were all below 20 %; the separating index between fertile and less fertile soils (Landon, 1991).

Table 2. Physico-chemical properties of sediment along Anantigha coastal area.

Sediment properties	Sampling stations			
	S1	S2	S3	S4
Particle size distribution				
Sand (g/kg)	573	623	53	570
Silt (g/kg)	387	87	837	360
Clay (g/kg)	40	290	110	70
Textural classification (USDA)	Sandy loam	Sandy clay loam	Silt	Sandy loam

Chemical properties				
pH (wet)	6.2	3.9	6.1	5.9
pH (dry)	2.3	3.3	2.3	2.2
Electrical conductivity (dsm-^{1})	2.73	0.77	1.70	2.81
Organic carbon (%)	3.75	1.66	3.57	7.06
Organic matter (%)	6.53	2.89	6.22	12.29
Exch. Ca (cmol/kg)	8.2	3.4	5.0	8.2
Exch. Mg (cmol/kg)	12.0	5.2	1.0	4.0
Exch. K (cmol/kg)	0.19	0.11	0.10	0.13
Exch. Na (cmol/kg)	0.14	0.08	0.07	0.10
Al^{3+} (cmol/kg)	32.8	8.8	37.0	20.0
H^{+} (cmol/kg)	13.6	0.8	7.2	8.0
Al saturation (%)	4.19	37.15	73.46	49.47
CEC(cmol/kg)	71.0	61.0	66.0	50.0
ECEC (cmol/kg)	66.79	23.71	50.37	40.43
BS (%)	20.53	8.79	6.17	12.43

SL = sandy loam; SL silt loam; LS = loamy sand; L = loam; C = clay; SCL = sandy clay loam; S1 = Anatigha Jamekon beach; S2 = Antigha fish pond; S3 = Anatigha slughter ; S4 = Ibesikpo timber

3. 2. Heavy metals concentration

The mean concentration of heavy metals in sediment samples at different sampling stations along Anantigha coastal area are presented in Table 3 and the result were found to be in order of Al>Fe>Mn>Cu>Zn (S1) and Al>Fe>Mn>Zn>Cu (S2, S3 and S4). Heavy metal content of soils is influenced by several factors among which soil organic matter content, soil reaction and clay content are the major ones (Adelekan and Alawode, 2011) as well as the nature of parent material and pedogenic processes (Lhendup K, Duxbury, 2008).

The mean concentration of manganese in the sediment samples were 6.20, 3.96, 3.63 and 6.34 mg/kg for stations S1, S2, S3 and S4. The Mn concentrations obtained for the study were lower than the permissible limits of 20-3,000 $mgkg^{-1}$ (Adelekan and Alawode, 2011) established for mineral soil environment and far below the background level of 850 mg/kg (Tables 3). Since Mn is below the maximum contaminant level (MCL) and natural background value (BGV), the soil can be utilized for crop cultivation.

However, caution should be taken, since Mn levels in soil above 1-5 g/kg critical limit can be injurious to the growth of crop plants (Black, 1968).

In the study soil, the mean copper contents for station S1, S2, S3 and S4 were 1.46, 0.44, 1.06 and 0.73 mg/kg. These values of Cu were all below the permissible limits of 2-100 $mgkg^{-1}$ (Lindsay, 1979) established for mineral soil environment. With these low contents of Cu, Anantigh coastal area is safe for crop growth and ecological sustainability (McLaughin *et al.*, 2000; McLaren, 2003).

The mean concentration of zinc in the sediment samples were 0.88, 0.65, 2.14 and 2.03 mg/kg for stations S1, S2, S3 and S4. The values of zinc recorded in this study were higher compared with the mean values obtained by Ephraim and Ajayi (2014) and Eddy and Ukpong (2005). The mean value obtained in this study is below the permissible limits of 10-300 $mgkg^{-1}$ established for mineral soils (Lindsay, 1979) and far below the background level of 95 mg/kg (Table 3). Ibia (1995) opined that exchangeable Zn level in soil between 4.5 mg/kg and 10 mg/kg would be detrimental to the growth of crop plants. However, the values of Zn obtained in this study fell far below this limit, implying that Anantigh coastal area is safe, and can be utilized for crop cultivation

The mean concentration of iron in the sediment samples were 140.14, 128.32, 126.63 and143.51 mg/kg for stations S1, S2, S3 and S4. The mean concentrations of Fe were higher when compared with the reported values of 2298.57 and 1920.94 mg/kg for surface and subsurface soil of Calabar Port Authority, Cross River State (Offiong et al., 2013) and lower than values reported by Jonah *et al.* (2014) in sediment samples from Ohii Miri river in Abia State. These changes may be attributed to the nature of the bedrock materials.

Comparing the values of Fe obtained for this study with the permissible limit (Lindsay, 1979), it is very clear that the values were far below the permissible values, but rated high. Thus, the high Fe content in soil (above the critical value of 2.5-5.0 mg/kg for crop production) means that Fe deficiency is not likely for crops grown on these soils. However, the presence of Fe in high concentrations in soils could lead to its precipitation and accumulation and upon complex chemical reactions can lead to the formation of phlintite (laterite) (Biwe, 2012). This upon alternate wetting and drying could irreversibly form hard indurated material (petrophlintite or ironstone) which could restrict root penetration and drainage. The result obtained for Fe is in strong agreement with other reports (Asaolu and Olaofe, 2014; Adefemi et al., 2007; Adefemi and Awokunmi, 2010) that iron occurs at high concentration in Nigerian soil and sediment.

The mean concentration of aluminium in the sediment samples were 41,900, 371,500, 734,600 and 494,700 mg/kg for stations S1, S2, S3 and S4. The mean concentrations of Al were at variant with the reported values of Ephraim and Ayaji (2014). The Al concentrations obtained for the study were far above the background level of 47,200 mg/kg except for station 1 (Tables 3). However, for all the sampling stations Zn and Cu were generally “low” to “medium” while Al, Fe and Mn values were rated high.

Nevertheless, except Al, other heavy metals including Fe, Zn, Cu and Mn for all stations were within the maximum permissible limits established for mineral soil environment based on soil quality guidelines (Lindsay, 1979). However, Al and Fe having higher values than Cu, Mn and Zn is in line with the findings of Esu (2010) who attributed this to the abundance of sesquioxides in the humid tropical soils. The high contents of the heavy metals in the soils could be associated with acidity of the soils and poor drainage.

Table 3. Concentration of heavy metals in sediment along Anantigha coastal area

Horizon Depth (cm)	Available micro-nutrient → mg/kg ←				
	Fe	Zn	Cu	Mn	Al
S1	140.14	0.88	1.46	6.20	41,900
S2	128.32	0.65	0.44	3.96	371,500
S3	126.63	2.14	1.06	3.63	734,600
S4	143.51	2.03	0.73	6.34	494,700
Overall mean	134.65	1.425	0.923	5.03	410,675
MPL	7,000-550,000	10-300	2-100	20-3,000	10,000-300,000
*Background value	46,700	95	45	850	47,200

***** World geochemical background value in average shale (Turekian KK, Wedepohl , 1961)

MPL = maximum permissible limits (Lindsay, 1979); S1 = Anatigha Jamekon beach; S2 = Antigha fish pond; S3 = Anatigha slughter; S4 = Ibesikpo timber

3. 3. Contamination indices

Contamination factor (CF), degree of contamination (Cd), enrichment factor (EF), geo-accumulation index (Igeo), pollution load index (PLI) and enrichment factor were the contamination indicators used for the assessment of the sediments in the present study. Calculated values of the pollution indices are presented in Tables 4, 5 and 6.

Contamination factor (Cf)

Based on Hakanson (1980) classification scheme for contamination factor, the result of the study (Table 4) has clearly indicated that the Cf values are less than unity for all the studied heavy metals for the four stations except for Al (Table 4). Considering the contaminations level terminologies associated with Cf values, it can be infer from the result that the sediment from Anantigha coastal area is low in Fe, Zn, Mn and Cu. However, Al showed low (station 1) to very high contamination level (station 3). The result obtained for this study is in agreement with the reports of Ephraim and Ayaji (2014) who also recorded a low Cf for Zn and Cu in Great Kwa River, Southeastern Nigeria and Rabee *et al.* (2011) who obtained a low Cf for Mn and Cu in Tigris River Sediment, Baghdad. However, the least Cf value recorded for Zn and Fe at Douglas creek in both wet and dry season by Mosses *et al*. (2015) far exceeds those reported for the present study.

Degree of contamination (C_d)

The result for degree of contamination is also presented in Table 4. Station 1 had a value of 0.932 indicating a low degree of contamination. Stations 2 and 4 had 7.89 and 10.53 degree of contamination respectively. The two stations values agreed with the second class rating ($7 \leq Cd < 14$), indicating a moderate degree of contamination of the areas. However, station 3 with value of 15.61 had considerable degree of contamination. This seems to be contrary with the findings of Jonah *et al.* (2014) who obtained 2.071 and 4.221 for rainy and dry season respectively, in Ohii Miri river in Abia State, Nigeria and comparable with the least value of 7.0 reported by Mosses *et al.* (2015) in Ekpene Ukpa within Qua Iboe River Estuary, South-South, Nigeria.

Pollution load index (PLI)

The results of the pollution load index (PLI) calculated for each station according to the method of Tomlinson *et al.* (2013) is presented in Table 4 and the results showed that the values recorded for all the stations were below 1, indicating an unpolluted condition for the assessed heavy metals. The results of the present evaluation revealed that the sediment of the Anantigha coastal marine sediment is unpolluted by heavy metals even though there is high degree of contamination from Al for stations 2, 3 and 4. This result affirmed those reported for degree of contamination earlier in which the values of heavy metals in the sediments were below permissible limit for contaminations (Table 4) except for Al in some of the locations. This indicates that the sediment of the area is not polluted by heavy metals. The result of the present study is comparable with those of Andem *et al.* (2015) who reported that the sediment of Okporku River, Nigeria is unpolluted by heavy metals but differs from those of Barakat *et al.* (2012) in Day River, Morocco whose values lies between 1.57-2.20, indicating that the concentration levels of the studied metals in most of the stations exceeded the background values. However, the low PLI obtained for the present study are not static, there is tendency for increase as a result of increased human input and activities (2010), and hence there is a need for regular check.

Table 4. Contamination factor, degree of contaimnation and pollution index of heavy metals in sediment along Anantigha coastal area.

Stations	Cf-Fe	Cf-Zn	Cf-Cu	Cf-Mn	Cf-Al	Cd	PLI
S1	0.0030	0.0093	0.032	0.0073	0.88	0.932	0.022
S2	0.0028	0.0068	0.0098	0.0047	7.87	7.89	0.023
S3	0.0027	0.022	0.024	0.0043	15.56	15.61	0.039
S4	0.0031	0.021	0.016	0.0075	10.48	10.53	0.038
mean	0.0029	0.0148	0.020	0.0059	8.69	8.74	0.031

Cf = Contamination factor; Cd = Degree of contamination; PLI = pollution load index

Geo-accumulation index (Igeo)

The calculated Igeo values are presented in Table 5. The calculated results of Igeo of heavy metals in the sediment soil investigated a mean value of -9.023, -6.827, -6.328, -8.03and 1.953 for Fe, Zn, Cu, Mn and Al respectively. From the result it is evident that the Igeo values for all the heavy metals except Al fell in class '0' in sampling stations 1 to 4 indicating practically uncontaminated conditions in these stations. However, considering Al, station 1 was practically uncontaminated whereas, Station 2 and 4 fell in class "3" indicating moderately to heavily contaminated soil, while station 3 fell in class "4" indicating that the sediment was heavily contaminated with aluminium. The values of Igeo of the present study are comparable with those reported in a number of previous studies (Rabee *et al.*, 2011; Bentum *et al.*, 2011; Barakat *et al.*, 2012; Jonah *et al.*, 2014; Andem *et al.*, 2015). In one of such studies in Okporku River, Yala in Cross River State, Nigeria, the highest Igeo values for metals were found as -1.67 for Cu and -1.76 for Fe, these indicates practically uncontaminated conditions, but in surface sediment in Ona River, Western Nigeria, the Igeo value of Cu has reached 2.92 (Akpan and Thompson, 2013). The result of the present study is also in line with what was reported by Barakat *et al* (2012), where calculated Igeo index for heavy metal concentrations in Day sediment in River at Beni-Mellal Region, Morocco ranged from (-0.17 to 0.49) and (-1.04 to -0.54) for Zn and Fe respectively. Their result indicates uncontaminated to moderately contaminated condition.

Enrichment Factor (EF)

Table 5. Geoaccumulation Index and enrichment factor for sediment samples from Anantigha coastal area.

Stations	I_{geo}-*Fe*	I_{geo} - *Zn*	I_{geo} -*Cu*	I_{geo} -*Mn*	I_{geo} -*Al*	*EF- Fe*	*EF- Zn*	*EF- Cu*	*EF- Mn*
S1	-8.96	-7.34	-5.53	-7.68	-0.76	0.0034	0.010	0.037	0.0082
S2	-9.09	-7.78	-7.26	-8.33	2.39	0.00035	0.00087	0.0012	0.00059
S3	-9.11	-6.057	-5.99	-8.46	3.37	0.00017	0.0015	0.0015	0.00027
S4	-8.93	-6.13	-6.53	-7.65	2.81	0.00029	0.0020	0.0016	0.00071
mean	-9.023	-6.827	-6.328	-8.03	1.953	0.001053	0.00359	0.01032	0.00071

I-geo = Geoaccumulation index; *EF* = Enrichment factor

The Enrichment Factors (EF) of all the heavy metals measured in the sediment samples of Anantigha coastal sediment is presented in Table 5. The computed EF values in the sediment indicates that the area is not enriched by the studied heavy metals, since all their EF values are less than 1.0. However, when interpreted following the method used by Birch [58], it becomes obvious that the investigated sediments had not been enriched by the studied heavy metals. This indicates that all the metal assessed in the sediment originated predominantly from the background material and weathering process (Szefer et al., 1996). Nevertheless, the result is contrary to the report of Bentum *et al.* (2011) whose result indicated no enrichment to minor enrichment for Fe, moderately severe enrichment to extremely severe enrichment for Cu and moderate enrichment to severe enrichment for Zn in sediments from Fosu lagoon in Ghana. Also, results reported by Mosses *et al.* (2015) indicate no enrichment to minor enrichment for Fe and Zn respectively.

Ecological Risk Factors

The results from statistical calculation of the ecological risk factor (Table 6) for sediment in Anantigha coastal marine area showed that all the stations were classified as having low potential ecological risk with respect to individual heavy metals (Zn, Cu and Mn) considered. Similarly, the integrated ecological risk index also classified the sediments as having a low ecological risk values. The result for the present study was in line with what was reported by Ajani *et al.* (2015) in Lagos Lagoon sediments, South-western Nigeria where the values obtained showed low ecological risk and that of Jonah *et al.* (2014) in Ohii Miri river in Abia State, Nigeria where 0.203 and 0.367 were obtained for Cu in both rainy and dry season, but contrary to the findings of Gurumoorthi and Venkatachalapathy (2016) in Kanyakumari coastal sediments, Southern India where the potential ecological risk index of Cd, Cu, Pb, Zn from 15 stations were ranged from 64.96-111.48 which corresponds to moderately to considerably risk factor following the rating of Hakanson (1980).

Table 6. Ecological risk factor of heavy metals in sediment along Anantigha coastal area.

Stations	E_r -Zn	E_r -Cu	E_r -Mn	RI
S1	0.0093	0.016	0.0073	0.033
S2	0.0068	0.049	0.0047	0.061
S3	0.022	0.12	0.0043	0.15
S4	0.021	0.08	0.0075	0.11
Mean	0.0148	0.066	0.0059	0.088

3. 4. Correlation

Organic matter and clay can be bounded with some amount of metals and affect the metal enrichment rates of sediment (Eimers *et al.*, 2002). Also, pH controls the availability of nutrient including heavy metals (Adefemi and Awokunmi, 2010). So we correlated the sediment pH, organic matter and clay content with sediment metals concentration for different stations. The heavy metals showed negative correlation with pH, indicating that as pH increases, the concentration of the heavy decreases and vice versa.

All the heavy metals showed negative correlation with clay, indicating the adsorption of heavy metals on the finer sediments. A strong correlation of OM with Fe ($r = 0.776$), Zn ($r = 0.65$) and Mn ($r = 0.706$) were observed and this reveals the formation of organic complexes with these heavy metals as a ligand by flocculation and subsequently influences their distributions, due to its high specific surface area (Marchand *et al.*, 2006; Zourarah *et al.*, 2008).

Fe exhibits significant association with Mn (r = 0.992) along with OM (r = 0.776), which reveals its key control over the linkage of these metals with organic matrix by association as Fe-oxy-hydroxides (Rubio et al., 2000) and Mn-oxy-hydroxides (Selvam *et al.*, 2012), whereas the rest of heavy metal pairs showed no significant correlation with each other. High significant correlations of Fe with Mn alone, indicates same point source or common sink in the sediments for these two metals. The result further indicates that OM, Fe and Mn hydroxides are the main geochemical carriers of metals in Anantigha coastal marine sediment.

Table 7. Relationship between heavy metals and pH, organic matter and clay.

	pH	clay	OM	Fe	Zn	Cu	Mn	Al
pH	1							
clay	.965*	1						
OC	-.761	-.699	1					
Fe	-.550	-.663	.776	1				
Zn	-.698	-.486	.675	.079	1			
Cu	-.678	-.792	.118	.288	.062	1		
Mn	-.538	-.677	.706	.992**	-.005	.370	1	
Al	-.106	.159	.155	-.498	.772	-.398	-.590	1
*. Correlation is significant at the 0.05 level (2-tailed).								
**. Correlation is significant at the 0.01 level (2-tailed).								

3. 5. Hierarchical cluster analysis

Hierarchical cluster analysis was used to determine relationships and similarities among variables in their respective stations. With regard to the dendogram cross-section, the stations were divided into three groups. Figure 2 represents a cluster analysis dendrogram based on the measured parameters. The first group included station S1, and changes in this station were mainly due anthropogenic activities such as; sand mining and domestic/industrial effluents in the stations. The second group, which consisted of stations S2 and S4, as having similar relationship, was affected by residential sources of pollutants. The third group only includes station S3, and sediment quality in this station is mainly affected by sewage from slaughter house and effluents from the nearby market. Therefore the differences between the groups indicate the differences in the sources of pollution. Therefore the differences between the groups indicate the differences in the sources of pollution.

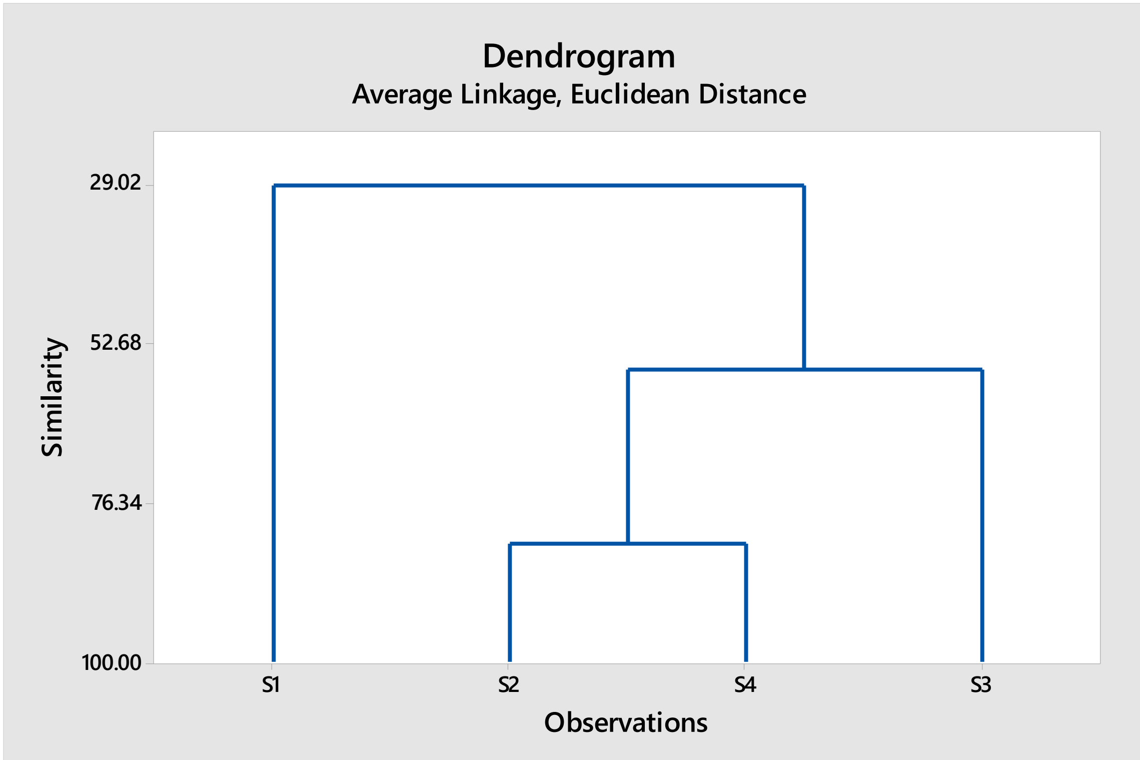

Figure 2. Dendrogram showing clustering of sampling stations

4. CONCLUSIONS

The results of the present investigation essentially contribute to the knowledge on the extent of pollution of sediments in Anatigha coatal area. The mean concentration levels of all the heavy metals in the sediment were lower than mean background value except Al. Fe exhibits significant association with Mn, which indicates same point source or common sink in the sediments for these two metals. Organic carbon, Fe and Mn hydroxides are the main geochemical carriers of metals in Anantigha coastal marine sediment. Analyzed data showed that the sediments in the area are contaminated with Al with Igeo result showing station 2 and 4 has been moderately to heavily contaminated with Al while station 4 heavily contaminated with aluminium. Station 1 had low degree of contamination, whereas station 2 and 4 had moderate degree of contamination and station 3 showing considerable degree of contamination. The PLI result indicates unpolluted condition and the area were not enriched by the studied heavy metals as shown by EF values. Hence, the sediment in Anantigha coastal marine area was classified as having low ecological risk factor. From the foregoing, the area can be utilized for cultivation of acid tolerant crops.

Recommendations

The levels of these metals are not static; therefore there should be need for continuous monitoring through adequate soil testing.

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