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Heavy Metal Enrichment and Sediment Quality Assessment of Yewa Creek, Southwest Nigeria

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Abstract
Surface sediment samples from the study area were analysed for their heavy metal contents, to determine level of enrichment, and assess sediment quality by employing the consensus based sediment quality guidelines. The mean probable effect concentration quotient (*mPECQ*), threshold effect and probable effect concentrations (TEC and PEC), and potential ecological risk index (RI) were used to evaluate the sediment quality. Pearson's correlation and cluster analyses were done to determine the interrelationship between heavy metals of concern and infer possible sources of these contaminants. In all the stations, sediments were not enriched in Cu, Pb, Co and Mn. The metals with significant enrichment are site-specific. Severe enrichment of Cd noticed at the uppermost reach of Yewa Creek has been adduced to contributions from untreated sewage sludge, mineral fertilizers and wastewater from agricultural activities. The Pearson's correlation matrix revealed that highly significant relationships exist between Co and Ni, As and Ni, As and Co, Cd and Ni, Cd and Co, and, Cd and As, implying that each of these pairs may have originated from the same contamination source(s). The result of hierarchical cluster analysis unveiled the association of Zn with Co, As and Ni, giving evidence of anthropogenic contribution, while, its association with Cu, Pb and Mn also indicated contribution from geogenic activities. The concentration of Cd in sediment from the second sampled station at the uppermost reach of Yewa Creek was below PEC, but its exceedance, based on comparison to PEL, suggested highly degraded sediments. Also, a very high risk index (RI) obtained in this station implied that sediment has been heavily impacted and harmful effects may be produced on vagrant and sessile organisms. Contrastingly, the calculated *mPECQ* values indicated that sediments in the study area are not toxic.

Keywords: *Heavy metals, Enrichment, Sediment, Yewa Creek, Southwestern Nigeria.*

Introduction

Sediments play highly significant role in maintaining the trophic status of any water body and are the major reservoir of heavy metal contaminants, hence, constitute ecologically important components of aquatic habitat (Singh *et al*., 1997; Mahino *et al*., 2014). Aquatic environment provides food and shelter for fishes, crustaceans, molluscs, sea turtles, whales, crocodiles, and nutrient supplies for economically important fish species (Zabadal *et al*., 2005). Due to natural (weathering and erosion of rocks) and anthropogenic activities, the concentrations of some trace metals such as Cr, Cd, Cu, Ni, As, Pb, Zn, Co, Fe, Mn, and Al are often enriched in sediments relative to Upper Continental Crust (Glasby *et al*., 2004; Shazili *et al*., 2006; Varol, 2011). These enriched trace metals may become a potential source of pollution (Islam *et al*., 2015). Consequent upon the bio-accumulative nature and persistency, concentration of heavy metals in sediments are significantly important in order to carry out sediment quality assessments.

Many researchers have proposed different sediment quality guidelines based on empirical data relating contaminant concentrations to harmful effects on sediment dwelling organisms. One of the most used guidelines related to freshwater systems are those developed and provided by MacDonald *et al*. (2000).

According to the PEC guideline, mean-Probable Effect Concentration Quotients (m-PECQs) provide an overall measure of heavy metal contamination and allow for evaluation of the combined effects of all contaminants considered in any given sediment (Veses *et al*., 2013). Based on the PEC guideline, mean-Probable Effect Concentration Quotients (m-PECQs) provide an overall measure of chemical contamination and support an evaluation of the combined effects of multiple contaminants on sediments (MacDonald *et al*., 2000; Ingersoll *et al*., 2001; Long *et al*., 2006). These quotients may help to classify samples as toxic or non-toxic according to reference values found by other researchers and allow for sample comparisons. Previous studies have used these quotients to predict the potential toxicity of sediment samples (Rippey *et al*. 2008; Ingersoll *et al*. 2009; MacDonald *et al*. 2011).

Yewa area in southwest Nigeria, hosts industries such as distilleries, battery production, asbestos making and brewery, releasing various effluents that are contaminating the environment (Adebowale *et al*., 2011). In Yewa South Local Government, the rural dwellers believed that these industrial activities have not impacted their aquatic habitats because the locations are far away from their area. Meanwhile, they engage in occupations or pursuits that require the use of water from Yewa River which receives most of the deleterious metals released to the environment through these industrial activities. The most popular occupation among the dwellers is agriculture involving the use of fertilizers as manure and artisanal fishing. Typical agricultural income generating activities are Garri frying; tomato, pepper, green vegetable production; and rearing of goats, cattle and pigs among others. The disposal of wastes arising from these activities could also contaminate the aquatic habitats in this environment. However, the southernmost part of Yewa River that empties its contents into Badagry Creek was sampled as the transport-energy dissipation at this segment is highly significant. Here, because of adsorption, hydrolysis and co-precipitation, only a small portion of free metal ions stay dissolved in water, and a large quantity of them get deposited in the sediment (*Cf*. Gaur *et al*., 2005). The accumulated metals in sediments could be biomagnified along the aquatic food chains (Gumgum *et al*., 1994; Yi *et al*., 2011), which in turn may enter into the human food chain resulting in health problems (Cook *et al*., 1990; Deniseger *et al*., 1990). It is therefore pertinent to extensively investigate heavy metal contamination in these sediments in order to effectively manage these ecosystems.

The principal objectives of this research are to (1) investigate heavy metal contents (Cd, Cr, Co, Cu, Ni, Pb, Zn and As) and level of enrichment in surface sediments; (2) assess sediment quality by employing the consensus based sediment quality guidelines (TEC and PEC approach); and (3) determine if the sources of metals are natural or anthropogenic, based on Pearson's correlation and cluster analyses of metal concentrations and enrichment factors in relative order.

The Study area

Yewa River lies approximately within latitudes 6.20º N and 7.75º N and longitudes 2.70º E and 3.00º E of the

Fig. 1: The map of Yewa Creek showing the stations sampled and their catchment areas in Southwest Nigeria.

Greenwich Meridian. It is a trans-boundary river between Republic of Bénin and The Federal Republic of Nigeria. Yewa may become urbanized in the next decade as a result of recently established Dangote Cement Factory at Ibese near the town. This area is located in the moderately hot, humid tropical climatic zone of southwest Nigeria. It is under the influence of the tropical continental air mass and the tropical maritime air mass (Adeaga *et al*., 2019). The narrow zone of convergence of the two air masses is called the Intertropical Convergence Zone (ITCZ), which usually shifts seasonally with the pressure belts and Isotherm. There are two distinct seasons: the wet season begins from March/April to October/November and the dry season which last for the rest of the year starts from October/November till March/April. The temperature is relatively high during the dry season with the mean annual temperature of about 26 ºC in the south and 28 ºC in the north with an annual range of ± 4 ºC (Adeaga *et al*., 2019). Yewa River flows through Yewa South and Ado-Odo to Atlantic Ocean.

The investigated creek lies within latitudes 6^0 26'N and 6^0 34'N and longitudes 2^0 50'E and 2^0 55'E (Fig. 1). This creek has shallow water depth with an average of 1.0 m at the centre, reaching a maximum of 3.0 m where it opens into the Badagry Creek (Phillips *et al*., 2017).

Materials and Methods

Sampling and Measurements

Surface sediment samples were collected from 11 stations in Yewa Creek using van Veen grab that was well wrapped with polyethylene material around the stainless steel clamshell bucket to avoid contamination. The bucket was washed with water immediately after every sampling. Sampling stations were positioned with the use of handheld GPS (Garmin etrex). At each sampling site, 300 g of the uppermost 2 cm of the surface sediment was collected with a plastic spatula and kept in labelled cellophane bag. The samples were air dried at room temperature and sieved through 2 mm aperture sieve to remove gravel sized materials. The < 2 mm fractions were subsequently used for particle size and chemical analyses. The sand size fractions were separated from mud fractions by wet sieving through a stainless steel 63 mm aperture sieve; and silt and clay fractions separated by using standard pipette method of Gale and Hoare (1991). All water samples were collected from the surface (30 cm) into labelled plastic bottles indicating the various stations, and measurements of temperature and pH were done during sampling. The pH was measured with pH meter (Hanna H 19625, Precision 0.01); and temperature with a mercury thermometer. Salinity was determined in the laboratory with a Conductivity Salinometer (WTWLF 325, Probe WTW Tetracon 325, Precision 0.1g/l).

Analytical Techniques

The samples for chemical analysis were pulverized using agate mortar and pestle, and the dried homogenized samples were sieved through 75 mm screen. The pulverized samples were sent to ACME analytical laboratory in (Vancouver), Canada, where samples were digested using the Aqua regia technique following the procedure described by Loring and Rantala, 1992. Also, Inductively Coupled Plasma-Emission Spectrometer was used for trace metal quantification and report submitted with certificate number VAN 13002288.1.

Assessment of Sediment Contamination

The mean concentrations of heavy metals were compared to the values documented by Buchman (1999) since there were no background values for the study area. Also, the unit of measurement of concentration was converted to part per million to allow direct comparison of values. Where a range of values were given, the median values were chosen for calculations and interpretation of indices of contamination.

Enrichment Factor (EF)

Enrichment factor is used to quantitatively assess the contribution of anthropogenic sources on the concentrations of heavy metals (Sakan *et al*., 2009; Hu *et al*., 2013). The EF is computed using the relationship below:

EF = (Metal/Fe) Sample / (Metal/Fe) Background

In this study, iron (Fe) was used as the reference element for geochemical normalization because of the following reasons: (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals and (3) its natural concentration tends to be uniform (Bhuiyan *et al*., 2010). EF values were interpreted as suggested by Sakan *et al*. (2009), where: EF < 1 indicates no enrichment; <3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and >50 is extremely severe enrichment.

Potential Ecological Risk Index (PERI)

In order to assess the extent of potential ecological risk that could be posed by metals in sediments, the quantitative method proposed by Hakanson (1980) was employed. Risk index (RI) is widely used in assessing ecological risk of heavy-metal pollution in sediments. RI is calculated as follows:

$RI = \Sigma Ei$

$Ei = T fi$

$Fi = Ci/Cb$

RI refers to the sum of all risk factors in the sediment samples and *Ei* is the monomial potential ecological risk factor for an individual heavy metal. Ti refers to the metal toxic response factor (i.e. As = 10, Cd = 30, Cu = Pb = Ni = Co = 5, Cr = 2 and Zn = Mn = 1), *Fi* refers to the metal pollution factor, Ci is the measured concentration of heavy metal in the sediment sample, and Cb is the background value of the reference metal. The RI values were categorized as follow: RI<150 indicates low ecological risk, 150=RI<300 indicates moderate ecological risk, 300=RI<600 indicates considerable ecological risk, and RI=600 indicates very high ecological risk for the sediment (Hakanson *Op cit*). Half the detection limit was used for heavy metals reported below the method detection limit.

Multivariate Statistics

The Paleontological Statistical Software of Hammer *et al*. (2007) was employed for multivariate analyses. Multivariate analyses including Pearson's correlation and cluster analysis (CA) were assigned to define the source apportionment of heavy metals. The Pearson's correlation analysis was done to determine the strength of interrelationship between metals of interest contained in the sediments investigated. Cluster analysis was performed using the enrichment factors (EF) to unveil the similarity in pattern of enrichment among the metals investigated, and determine possible anthropogenic or common source influence. The hierarchical agglomerative cluster analysis was done by employing the pair group method and Pearson's correlation as a measure of similarity.

Sediment Quality Guidelines

Assessment of sediment quality was done by considering the mean Probable effect concentration quotient (m-PECQ) and the comparison of concentrations measured with the consensus-based TEC and PEC values provided by MacDonald *et al*. (2000). The m-PECQ was calculated by the equation below as suggested by Ingersoll *et al*. (2001), where *Ci* is the measured concentration of individual heavy metal, *PECi* is the individual PEC value, *n* represents number of heavy metals considered, *i* denotes single / a heavy metal in consideration.

$$m\text{-}PECQ = \left(\sum_i^n C_i / PEC_i\right) / _n$$

As suggested by Ingersoll *et al*. (2001), five ranges of the *m-PECQ* were used for ranking samples in terms of incidence of toxicity: <0.1; 0.1–<0.5; 0.5–<1.0; >1.0; >5.0. These levels correspond to the percentage possibility of sediment toxicity represented as 10%; 17%; 56%; 97%; 100% in relative order.

Results and Discussion

Sediment and Water Characteristics

The composition of grain sizes showed the order of clay (42.00-80.04 %; Mean: 55.70 %) > sand (13.86-46.59 %; mean: 28.83 %) > silt (3.00-26.00 %; mean: 15.46 %) (Table 1). Based on the grain size composition, all sediments in this creek are sandy mud. Grain size affects entrainment, transport and deposition, providing clues for provenance, and functioning as the main controlling parameter in the determination of physiochemical properties of sediments (Pye, 2004). Grain size property has significant importance in reconstruction of paleoecologic peculiarities and also influences organic and inorganic matter concentrating in sediments (Maslennikova *et al*., 2012). Consequently, the prevalence of clay sized particles in Yewa Creek may enable concentration of more available heavy metals due to relatively larger surface-to-volume ratio when compared to other sizes (Salomons and Forstner, 1984; Martincic *et al*., 1990). Stations Y6 near Banimgbe catchment area at the lower reach, Y3 and Y1 at the upper reach of Ogun State segment of the creek (Fig. 1), have the highest clay sized fractions of 80.04 %, 70.25 % and 70.00 % respectively. The same order of heavy metal concentration may therefore results. The pH, temperature, dissolve oxygen concentration and water turbulence affect precipitation, sorption and dissolution responsible for heavy metal concentration (Simpson *et al*. 2004; Abdel-Ghani and Elchaghaby 2007; Atkinson *et al*. 2007). Though slightly alkaline, pH values are more alkaline at stations Y2 (8.80), Y8 (8.40), Y10 (8.20) and Y6 (8.10) than others that are indicating similar values for coastal water (Riley and Chester, 1971). Contrastingly, the pH of water in station Y1 (6.90) is slightly acidic and hence heavy metal precipitation may differ. It is therefore anticipated that more heavy metals will be precipitated and adsorbed onto sediment surfaces at stations indicating pH of coastal water in increasing order of values than station Y1 (Duncan *et al*., 2018). Also, metals will be more easily released from sediments into the water at station Y1 where though there is no marked temperature difference from other stations but characterized by a low pH (Table 1). The shallow water creek (1.0-2.9 m) is generally non-saline (0.00-1.00 $^{0}/_{00}$) as it is overwhelmed by fluvial activities.

Table 1: Sediments' description and water characteristics for Yewa Creek, Southwest Nigeria

S/N	Sample stations	Depth (m), Sediment-Water Surface	pH	Salinity ($^{0}/_{00}$)	Temperature (^{0}C)	Sediment Description			Remark(s)
						% Sand	% Silt	% Clay	
1	Y1	1.9	6.90	0.00	27.7	18.01	11.99	70.00	Sandy Mud
2	Y2	1.6	8.80	1.00	27.6	25.42	20.08	54.50	Sandy Mud
3	Y3	1.1	7.90	0.00	27.7	15.05	14.70	70.25	Sandy Mud
4	Y4	1.6	7.60	0.00	27.1	44.28	6.72	49.00	Sandy Mud
5	Y5	1.0	8.00	0.00	28.0	24.00	26.00	50.00	Sandy Mud
6	Y6	1.1	8.10	0.00	28.0	13.86	6.10	80.04	Sandy Mud
7	Y7	1.9	7.90	0.00	28.1	30.61	20.09	49.30	Sandy Mud
8	Y8	1.2	8.40	0.00	28.2	46.59	3.00	50.41	Sandy Mud
9	Y9	1.8	7.80	0.00	27.8	23.83	21.07	55.10	Sandy Mud
10	Y10	2.9	8.20	0.00	27.8	37.67	20.33	42.00	Sandy Mud
11	Y11	2.0	8.00	0.00	27.8	37.82	20.00	42.12	Sandy Mud

Heavy Metal Concentrations and Sediment Quality Assessment

The concentration in part per million (ppm) of Cu at the Upper reach of the Yewa Creek (Y1-Y5) ranged from 11-15 at the Ogun State end, and at the lower reach in Lagos State segment, from 10-19 (Table 2). The sample from the boundary between Ogun and Lagos states (Y6) contained the lowest content of Cu, implying that there may be no direct connection between the sources of Cu in the two segments. The Cu content is generally very low in sediments of Yewa Creek as the background concentration of Buchman, 1999 (18.0 ppm) surpasses the average recorded (12.8 ±1.25), hence poses no threat (Table 2). Also, Pb (mean: 8.18 ±0.75), Zn (mean: 75.9 ±16.4), Ni (mean: 21.7 ±0.79), Mn (mean: 436 ±74.5), Fe in % unit (mean: 6.13 ±0.45), As (mean: 2.55 ±0.24) and Al in % unit (mean: 1.67 ±0.16) have their lowest contents in sediment from the station at the boundary between Ogun and Lagos states (Y6). Contrastingly, besides station Y2, the highest concentration of Cd was measured in station Y6.

Table 2: Heavy metal concentrations and mPECQ values for sediments of Yewa Creek, and TEC and PEC values extracted from MacDonald et al. (2000). All values in mg/kg have been converted to ppm.

Trace metals (MDL)	Stations											Mean (standard error)	TEC	PEC
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11			
Cu (1)	11	14	15	15	12	2	13	10	14	16	19	12.8(±1.25)	31.6	149
Pb (3)	7	6	11	6	8	3	12	10	10	8	9	8.18(±0.75)	35.8	128
Zn (1)	88	65	239	52	55	31	55	48	53	72	77	75.9(±16.4)	121	459
Ni (1)	21	28	21	20	23	17	20	22	22	21	24	21.7(±0.79)	22.7	48.6
Co (1)	26	32	25	19	28	28	23	26	26	31	29	26.6(±1.05)	-	-
Mn (2)	423	248	325	391	351	140	324	405	398	1104	690	436(±74.5)	-	-
Fe % (0.01)	7.11	4.95	5.77	6.29	6.61	2.11	5.77	7.03	6.68	7.85	7.25	6.13(±0.45)	-	-
As (2)	3	3	3	3	3	1	3	2	3	1	3	2.55(±0.24)	9.79	33.0
Cd (0.5)	0.6	4.0	0.25	0.25	1.1	1.2	0.25	0.8	0.5	0.25	1.1	0.94(±0.31)	0.99	4.98
Al % (0.01)	1.67	1.97	1.86	1.87	1.84	0.40	1.66	1.62	1.91	1.1	2.52	1.67(±0.16)	-	-
mPECQ	0.16	0.29	0.22	0.10	0.17	0.12	0.14	0.15	0.16	0.15	0.20	0.17(±0.01)	-	-

According to Hakanson (1980), the sediment from station Y1 indicated considerable contamination with Zn (3.91), Cd (3.0) and Fe (5.10); moderate contamination with Ni (2.12), Co (2.60), Mn (1.06) and As (2.73); and low contamination with Cu (0.63) and Pb (0.67). The sediments of this creek are highly enriched in Al (CFs: 1.54-9.69) (Table 3). Approximately 63.63 % of representative sediments from Yewa Creek exhibited moderate contamination with Zn, whereas 27.27 % and 9.09 % showed considerable and very high contamination respectively. More sediments indicated considerable to very high contamination by Cd (CFs from 3 to 20) in Yewa Creek where the least contaminated station (Y6) still indicated very high contamination with Cd (6.0). The Cu and Pb have the least contamination factors in all the sediments analysed, while Ni, Co, Mn and As showed more of moderate contamination in sediments. The average values of CFs < 1 recorded in most stations of the creek for Cu and Pb suggested lithogenic source (Decena *et al*., 2018).

Table 3: The contamination factors (CF) of heavy metals in surface sediments of Yewa Creek, southwest Nigeria

Trace metals	Stations										
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11
Cu	0.63	0.80	0.86	0.86	0.69	0.11	0.74	0.57	0.80	0.91	1.09
Pb	0.67	0.57	1.05	0.57	0.76	0.29	1.14	0.95	0.95	0.76	0.86
Zn	3.91	2.89	10.62	2.31	2.44	1.38	2.44	2.13	2.36	3.20	3.42
Ni	2.12	2.83	2.12	2.02	2.32	1.72	2.02	2.22	2.22	2.12	2.42
Co	2.60	3.20	2.50	1.90	2.80	2.80	2.30	2.60	2.60	3.10	2.90
Mn	1.06	0.62	0.81	0.98	0.88	0.35	0.81	1.01	1.00	2.76	1.73
Fe	5.10	3.55	4.14	4.51	4.74	1.51	4.14	5.04	4.79	5.63	5.20
As	2.73	2.73	2.73	2.73	2.73	0.91	2.73	1.82	2.73	0.91	2.73
Cd	3.00	20.00	1.25	1.25	5.50	6.00	1.25	4.00	2.50	1.25	5.50
Al	6.42	7.58	7.15	7.20	7.08	1.54	6.38	6.23	7.35	4.23	9.69

In evaluating enrichment factor (EF), Fe was being used as a reference element in this study. The heavy metals EF values followed the order Cd > Zn > Co > As > Ni > Pb > Cu (Table 4). The sediments are not enriched in Cu, Pb, Co and Mn in any of the stations, whereas, minor enrichment of Zn, Ni and As were noticeable at stations Y3, Y5 and Y5 respectively. Minor enrichment, moderate enrichment and moderately severe enrichment of Cd were indicated in sediments from stations Y10 and Y11, Y5, and Y2 in relative order (Table 4). The marked enrichment of Cd is an indication of anthropogenic activities in the catchment areas. Such activities may include agricultural runoffs and indiscriminate manner of waste disposal. The major sources of Cd are untreated sewage sludge, mineral fertilizers and wastewater from industrial and agricultural activities (Satarug *et al*., 2003). The enrichment of sediment with Zn could also be linked to large-scale use of agrochemicals and fertilizers. Exemption of stations Y9 and Y11, all stations showed minor enrichment of Al. It is important to note that bioavailability and toxicity of heavy metals in sediments largely depend on their concentrations and chemical form. As a result, heavy metals in sediment samples with high enrichment factor values, along with high labile fractions in sediments, possess the potential for mobility and bioavailability in aquatic ecosystem (Islam *et al*., 2015).

Table 4: The enrichment factors (EF) of heavy metals in surface sediments of Yewa Creek, southwest Nigeria

Trace metals	Stations										
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11
Cu	0.123	0.225	0.207	0.190	0.076	0.180	0.113	0.167	0.161	0.209	0.145
Pb	0.131	0.161	0.253	0.133	0.189	0.276	0.189	0.199	0.135	0.165	0.161
Zn	0.767	0.814	2.568	0.513	0.911	0.591	0.423	0.492	0.569	0.658	0.516
Ni	0.416	0.826	0.513	0.448	1.136	0.488	0.441	0.464	0.377	0.466	0.490
Co	0.510	0.902	0.604	0.421	1.852	0.556	0.516	0.543	0.551	0.558	0.591
Mn	0.208	0.174	0.196	0.217	0.231	0.196	0.201	0.208	0.490	0.332	0.185
As	0.535	0.769	0.659	0.605	1.202	0.659	0.361	0.570	0.323	0.525	0.576
Cd	0.588	5.630	0.302	0.277	3.970	0.302	0.790	0.523	0.220	1.060	1.160
Al	1.260	2.135	1.730	1.595	1.018	1.543	1.236	1.534	0.752	1.722	0.129

Results of Multivariate Analyses

Correlation Analysis

Pearson's correlation matrix and cluster analysis were employed to further interpret the enrichment factors of heavy metals in sediments. The results of Pearson correlation analysis (Table 5) revealed highly significant correlation between Co and Ni (r= 0.959), As and Ni (r= 0.923), As and Co (r= 0.886), Cd and Ni (r= 0.845), Cd and Co (r= 0.705), and Cd and As (r= 0.660), implying that each of these pairs of heavy metals may have originated from the same contamination source or share similar geochemical behaviour (Gupta *et al*., 2014; Liu *et al*., 2014). The correlation matrix also showed that there was weak negative correlation between Cu and Co (r= -0.488). There was no marked correlation between Cu and Mn (r= 0.0285), Pb (r= 0.135), Zn (r= 0.274), Cd (r= -0.010), As (r= -0.247) and Ni (r= -0.302), while strong correlation was indicated with Al (r= 0.616). Weathering and erosion of soil and rocks from catchments and runoffs from nearby farm settlements could cause heavy metal enrichment in stream sediments. When natural activity like denudation takes place as earlier mentioned, and there is an increase in some heavy metals in sediments, strong positive correlation exists, and same source contribution is inferred. Also, if runoffs from farm settlements are emptied into a river, or polluted air from industrial / commercial activities finally dumps suspended heavy metals into such river, same situation arises. The former and the latter processes are referred to natural (lithogenic) and anthropogenic activities respectively. Upon these premises, the negative correlation between Cu and Co may imply different sources, since the correlation matrix showed increase in Cu with corresponding decrease in Co contents of sediments.

Table 5: Pearson's Correlation matrix for heavy metals in sediments of Yewa Creek, Southwest Nigeria.

	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Al
Cu									
Pb	0.13502								
Zn	0.27352	0.46399							
Ni	-0.30192	0.09550	0.13627						
Co	-0.48814	0.07559	0.11527	**0.95891**					
Mn	0.02847	-0.36532	-0.16634	-0.25257	-0.08752				
As	-0.24689	0.23743	0.24359	**0.92300**	**0.88557**	-0.39034			
Cd	-0.00980	-0.12906	-0.01192	**0.84457**	**0.70485**	-0.25166	**0.65929**		
Al	**0.61615**	0.26247	0.28866	0.10105	-0.08132	-0.24799	0.13007	0.24723	

Cluster Analysis

The result of hierarchical agglomerative cluster analysis rendered a dendrogram (Fig. 2), where all the heavy metals are grouped into two major statistically significant clusters. Also, Al and Cd at opposite ends as outliers, indicating different sources of their enrichment in sediments. The sediments in the study area are mostly enriched in Cd, followed by Al. The two major clusters are pivoted by a minor outlier of Zn which is the nearest neighbour to Cd in the linkage group. Cluster I includes Cu, Pb and Mn representing group with no enrichment in the sediments analysed (Table 4) with EF less than unity. These metals are geogenically/lithogenically sourced. Cluster II contain heavy metals which only indicated minor enrichment in one station i.e. Co (Y5), As (Y5), Ni (Y5) and Zn (Y3), all in the Ogun State segment of Yewa Creek (Figs. 1 and 2). The association of Zn with Co, As, Ni are indicative of anthropogenic source, and inferring lithogenic source with Cu, Pb and Mn. Cadmium and Aluminium are grouped as outliers for both clusters, hence, are from anthropogenic and lithogenic sources. Aluminium is a major component of continental rock and soil. They are extremely resistant to weathering, and therefore, well conserved in terrigenous sediments. The study area is marked by mainly sandy mud, unarguably deposited under low energy hydrodynamic regime when fine matter would be preferentially deposited. The enrichment of Al may be justified on this basis, since, Al is generally characterized by high affinity for fine sediments. The anthropogenic sources may include disposal of solid waste, primarily associated with industrial process such as aluminium production. Also, tea leaves may contain very high concentration of Al (Dong *et al*. 1999). The EF of Cd largely indicate anthropogenic contribution in stations where there are moderate to severe enrichment. The most likely sources of Cd in the study area are untreated sewage sludge, mineral fertilizers and waste water from agricultural activities. However, few stations have no enrichment of Cd.

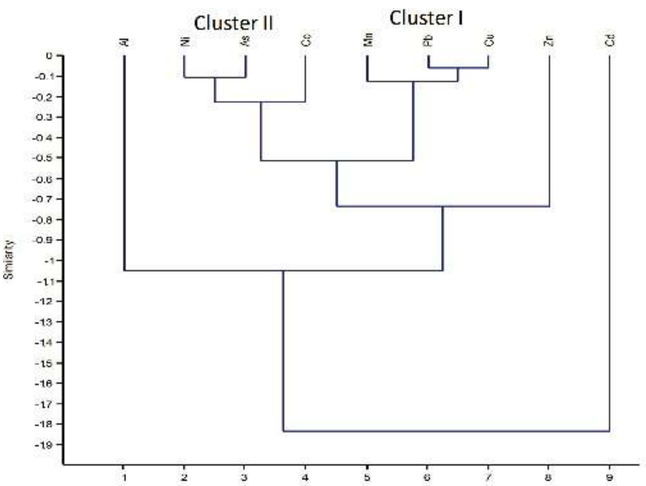

Fig. 2: Dendrogram showing clustering of enrichment factors for the heavy metals in sediments of Yewa Creek, Southwest Nigeria.

Sediment Quality Assessment

Application of Sediment Quality Guidelines

It is important to determine whether the concentrations of heavy metals in sediments pose a threat to aquatic life. Heavy metal concentrations in sediment samples analysed were compared with the consensus-based threshold effect concentration (TEC) and probable effect concentration (PEC) values of sediment quality guidelines (MacDonald *et al*., 2000). The concentrations of Cu, Pb, Zn and As are lower than their TEC in all sediments (Table 2), hence, PEC values were not considered for assessment of sediment quality. This implies that the concentrations of these heavy metals have no negative effect on the sediment quality. Though below PEC, the concentrations of Ni and Cd are more than TEC in 27.3 % and 36.4 % of samples from all stations respectively. The concentration of Cd (4.00 ppm) in station Y2 at the upper reach of Yewa Creek, the Ogun State segment, is above probable effect level (PEL) of 3.53 ppm (MacDonald *et al*., 2000). Above PEL, the concentrations are likely to result in harmful effects on sediment-dwelling organisms considering the empirical-based sediment quality guidelines. An index of sediment toxicity ranking, *mPECQ,* was evaluated in this study. Samples from stations Y2 (0.29) and Y3 (0.22) at the Ogun State segment have the highest *mPECQ* values hence the percentage possibility of toxicity did not exceed 17 % (Ingersoll *et al*. 2001). The *mPECQ* values ranged from 0.1 (Y4) to 0.29 (Y2) indicating that all the sediments from the creek are not above 17 % possibility of being toxic, though, are above 10 % in the ranking. The overall assessment of sediments from Yewa Creek based on mean probable effect concentration quotient (*mPECQ*) is favourable, since no individual value measured up to 0.5, indicating non-toxicity (Varol, 2011).

Potential Ecological Risk Index (RI)

The product of the individual heavy metal toxic response factor (*T*) and metal pollution factor (*fi*) calculated as contamination factor are added in each sediment to evaluate its risk index (RI). The RI has been proven as a highly effective tool to assess the extent of contamination of sediments of an aquatic ecosystem (Lin et al., 2013). The monomial potential ecological risk factor for an individual heavy metal *Ei* and RI for the respective sampled station are shown in table 6. The mean *Ei* for each heavy metal of concern declined in the following order Cd>As>Co>Ni>Pb>Cu>Zn>Mn. This order is directly influenced by the toxic response factor of the individual metal and its concentration in sediment. The risk index for sediment sample from station Y2 is very high (RI = 667), implying that the station has been heavily impacted and deleterious effects may be produced on vagrant and sessile organisms. The potential ecological risk indices (PERI) for stations Y1, Y5, Y6, Y8 and Y11 interpreted moderate ecological risk whereas, low ecological risk was revealed from sediments collected at stations Y3, Y4, Y7, Y9 and Y10.

Conclusions

Sandy mud dominates the surface sediments of Yewa Creek. The creek is a shallow water, non-saline with an overwhelming pH of coastal water. The physiochemical characteristics of water and sediments are preponderantly similar in most stations, except station Y1 at the uppermost reach of the creek where the water is slightly acidic. However, this does not make much difference in the concentration of metals retained in sediments as the water acidity is insignificant. In this study, heavy metal enrichment factors followed the decreasing order of Cd>Zn>Co>As>Ni>Pb>Cu. However, there are variations in the enrichment factors of metals at the various stations, because the variation in heavy metal concentration is site-specific. For example, no enrichment of Cu, Pb, Co and Mn in all stations, whereas, minor, moderate and moderately severe enrichment of Cd were indicated in sediments from stations Y10 and Y11, Y5, and Y2 respectively.

Pearson's correlation analysis revealed highly significant relationship between Co and Ni, As and Ni, As and Co, Cd and Ni, Cd and Co, and, Cd and As, implying that each of these pairs may have originated

Table 6: The potential ecological risk indices (RI) of trace metals in surface sediments of Yewa Creek, Southwest Nigeria.

Sampling Stations	Ecological risk index of heavy metals, Ei								RI
	Cu	Pb	Zn	Ni	Co	Mn	Cd	As	
Y1	3.14	3.33	3.91	10.61	13	1.06	90	27.3	152
Y2	4.00	2.86	2.89	14.14	16	0.62	600	27.3	667
Y3	4.29	5.24	10.62	10.61	12.5	0.81	37.5	27.3	109
Y4	4.29	2.86	2.31	10.10	9.5	0.98	37.5	27.3	95
Y5	3.43	3.81	2.44	11.62	14	0.88	165	27.3	228
Y6	0.57	1.43	1.38	8.59	14	0.35	180	9.09	215
Y7	3.71	5.71	2.44	10.10	11.5	0.81	37.5	27.3	98.8
Y8	2.86	4.76	2.13	11.11	13	101	120	18.2	173
Y9	4.00	4.76	2.36	11.11	13	1.00	75	27.3	128
Y10	4.57	3.81	3.2	10.61	15.5	2.76	37.5	9.09	105
Y11	5.43	4.83	3.42	12.12	14.5	17.3	165	27.3	234
Minimum	0.57	1.43	1.38	10.10	9.5	0.35	37.5	9.09	95
Maximum	4.57	5.71	10.62	14.14	15.5	2.76	600	27.3	667
Mean	3.66	3.95	3.37	9.92	13.32	1.09	140	23.2	200

from the same contamination source(s). The result of hierarchical cluster analysis unveiled the association of Zn with Co, As and Ni giving evidence of anthropogenic contribution, while, its association with Cu, Pb and Mn has also indicated additional contribution from geogenic activities. The enrichment factor of Cd largely indicate anthropogenic contribution in stations where there are moderate to severe enrichment. The most probable sources of Cd in the study area are suggested to be from untreated sewage sludge, mineral fertilizers and waste water from agricultural activities.

Inferring from the widely used international sediment quality guidelines (ISQG), which considers the consensus-based TEC and PEC values, Cu, Pb, Zn and As, have no negative effect on the sediment quality. In spite of the fact that the concentration of Cd in station Y2 is slightly below PEC, its exceedance based on comparison to PEL suggests that the sediment is highly degraded. Nonetheless, the overall assessment according to the calculated *mPECQ* values is favourable, because no individual value measured up to 0.5, indicating sediments are not toxic.

A very high risk index which was obtained at station Y2, implying that sediment has been heavily impacted and harmful effects may be produced on vagrant and sessile organisms.

References

Abdel-Ghani, N.T. and Elchaghaby, G.A. (2007). Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *International journal of Environmental Science and Technology,* 4:451–456.

Adeaga, O.A., Bello, A.A. and Akinbaloye, T. (2019). Water Resources Uncertainty in Yewa River Basin, Ogun State, Southwest Nigeria. *World Scientific News, an international scientific journal*, 131: 37-53.

Adebowale, O., Adebowale, O.O. and Oyesola, O.B. (2011). Perceived effect of industrial water pollution on the livelihood of rural dwellers in Yewa area, Ogun state, Nigeria. *European Journal of Social Sciences*, 22(1): 66-75.

Atkinson, C.A., Jolley, D.F. and Simpson, S.L. (2007). Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from contaminated marine sediments. *Chemosphere*, 69(9):1428–1437.

Bhuiyan, M.A.H., Parvez, L., Islam, M.A., Dampare, S.B. and Suzuki, S. (2010). Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. *Journal of Hazardous Materials*, 173: 384–392.

Buchman, M.F. (1999). NOAA Screening Quick Reference Tables, *NOAA HAZMAT Report* 99-1, Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12.

Cook, J.A., Andrew, S.M. and Johnson, M.S. (1990). Lead, zinc, cadmium and fluoride in small mammals from contaminated grass-land established on fluorspar tailings, *Water Air Soil Pollution*. 51: 43–54.

Decena, S.C.P, Arguilles, M.S. and Robel, L.L. (2018). Assessing heavy metal contamination in surface sediments in an Urban River in the Philippines. *Polish Journal of Environmental Studies*, 27(5): 1983-1995.

Deniseger, J., Erickson, J., Austin, A., Roch, M. and Clark, M.J.R. (1990). The effects of decreasing heavy metal concentrations on the biota of Buttle Lake, *Water Research*, 24: 403–416.

Dong, D., Xie, Z., Du, Y., Liu, C. and Wang, S. (1999). Influence of soil pH on aluminum availability in the soil and aluminum in tea leaves (J). *Commun. Soil Sci. Plant Anal.* 30(5/6): 873–883.

Duncan, A.E., de Vries, N. and Nyarko, K.B. (2018). Assessment of heavy metal pollution in the sediments of the River Pra and its tributaries. *Water, Air and Soil Pollution*, 229:272.

Gale J.G. and Hoare P.G. (1991). The physical composition and analysis of regolith materials. In *Quaternary Sediments:* Petrographic Methods for the Study of Unlithified Rocks, *Belhaven Press*, New York, 87-94.

Gaur, V.K., Gupta, S.K., Pandey, S.D., Gopal, K. and Misra, V. (2005). Distribution of heavy metals in sediment and water of River Gomti, India. *Environmental Monitoring Assessment*. 102: 419–433.

Glasby, G. P., Szefer, P., Geldon, J. and Warzocha, J. (2004). Heavy-metal pollution of sediments from Szczecin Lagoon and the Gdansk Basin, Poland. *Science of the Total Environment*, 330(1–3), 249–269.

Gumgum, B., Unlu, E., Tez, Z. and Gulsun, Z. (1994). Heavy-metal pollution in water, sediment and fish from the Tigris River in Turkey. *Chemosphere* 29: 111–116.

Gupta, S.K., Chabukdhara, M., Kumar, P., Singh, J. and Bux, F. (2014). Evaluation of ecological risk of metal contamination in river Gomti, India: A biomonitoring approach. *Ecotoxicol. Environ. Saf.* 110: 49.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, 14, 975, 1980.

Hammer, Æ., Harper, D.A.T. and Ryan, P.D. (2007): Paleontological Statistics Software Package (PAST) for education and data analysis. Version 1.67, 83.

Hu, Y., Liu, X., Bai, J., Shih, K., Zeng, E.Y. and Cheng, H. (2013). Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. *Environmental Science Pollution Research,* 20: 6150.

Ingersoll, C. G., MacDonald, D. D., Wang, N., Crane, J. L., Field, L. J., Haverland, P. S., Kemble, N. E., Lindskoog, R. A., Severn, C. and Smorong, D. E. (2001). Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. *Arch. Environ. Contam. Toxicol*., 41: 8–21.

Ingersoll, C. G., Kemble, N. E., Kunz, J. L., Brumbaugh, W. G., MacDonald, D. D. and Smorong, D. (2009). Toxicity of sediment cores collected from the Ashtabula River in Northeastern Ohio, USA, to the amphipod Hyalella azteca. *Arch. Environ. Cont. Tox*., 57: 826–827.

Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M. and Islam, M.K. (2015). Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecological Indicators*, 48: 282–291.

Lin, C., He, M., Liu, X., Guo, W. and Liu, S. (2013). Contamination and ecological risk assessment of toxic trace elements in the Xi River, an urban river of Shenyang city, China. *Environ. Monit. Assess*. 185:4321.

Liu, J., Wu, H., Feng, J., Li, Z. and Lin, G. (2014). Heavy metal contamination and ecological risk assessments in the sediments and zoo-benthos of selected mangrove ecosystems, South China. *Catena*, 119: 136–142.

Long, E. R., Ingersoll, C. G. and MacDonald, D. D. (2006). Calculation and uses of mean sediment quality guideline quotient, a critical review. *Environ. Sci. Technol*., 40: 1726–1736.

Loring, D.H. and Rantala, R.T.T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth Sci. Rev*. 32: 235-283.

MacDonald, D.D., Ingersoll, C.G. and Berger, T.A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Systems. *Archives of Environmental Contamination and Toxicology*, 39(1):20-31.

MacDonald, D. D., Ingersoll, C. G., Kemble, N. E., Smorong, D. E., Sinclair, J. A., Lindskoog, R., Gaston, G., Sanger, D., Carr, R. S., Biedenbach, J., Gouguet, R., Kern, J., Shortelle, A., Field, L. J. and Meyer, J. (2011). Baseline ecological risk assessment of the Calcasieu Estuary, Louisiana: Part 3. An evaluation of the risks to benthic invertebrates associated with exposure to contaminated sediments. *Arch. Environ. Cont. Tox*., 61, 29–58.

Mahino, F., Usmani, N. and Hossain, M.M. (2014). Heavy Metal in Aquatic Ecosystem Emphasizing its Effect on Tissue Bioaccumulation and Histopathology: A Review. *Journal of Environmental Science and Technology* 7(1): 1-15.

Martincic, D., Kwokal, Z. and Branica, M. (1990). Distribution of zinc, lead, cadmium and copper between different size fractions of sediments I. The Limski Kanal (North Adriatic Sea). *Sci Total Environ* 95: 201–215.

Maslennikova, S., Larina, N. and Larin, S. (2012). The effect of sediment grain size on heavy metal content. *Lakes, reservoirs and ponds*, 6(1): 43-54.

Phillips, O.A., Falana, A.O. and Adebayo, A.J., 2017. The geochemical composition of sediment as a proxy of provenance and weathering intensity: a case study of southwest Nigeria's coastal creeks. *Geology, Geophysics and environment,* 43 (3):229-248.

Pye, K. and Blott, S.J. (2004). Particle size analysis of sediments, soils and related particulate materials for forensic purposes using laser granulometry. *Forensic Science International*, 19-27.

Riley, J.P. and Chester, R. (1971). Introduction to Marine Chemistry. *Academic Press*, London, 465.

Rippey, B., Rose, N., Yang, H., Harrad, S., Robson, M. and Travers, S. (2008). An assessment of toxicity in profundal lake sediment due to deposition of heavy metals and persistent organic pollutants from the atmosphere. *Environ. Int*., 34, 345-356.

Sakan, S.M., Djordjevic, D.S., Manojlovic, D.D. and Polic, P.S. (2009). Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *Journal of Environmental Management*, 90: 3382–3390.

Salomons, W. and Forstner, U. (1984). Metals in hydrocycle. Springer, Berlin Heidelberg New York, 349.

Satarug, S., Baker, J.R, Urbenjapol, S., Haswell-Elkins, M., Reilly, P.E., Williams, D.J., and Moore, M.R. (2003). "A global perspective on cadmium pollution and toxicity in non-occupationally exposed population." Toxicology Letters 137: 65-83.

Shazili, N. A. M., Yunus, K., Ahmad, A. S., Abdullah, N. and Rashid, M. K. A. (2006). Heavy metal pollution status in the Malaysian aquatic environment. *Aquatic Ecosystem Health & Management*, 9(2): 137-145.

Simpson, S.L., Angel, B.M. and Jolley, D.F. (2004). Metal equilibration in laboratory-contaminated (spiked) sediments used for the development of whole-sediment toxicity tests. *Chemosphere*, 54(5):597–609.

Singh, M., Ansari, A.A., Muller, G. and Singh, I.B. (1997). Heavy metals in freshly deposited sediments of Gomti river (a tributary of the Ganga river): effects of human activities, *Environ. Geol*. 29: 246–252.

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous materials*, 195: 355-364.

Veses, O., Mosteo, R., Ormad, M.P. and Ovelleiro, J.I. (2013). Sediment quality assessment of two industrialized areas of Spain. *Int. J. Environ. Res*., 7(4): 1039-1046.

Yi, Y., Yang, Z. and Zhang, S. (2011). Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environmental Pollution*, 159: 2575–2585.

Zabadal, J.R.S., Vilhena, M.T.M.B., Bogado, S.Q. and Pofal, C.A. (2005). Solving unsteady problems in water pollution using Lie symmetries. *Ecol. Mod*., 186(3): 271-279.