ASSESSMENT OF POLLUTION BY HEAVY METALS IN SEDIMENTS OF RIVER OYI AND ITS TRIBUTARY, SOUTHWESTERN NIGERIA

Adisa, A. L.[1*] and Adekoya, J. A.[2]

[1] Department of Applied Geology, Federal University of Technology Akure, Nigeria.
[2] Department of Geological Sciences, Osun State University, Osogbo, Osun State, Nigeria.
Corresponding e-mail: adeshina4me2000@gmail.com.

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ABSTRACT

The sediments of Rivers Oyi and Wara were sampled in order to assess the pollution status of these rivers by heavy metals. Thirty stream sediment samples were collected along channels of Rivers Oyi and Wara, bounded by Latitudes 8° 39'N and 8° 50'N and Longitudes 5° 00'E and 5° 09'E. The samples were analyzed for eight heavy metals, namely, Co, Cu, Cr, Fe, Mn, Pb and Ni after they had been partially extracted using aqua-regia digestion and analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The geochemical data obtained were then subjected to univariate statistical and correlational analyses. Enrichment Factor (EF), pollution load index (PLI), geo-accumulation index (Igeo) as well as USEPA sediment quality guidelines were evaluated in order to assess the degree of pollution of the stream sediments. All the analysed heavy metals were widely distributed in the drainage system. The ranges in the concentrations of the elements were: 2.52-50.88 ppm for Cu, 1.20-12.80 ppm for Co, 5.60-41.80 ppm for Cr, 0.28-1.72 % for Fe, 89-619 ppm for Mn, 2.46-19.34 ppm for Pb, 4.80-70.60 ppm for Zn and 1.40-12.30 ppm for Ni while the mean concentrations were as follows: 10.5 ppm for Cu, 5.07 ppm for Co, 20.82 ppm for Cr, 0.83 % for Fe, 248.80 ppm for Mn, 5.79 ppm for Pb, 15.06 ppm for Zn and 6.29 ppm for Ni. Pearson correlation coefficient produced strong positive correlation between Cu-Zn, Fe-Co, Mn-Co, Co-Cr etc. The enrichment factor (EF), pollution load index (PLI) as well as the geo-accumulation index (Igeo) results indicated that the rivers/streams were practically unpolluted with respect to heavy metals. The slightly high values of some elements could be due to anthropogenic sources. In conclusion, the levels of concentrations of heavy metals in the stream sediments of the study area did not constitute any serious environmental risk.

Keywords: Pollution, Enrichment Factor, Mineralization, Lithology.

INTRODUCTION

This paper assessed the pollution of aquatic environment of River Oyi and its tributaries in southwest Nigeria, using potentially toxic heavy metals such as Cu, Co, Ni, Pb, Fe, Mn and Zn. These heavy metals usually occur in very small amounts and are, therefore, not normally harmful to our environment. However, they become source of concern when they occur in higher concentrations (Estifanos, 2013). Stream sediments have been widely employed by researchers in the study of heavy metal pollution because they act as sink for aquatic pollutants and therefore, reflect the quality of the aquatic system as well as providing valuable information such as sources, distribution and the impact of man.

The sources of heavy metals in the aquatic system may be natural or anthropogenic. These metals are naturally discharged into the drainage system through processes, such as weathering and erosion of rocks (Muwanga, 1997; Zvinowanda *et al.*, 2009; Libes, 2009) where they become immobilized and could be absorbed, co-precipitated or form inorganic complexes. They could also occur in particulate form or co-precipitate as oxides, and hydroxides of Fe and Mn (Awofolu *et al.*, 2005; Mwiganga and Kansiime, 2005; Okafor and Opuene, 2007). Anthropogenic sources, which are as a result of human activities, include input from domestic waste, industrial waste water, mining, leaching from solid waste dump etc. (Ladigbolu and Balogun, 2011). The effect of these human activities on the aquatic environment is the alteration of the physical and chemical properties of both water and sediment. Consequently, the concentrations of heavy metals may reach potentially dangerous levels in these media, thereby given rise to concern for human health.

The objectives of this study are therefore to: (i) assess the contents of the heavy metals in the sediments of the River Oyi and its tributary; (ii) examine the occurrence and the distribution of the metals; (iii) establish the relationship among the metals; and (iv) assess the pollution status of the River Oyi drainage system.

Description of the Study Area

The Lafiagi study area lies between Latitudes 8° 39'N and 8° 50'N and Longitudes 5° 00'E and 5° 09'E (Fig. 1). It is situated about 110 km northeast of Ilorin. The climatic condition of the study area is characterized by two seasons: the wet and dry seasons. The wet season, a period marked by heavy rainfall begins at about the end of March and lasts till October while the dry season begins in November and ends in early March. The average annual precipitation is 1,200 mm while the average annual temperature is about 36°C.

These climatic conditions allow the growth of both root and grain crops such as millet, beans, cowpea, groundnut, melon etc. which are widely grown in the area. The human settlements in the area, which include Ologomo, Share, Bishewa, Fawole etc. are essentially rural to semi-urban. Ferruginous tropical soil which supports guinea savannah vegetation characterized the land. The vegetation has characteristic grass cover together with shrubs and medium – sized trees. The study area is drained by River Oyi (the major river) and its tributaries. River Oyi runs essentially northward before it discharges into the River Niger. Some of the streams in the area are seasonal, as most of their channels are dry during the dry season. The drainage pattern is dendritic.

The study area is underlain by both the Precambrian Basement Complex rocks and the Cretaceous Sandstone of the Bida Basin (Figure 2). The Basement Complex is one of the three major litho-petrological components that make up the geology of Nigeria (Obaje, 2009). The Cretaceous to Tertiary sedimentary rocks and the younger Granite being the other components (Grant, 1970; McCurry and Wright, 1971 and Rahaman, 1976). The area lies at the reactivated part of the Pan-African belt. It is Precambrian in age and polycyclic, bearing imprints of at least four previous orogenies, viz: Liberian (c. 2800Ma), Eburnean (c. 2000 Ma), Kibaran (1100 Ma) and Pan African (c. 600 Ma) (Grant, 1970 and Rahaman, 1988). Workers such as Oyawoye (1972), McCurry (1976), Odeyemi (1981), Ajibade *et al.* (1987), Adekoya (1991) and Adekoya *et al.* (2003) have grouped the rocks of the Basement complex into four petro-lithological units: The Migmatite-Gneiss-Quartzite Complex; The Schist Belt; The Pan-African granitoids (Older Granites) with associated charnokitic rocks and syenites; and The minor felsic and mafic intrusive.

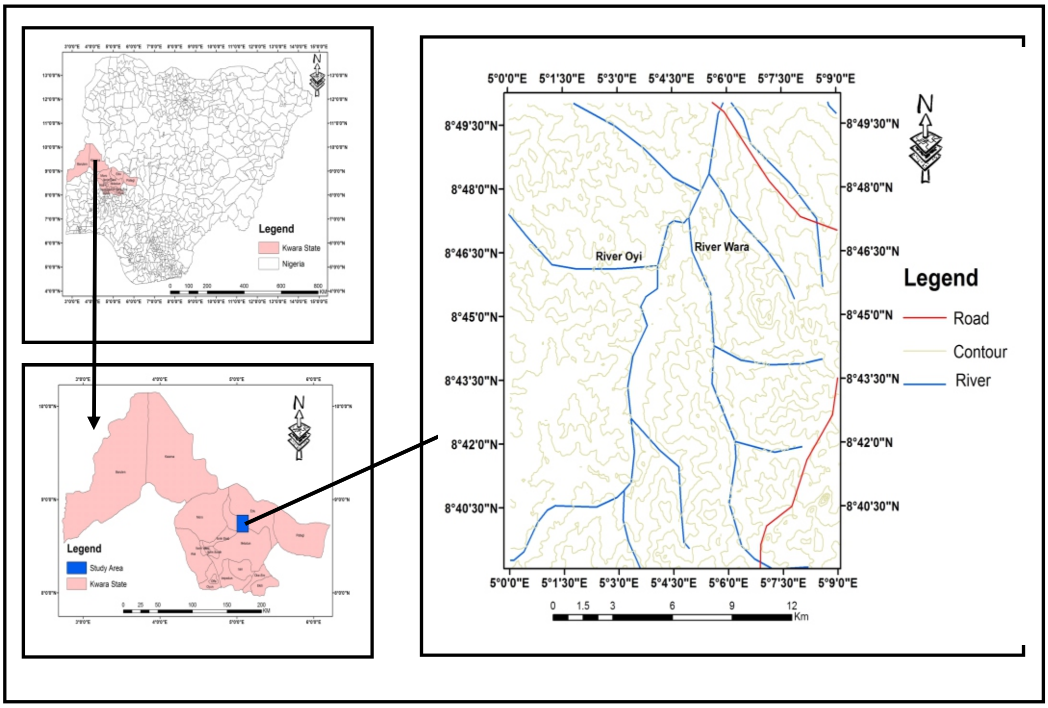


Figure 1: Map of Kwara State Showing the Study Area

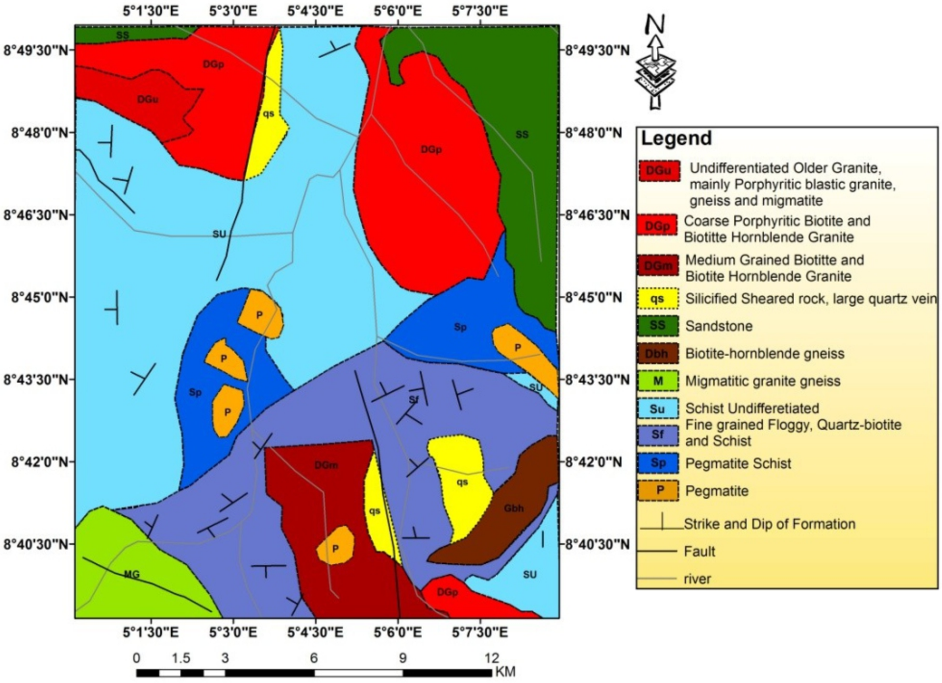


Fig. 2: Geological Map of the Study Area. (adapted from Nigeria Geological Survey Agency (NGSA), 2006)

The Basement Complex rocks underlying the study area as shown on the geological map of Lafiagi (1: 250,000, NGSA, 2006) consist of: fine-grained flaggy, quartz-biotite and schist; undifferentiated schist; pegmatite; undifferentiated Older granite etc. The undifferentiated schist dominated the study area as it covers about half of the area. Next in dominance, is the fine-grained flaggy, quartz-biotite and schist which covers the southern part of the area sharing boundary with the pegmatized schist to the northwest and migmatitic granite gneiss to the southwestern part of the area. Rocks of the Older Granite suite, which include the medium-grained biotite and biotite-hornblende granite, and the undifferentiated granite etc., occupy the northwestern, southern and the northeastern parts of the area.

The rocks in the Lafiagi area are suspected to host gold mineralization. The host rocks for the gold mineralization are the schists and the gneisses at Bishewa and Ologomo (Malomo, 2012). The sandstone beds in Gidan Sani at the contact between the Basement Complex and the Cretaceous sediments of the Bida Basin also host gold mineralization (Malomo, 2012). The pegmatites in the study area also host to Ta-Nb mineralization. According to Adedoyin *et al.*, (2006), the pegmatite in the Lema-Ndeji pegmatite field in the Lafiagi area, are hosted by Older Granite. These pegmatites are host to metals such as niobium, tin, tungsten, columbite as well as mica, feldspar, quartz, and a host of gemstones, including black tourmaline, beryl etc. Megwara and Udensi (2014) also reported that some of the lineaments in the Share area have been observed to be associated with the occurrence of kaolin.

MATERIALS AND METHOD OF STUDY

Sampling and Analytical Methods

Stream sediment sampling was carried out in 2010 using the 1: 100,000 topographic sheet No. 203 (Lafiagi) which served as base map. The samples were collected from thirty sites along the channels of Rivers Oyi and Wara (Figure 3). The sampling intervals varied between 1.0 km to 1.5 km and the samples were collected at a depth of 15 cm. At each sampling site, the samples were collected in a clean sampling bag using plastic scoop. The global positioning system (GPS) was used in recording the geographic coordinates of sampling points accurately which were later plotted on the topographic map.

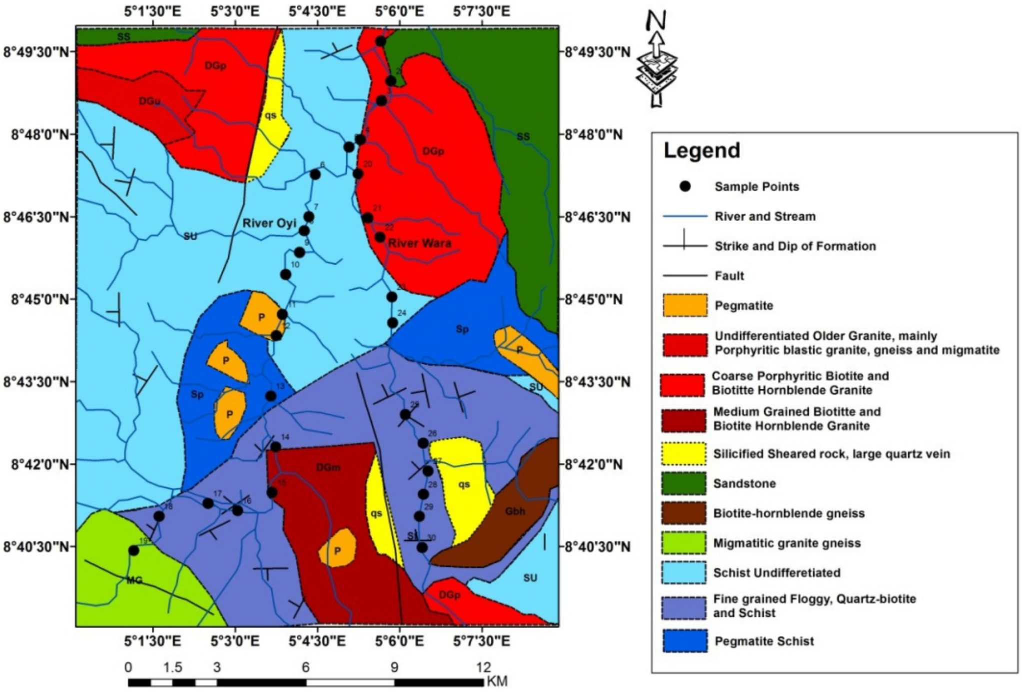


Fig. 3: Geological Map of the Study Area showing the Sample Locations (NGSA, 2006).

The samples were later disaggregated and quartered, after they had been air-dried, using ceramic mortar while ensuring there was no contamination of the samples. The samples were then sieved using -80 (<177 micron) sieve with nylon screen (Rose *et al.*, 1979; Thompson, 1986). Thereafter, 0.5 g of the sieved samples were then digested with aqua regia (1:3 HNO_3: HCL) for 2 hrs at 95°C. The resulting solutions were analyzed for eight heavy metals namely: Cu, Co, Cr, Fe, Mn, Pb, and Zn by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Both the digestion and the ICP-MS analysis were done at ACME Analytical Laboratories, Vancouver, Canada. Aqua regia attack as a method of digestion was preferred to the other methods because of its strong oxidising power.

For quality control, duplicates were used to assess data quality and accuracy was determined by using ACME's in-house reference materials. The statistical analysis of the duplicates indicated that only few elements had much larger relative error (P>15%). Also contributions from blanks were negligible as the contents of all the elements in the blanks were below the detection limits. Therefore, both analytical precision and accuracy were found to be reasonable and satisfactory.

Statistical Analysis of Data

Univariate statistical analysis such as minimum, maximum (range) values, the mean, median, standard deviation etc. were computed for each of the analyzed heavy metals in the stream sediments. The data were also compared with the US Environmental Protection Agency (USEPA) sediment quality guidelines. In order to have an insight into the inter-element relationship, Pearson linear correlation matrix was generated from the data. Enrichment factors and pollution load index (PLI) were also plotted in form of histograms. These statistical computations were carried out using SPSS software version 16.0.

Determination of Enrichment Factor (EF)

The enrichment factor, according to Hernandez *et al.*, (2003), is the relative abundance of a chemical element in soil (sediment) compared to the bedrock. The baseline concentration of these heavy metals in unpolluted sediments must be known in order to quantify the enrichment of these heavy metals in the sediment. The worldwide standard given by Turekian and Wedephol (1961) was adopted, in this study, as the reference for unpolluted sediments. The degree of sediment contamination is, therefore, assessed by computing the enrichment factors (EFs) of the heavy metals in the stream sediments using the formula

$$EF_m = (C_n / Fe)_{sample} / (C_n / Fe)_{background}$$

where, C_n is the concentration of trace element "n". $(C_n/Fe)_{sample}$ is the ratio of concentration of trace element (C_n) to that of Fe (C_{Fe}) in the stream sediment sample and $(C_n / Fe)_{background}$ is the same reference ratio in the "world shale". The background value is that of average shale (Turekian and Wedephol, 1961).

Fe is adopted as the normalising element in determining the EF values because of its high mobility in an oxidising surface environment, low occurrence variability and its occurrence in the environment in trace amounts (Loska *et al.*, 2003; Nyangababo *et al.*, 2005; kamaruzzamal *et al.*,2008; Chakravarty and Patgiri, 2009;). Elements which have an EF value of nearly unity are naturally derived, while those of anthropogenic origin have EF values of several orders of magnitude.

Determination of Pollution Load Index (PLI)

Pollution load index (PLI) was computed by obtaining the n-root from the n-CFs that were obtained for all the metals (Soares *et al.*, 1999) according to the method of Tomilson *et al.*, (1980):

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

where n is the number of metals in this study and CF is the contamination factor defined as the quotient obtained by dividing the concentration of each metal in the sediments by the background value (Rabee *et al.*, 2011):

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

i.e. $CF = C_{metal} / C_{Background\ value}$

For easy interpretation, the PLI values were plotted against the sample sites. The plotting was done using using SPSS version 16.0 software.

Determination of Geo-accumulation Index (Igeo)

The degree of pollution of the sediments were also evaluated by computing the geo-accumulation index

$$Igeo = \log_2[C_n / (1.5 B_n)]$$

Where, C_n is the measured concentration of the analyzed metal (n) in the sediment. B_n is the geochemical background concentration of the metal (n), and factor 1.5 is the background matrix correction due to lithogenic effects.

RESULTS AND DISCUSSION

Distribution of Heavy metals

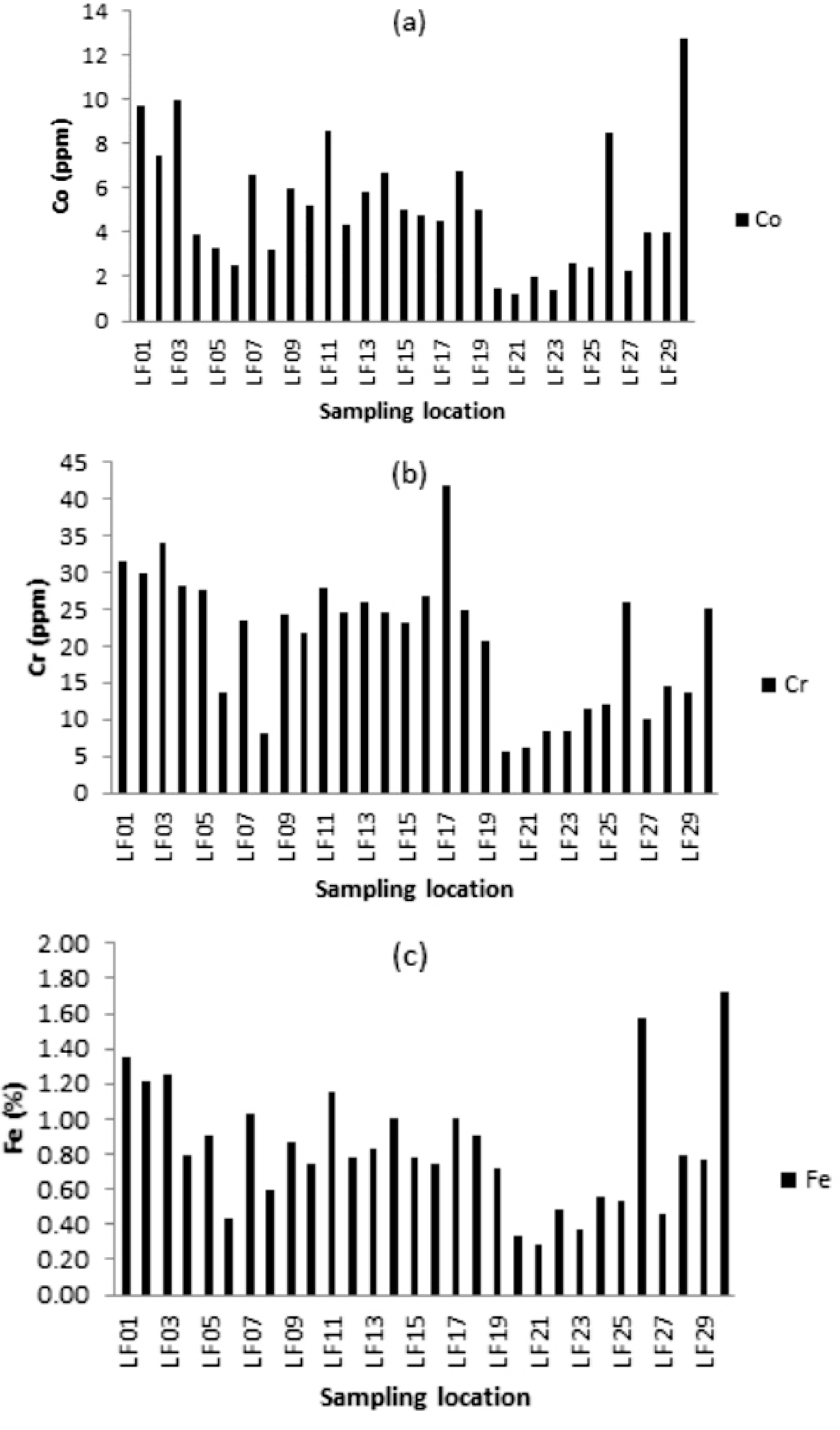
The results of the geochemical analysis are summarized in Table 1. Included in the table are the mean, median and range values of the heavy metals concentrations in the stream sediments of the study area as well as the USEPA, 1999 sediment quality guidelines values.

The table shows that all the elements are widely distributed in the study area as they were detected in all the stream sediments analyzed. The range of concentrations of heavy metals are Cu (2.52-50.88 ppm), Co (1.2-12.8 ppm), Cr (5.6-41.8 ppm), Fe (0.28-1.72 %), Mn (89-619 ppm), Pb (2.46-19.34 ppm), Zn (4.8-70.6 ppm) and Ni (1.4-12.3 ppm) (Table 1 and Figure 4). The mean and median concentrations of Cu are 10.50 ppm and 7.77 ppm. Both of these values are lower than the 45 ppm value for Cu concentration in "average world shale" as well as the 16 ppm value for the USEPA guideline (Table 1). The maximum concentration of Cu (50.88 ppm at LF 26) is, however, higher than both the average world shale and the USEPA guideline values. This, therefore, suggests that the site LF 26 is polluted with respect to Cu. Cr has 20.82 and 23.95 as its mean and median concentrations respectively, both values are lower than the 90 ppm value in "average world shale" as well as the USEPA guideline value of 25 ppm. This indicates that Cr does not pose any environmental risk. However, the concentrations of Cr is higher than corresponding USEPA guideline value at eleven sites viz: LF 1, 2, 3, 4, 5, 11, 13, 16, 17, 26 and 30 (Table 1 and Fig. 4), suggesting the possibility of pollution by Cr at these sites. For the other elements, the average concentrations are 5.07 ppm, 248.8 ppm, 5.79 ppm, 15.06 ppm and 6.29 ppm for Co, Mn, Pb, Zn and Ni respectively. These values are found to be low when compared with the corresponding values in the "average world shale " and the USEPA guideline values except for Mn whose USEPA guideline value of 30 ppm is lower than the average concentration (Table 1). Therefore, according to USEPA, the sediments of River Oyi and its tributary were unpolluted by these heavy metals.

Table 1: Heavy Metal Concentration in the Sediment (< 177um) of River Oyi and its Tributary

Sample	Cu	Co	Cr	Fe	Mn	Pb	Zn	Ni
LF01	37.22	9.70	31.50	1.35	608.00	7.74	39.40	12.30
LF02	9.38	7.50	30.00	1.21	308.00	6.57	18.20	10.10
LF03	12.39	10.00	34.00	1.25	528.00	7.80	16.40	11.50
LF04	10.80	3.90	28.30	0.79	292.00	7.12	13.90	5.60
LF05	6.84	3.30	27.50	0.91	200.00	19.34	12.40	4.20
LF06	2.52	2.50	13.80	0.44	130.00	2.63	5.00	3.00
LF07	12.30	6.60	23.50	1.03	273.00	4.98	19.60	8.50
LF08	4.73	3.20	8.10	0.60	157.00	2.64	12.30	3.50
LF09	9.88	6.00	24.40	0.87	246.00	4.79	13.90	7.50
LF10	7.01	5.20	21.90	0.75	227.00	3.37	12.30	6.70
LF11	16.95	8.60	27.90	1.16	344.00	5.58	20.60	11.50
LF12	7.11	4.30	24.50	0.78	195.00	5.40	10.30	5.40
LF13	9.62	5.80	26.00	0.83	295.00	6.14	12.30	6.80
LF14	9.80	6.70	24.50	1.00	265.00	5.12	17.20	9.00
LF15	5.76	5.00	23.10	0.78	258.00	4.55	10.40	6.30
LF16	5.54	4.80	26.70	0.74	218.00	5.50	9.50	5.70
LF17	8.49	4.50	41.80	1.00	227.00	9.73	10.60	5.60
LF18	6.91	6.80	24.90	0.90	302.00	4.93	11.60	8.30
LF19	7.19	5.00	20.70	0.72	215.00	3.95	11.50	6.20
LF20	3.42	1.50	5.60	0.33	214.00	2.46	4.90	1.40
LF21	3.35	1.20	6.20	0.28	89.00	2.68	4.80	1.70
LF22	7.94	2.00	8.30	0.48	124.00	2.51	8.00	3.50
LF23	5.15	1.40	8.30	0.37	98.00	6.19	7.40	1.90
LF24	5.78	2.60	11.50	0.56	137.00	4.56	10.50	4.00
LF25	8.35	2.40	12.10	0.53	118.00	7.85	12.20	3.00
LF26	50.88	8.50	26.00	1.58	311.00	8.63	70.60	11.30
LF27	6.46	2.30	10.10	0.46	106.00	3.63	8.00	3.40
LF28	7.60	4.00	14.50	0.79	182.00	5.90	12.30	5.10
LF29	9.90	4.00	13.60	0.77	178.00	3.71	12.10	4.90
LF30	15.68	12.80	25.20	1.72	619.00	7.84	23.70	10.70
Range	2.52-50.88	1.2-12.8	5.6-41.8	0.28-1.72	89-619	2.46-19.34	4.8-70.6	1.4-12.3
Mean	10.50	5.07	20.82	0.83	248.80	5.79	15.06	6.29
Median	7.77	4.65	23.95	0.79	222.50	5.26	12.25	5.65
Minimum	2.52	1.20	5.60	0.28	89.00	2.46	4.80	1.40
Maximum	50.88	12.80	41.80	1.72	619.00	19.34	70.60	12.30
*Average Shale	45	19	90	4.7	850	20	95	68
**USEPA SQG	16	-	25	30	30	40	110	16

* World geochemical background value in average shale (Turekian and Wedepohl, 1961).
Values in ppm except Fe in %. **US Environmental Protection Agency Sediment Quality Guidelines.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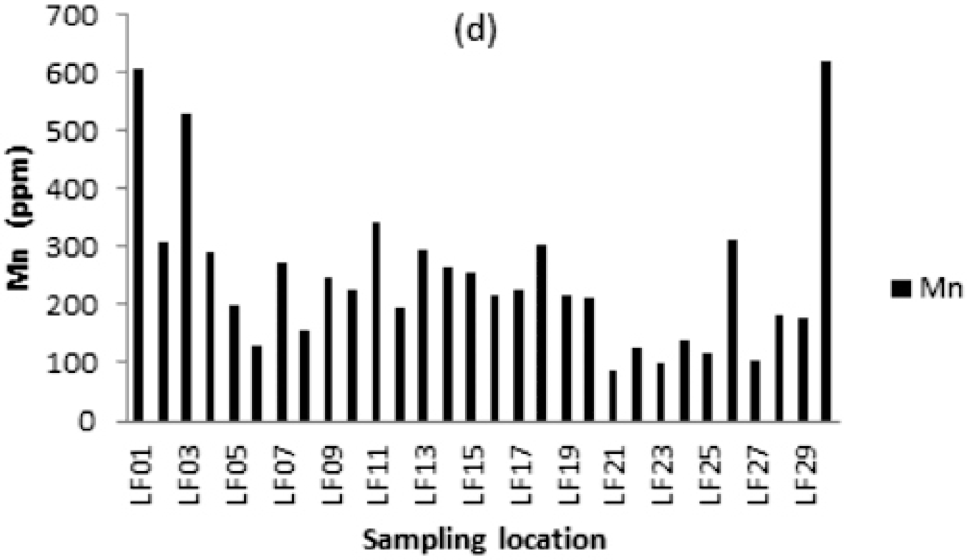
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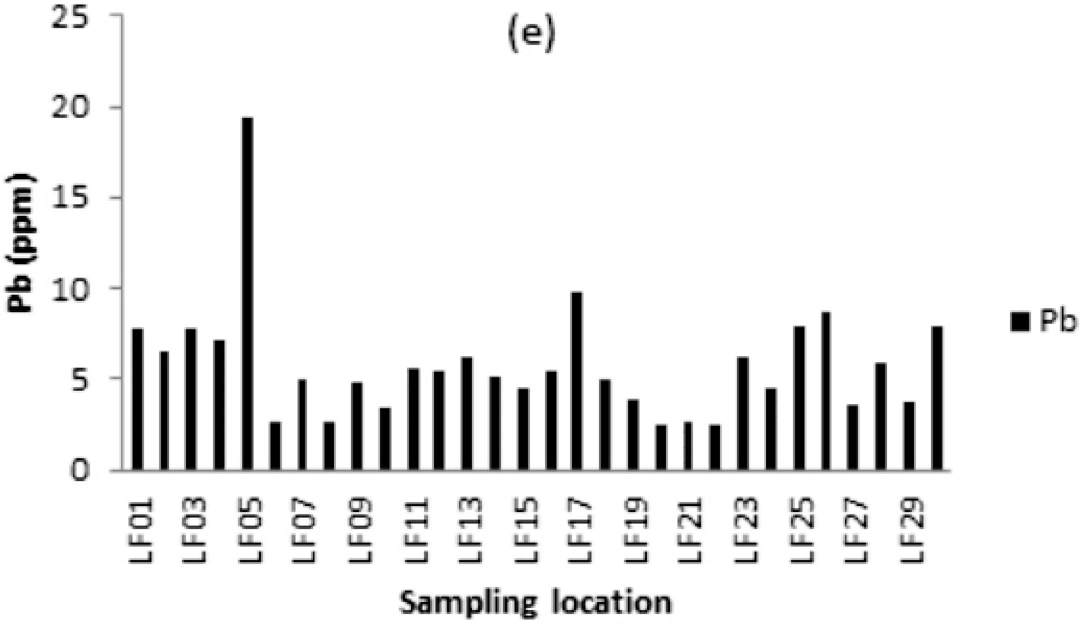
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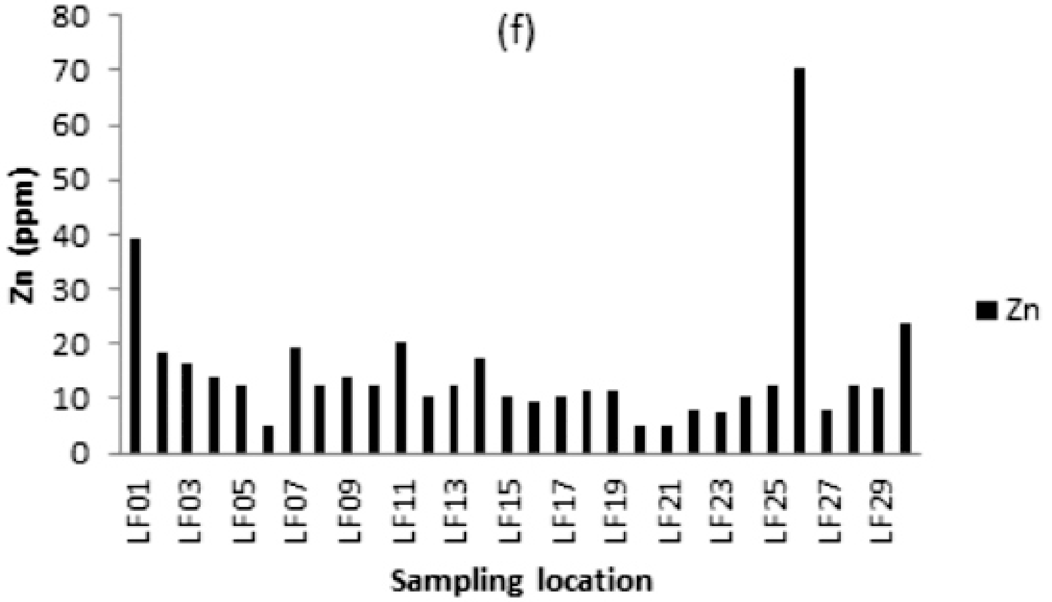
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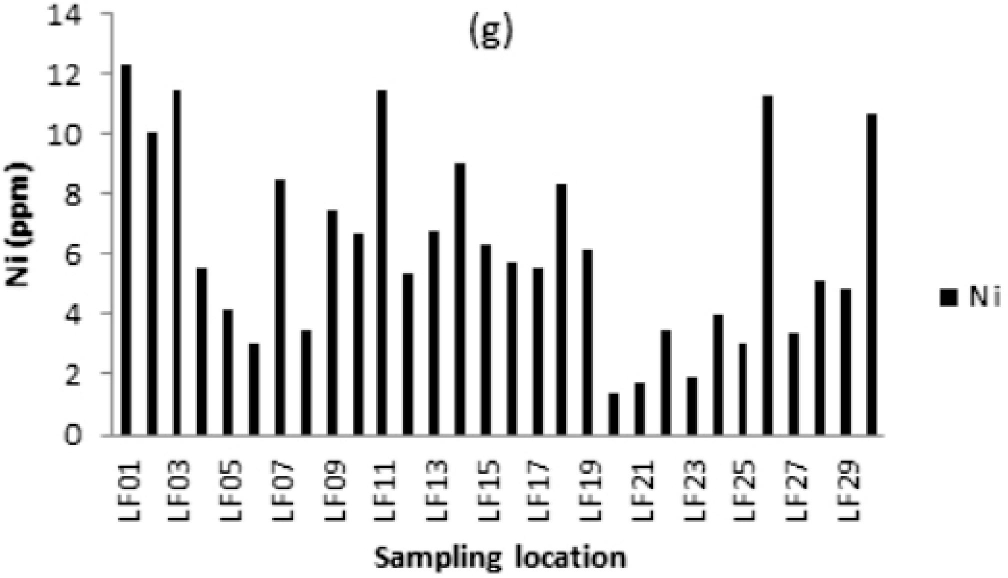

Figure 4: Spatial Variation of Heavy Metals in the Sediments of River Oyi and Its Tributary

Inter-element association was evaluated by Pearson Correlation coefficient. The correlation matrix (Table 2) shows that the coefficient "r" ranges from 0.238 for Ni/Pb to 0.975 for Cu/Zn. Some elemental pairs e.g. Co/Cr, Co/Fe, Co/Mn etc. showed strong positive correlations, which indicate a common source for these heavy metals, while pairs such as Co/Pb, Pb/Mn etc. show a weak positive correlation. The positive correlation of some elements with Fe and Mn, such as Fe-Ni, Fe-Co, and Mn-Co, may indicate the scavenging actions of both Fe- and Mn- oxides on these metals. The association of Co and Mn-oxides may result from the adsorption of Co on Mn-oxide surfaces or the structural substitution of Co for Mn (Lecomte and Sondag, 1980). Horsnail and Elliot (1971) have also reported that Mn-rich precipitates have high Co contents in the drainage channels in British Columbia.

The strong positive correlation between Cu/Zn could be as a result of the sulphide often found in association with gold mineralization. Oyinloye and Steed (1996) reported the association of pyrite, pyrrhotite, chalcopyrite, argentopyrite and sphalerite with the Iperindo primary gold deposit.

Assessment of Stream Sediment Pollution
Enrichment Factor

The values of the enrichment factors (EF) for the seven analyzed heavy metals in the stream sediments of the study area are presented in Table 3. Zhang and Liu (2002) classified EF values into two: EF values of less than 1.5 suggest that the heavy metals are derived from natural sources while EF values greater than 1.5 suggest anthropogenic sources. In this study, the classification of Sutherland (2000) was adopted. Sutherland (2000) recognised six categories of enrichment factor (EF) as outlined below:

Table 2: Pearson Correlation Matrix for Stream Sediment Geochemical Data of Oyi Drainage System

	Cu	Co	Cr	Fe	Mn	Ni	Pb	Zn
Cu	1.000							
Co	0.592	1.000						
Cr	0.381	0.693	1.000					
Fe	0.705	0.942	0.746	1.000				
Mn	0.553	0.921	0.649	0.846	1.000			
Ni	0.668	0.954	0.739	0.918	0.848	1.000		
Pb	0.275	0.247	0.540	0.449	0.283	0.238	1.000	
Zn	0.975	0.605	0.375	0.736	0.512	0.673	0.292	1.000

Correlations are significant at $p < 0.05$.

Table 3: Enrichment Factor for studied heavy metals in sediments (<177um) of River Oyi and its Tributary.

Sample	Cu	Co	Cr	Mn	Pb	Zn	Ni
LF01	2.88	1.78	1.22	2.49	1.35	1.44	0.63
LF02	0.81	1.53	1.29	1.41	1.28	0.74	0.58
LF03	1.04	1.98	1.42	2.34	1.47	0.65	0.64
LF04	1.43	1.22	1.87	2.04	2.12	0.87	0.49
LF05	0.79	0.90	1.58	1.22	4.99	0.67	0.32
LF06	0.60	1.41	1.64	1.63	1.40	0.56	0.47
LF07	1.25	1.59	1.19	1.47	1.14	0.94	0.57
LF08	0.82	1.32	0.71	1.45	1.03	1.01	0.40
LF09	1.19	1.71	1.46	1.56	1.29	0.79	0.60
LF10	0.98	1.72	1.52	1.67	1.06	0.81	0.62
LF11	1.53	1.83	1.26	1.64	1.13	0.88	0.69
LF12	0.95	1.36	1.64	1.38	1.63	0.65	0.48
LF13	1.21	1.73	1.64	1.97	1.74	0.73	0.57
LF14	1.02	1.66	1.28	1.47	1.20	0.85	0.62
LF15	0.77	1.59	1.55	1.83	1.37	0.66	0.56
LF16	0.78	1.60	1.88	1.63	1.75	0.64	0.53
LF17	0.89	1.11	2.18	1.26	2.29	0.52	0.39
LF18	0.80	1.87	1.44	1.86	1.29	0.64	0.64
LF19	1.04	1.72	1.50	1.65	1.29	0.79	0.60
LF20	1.08	1.12	0.89	3.59	1.75	0.73	0.29
LF21	1.25	1.06	1.16	1.76	2.25	0.85	0.42
LF22	1.73	1.03	0.90	1.43	1.23	0.82	0.50
LF23	1.45	0.94	1.17	1.46	3.93	0.99	0.35
LF24	1.08	1.15	1.07	1.35	1.91	0.93	0.49
LF25	1.65	1.12	1.19	1.23	3.48	1.14	0.39
LF26	3.36	1.33	0.86	1.09	1.28	2.21	0.49
LF27	1.47	1.24	1.15	1.27	1.85	0.86	0.51
LF28	1.00	1.25	0.96	1.27	1.76	0.77	0.45
LF29	1.34	1.29	0.92	1.28	1.13	0.78	0.44
LF30	0.95	1.84	0.77	1.99	1.07	0.68	0.43

EF⩽1: background concentration
1< EF<2: Depletion to Minimal enrichment
2< EF<5: moderate enrichment
5< EF<20: significant enrichment
20< EF<40: very high enrichment
⩾40: extremely high enrichment.

A critical study of the enrichment factor reveals that most of the sample sites in the study area have EF values >1 for the various metals except for Ni and Zn. The percentages of the sampling sites where the EF values are <1 are as follows: Mn (0%), Cu (36.7% of the sampling sites), Co (6.67%), Cr (23.3%), Pb (0%), Zn (86.7%) and Ni (100%). The above mentioned metals, therefore, fall in the range of background concentration at these sampling sites (Fig. 5). Those that fall within the range of minimal enrichment (i.e. 1<EF<2) are as follows: Cu (56.7%), Pb (80%), Co (93.3%), Cr (76.7%), Zn (10.0%) and Mn (86.7%). This implies that, these elements pose no risk of contamination or pollution in the stream sediments and associated medium (water) of the environment at these sampling sites. Some of the sampling sites also fall in the category of moderate enrichment (i.e. 2<EF<5). These are 6.7% of the sampling sites for Cu (at LF 01 and LF 26), Mn (13.3%) at LF 01, LF 03,LF 04.and LF 20, and Pb (16.7%) at LF 04,05, 17, 21, 23 and LF 25 (Fig. 5). Based on these observations, there is no significant enrichment of Co, Cr, Zn and Ni in the stream sediments, except for Cu, Pb and Mn . Sites LF 01, 03 and 04 are areas with recorded high human activities and these sampling sites are also close to the overhead bridge on Lafiagi Road.

Pollution load Index (PLI)

Priju and Narayana (2006) noted that both the CF and PLI are indices of sediment toxicity. These indices, therefore, serve as a quick tool for comparing the pollution status of the different sampling sites (Adebowale *et al.*, 2009). PLI value > 1 is an indication of pollution whereas PLI < 1 is unpolluted (Chakravarty and Patgiri, 2009; Seshan *et al.*, 2010). It is apparent from Table 4 and Fig. 6, that the calculated PLI values for all the sampling sites are less than 1 indicating non-pollution.

Geoaccumulation Index (I_{geo})

The computed geoaccumulation index (Igeo) values based on the average shale for the heavy metals in the stream sediments of the study area are presented in Table 5. Muller (1981) distinguished seven classes of I_{geo} (Table 6).

The Igeo values for all the elements in the stream sediments are less than 0 (i.e. Igeo < 0). According to Muller's classification, these values fall in Class 0 indicating background concentrations. Therefore, all the thirty stream sediment samples are uncontaminated by these heavy metals.

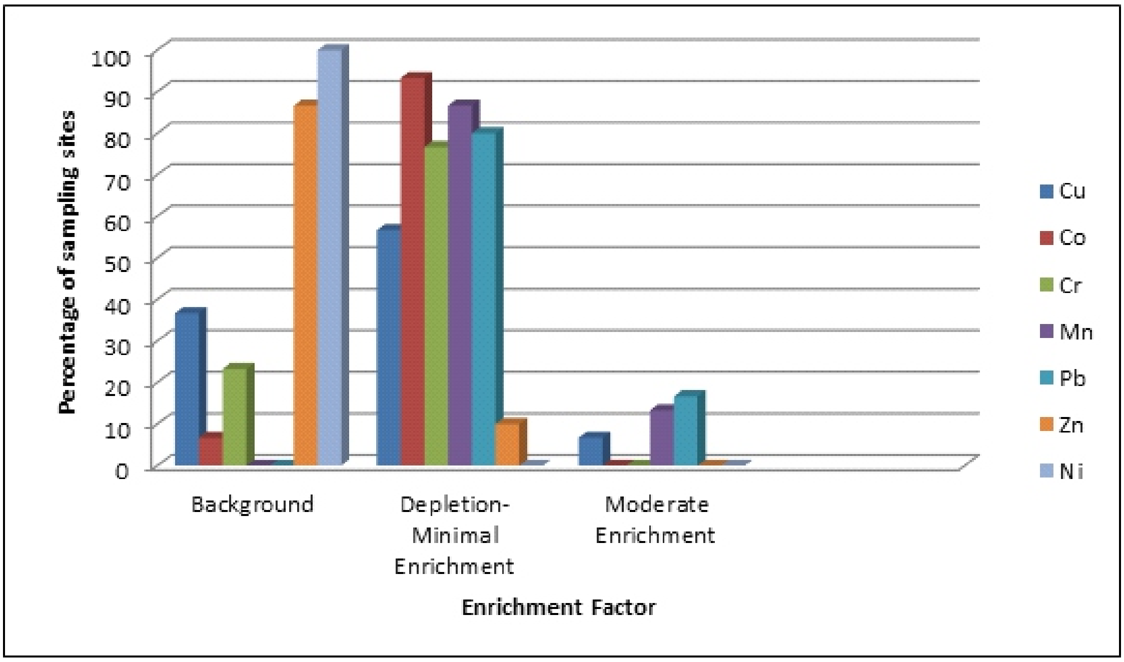

Fig. 5: Percentage Enrichment of Heavy Metals in the Stream Sediments of River Oyi and its Tributary.

Table 4: Pollution Load Index (PLI) for metals in Sediments (< 177um) of River Oyi and its Tributary

Sample	Cu	Co	Cr	Fe	Mn	Pb	Zn	Ni	PLI
LF01	0.83	0.51	0.35	0.29	0.72	0.39	0.41	0.18	0.42
LF02	0.21	0.39	0.33	0.26	0.36	0.33	0.19	0.15	0.26
LF03	0.28	0.53	0.38	0.27	0.62	0.39	0.17	0.17	0.32
LF04	0.24	0.21	0.31	0.17	0.34	0.36	0.15	0.08	0.21
LF05	0.15	0.17	0.31	0.19	0.24	0.97	0.13	0.06	0.20
LF06	0.06	0.13	0.15	0.09	0.15	0.13	0.05	0.04	0.09
LF07	0.27	0.35	0.26	0.22	0.32	0.25	0.21	0.13	0.24
LF08	0.11	0.17	0.09	0.13	0.18	0.13	0.13	0.05	0.12
LF09	0.22	0.32	0.27	0.19	0.29	0.24	0.15	0.11	0.21
LF10	0.16	0.27	0.24	0.16	0.27	0.17	0.13	0.10	0.18
LF11	0.38	0.45	0.31	0.25	0.40	0.28	0.22	0.17	0.29
LF12	0.16	0.23	0.27	0.17	0.23	0.27	0.11	0.08	0.17
LF13	0.21	0.31	0.29	0.18	0.35	0.31	0.13	0.10	0.22
LF14	0.22	0.35	0.27	0.21	0.31	0.26	0.18	0.13	0.23
LF15	0.13	0.26	0.26	0.17	0.30	0.23	0.11	0.09	0.18
LF16	0.12	0.25	0.30	0.16	0.26	0.28	0.10	0.08	0.17
LF17	0.19	0.24	0.46	0.21	0.27	0.49	0.11	0.08	0.22
LF18	0.15	0.36	0.28	0.19	0.36	0.25	0.12	0.12	0.21
LF19	0.16	0.26	0.23	0.15	0.25	0.20	0.12	0.09	0.17
LF20	0.08	0.08	0.06	0.07	0.25	0.12	0.05	0.02	0.07
LF21	0.07	0.06	0.07	0.06	0.10	0.13	0.05	0.03	0.07
LF22	0.18	0.11	0.09	0.10	0.15	0.13	0.08	0.05	0.10
LF23	0.11	0.07	0.09	0.08	0.12	0.31	0.08	0.03	0.09
LF24	0.13	0.14	0.13	0.12	0.16	0.23	0.11	0.06	0.13
LF25	0.19	0.13	0.13	0.11	0.14	0.39	0.13	0.04	0.13
LF26	1.13	0.45	0.29	0.34	0.37	0.43	0.74	0.17	0.42
LF27	0.14	0.12	0.11	0.10	0.12	0.18	0.08	0.05	0.11
LF28	0.17	0.21	0.16	0.17	0.21	0.30	0.13	0.08	0.17
LF29	0.22	0.21	0.15	0.16	0.21	0.19	0.13	0.07	0.16
LF30	0.35	0.67	0.28	0.37	0.73	0.39	0.25	0.16	0.36

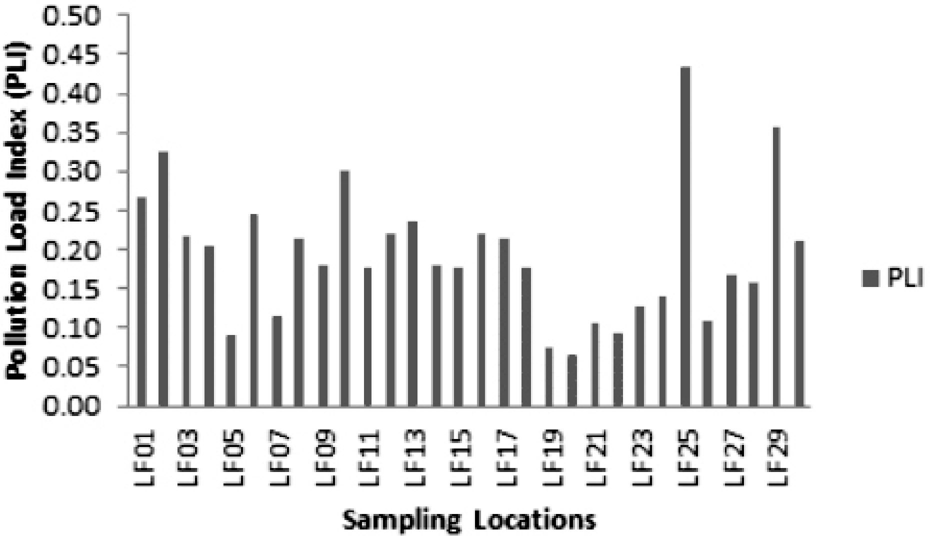

Fig. 6: Pollution Load Index (PLI) values of sampling sites at River Oyi and its tributaries

Table 5: Muller's Classification for the Geoaccummulation Index (Muller, 1981)

I_{geo} values	Class	Quality of Sediment
< 0	0	Unpolluted
0 -1	1	From unpolluted to moderately polluted
1 – 2	2	Moderately polluted
2 – 3	3	From moderately to strongly polluted
3 – 4	4	Strongly polluted
4 – 5	5	From strongly to extremely polluted
5 – 6	6	Extremely polluted

Table 6: Geo-accumulation Index for the Analyzed Heavy Metals in the Sediments (<177um) of River Oyi and its Tributary

Sample	Cu	Co	Cr	Fe	Mn	Pb	Zn	Ni
LF01	-2.85	-1.93	-2.17	-2.38	-2.05	-2.19	-2.97	-3.34
LF02	-2.45	-1.51	-1.99	-2.54	-1.27	-1.94	-3.12	-3.15
LF03	-2.64	-2.87	-2.25	-2.50	-2.13	-2.08	-3.36	-4.19
LF04	-3.30	-3.11	-2.30	-3.16	-2.67	-0.63	-3.52	-4.60
LF05	-4.74	-3.51	-3.29	-2.95	-3.29	-3.51	-4.83	-5.09
LF06	-2.46	-2.11	-2.52	-4.00	-2.22	-2.59	-2.86	-3.58
LF07	-3.83	-3.15	-4.06	-2.77	-3.02	-3.51	-3.53	-4.87
LF08	-2.77	-2.25	-2.47	-3.55	-2.37	-2.65	-3.36	-3.77
LF09	-3.27	-2.45	-2.62	-3.02	-2.49	-3.15	-3.53	-3.93
LF10	-1.99	-1.73	-2.27	-3.23	-1.89	-2.43	-2.79	-3.15
LF11	-3.25	-2.73	-2.46	-2.60	-2.71	-2.47	-3.79	-4.24
LF12	-2.81	-2.30	-2.38	-3.18	-2.11	-2.29	-3.53	-3.91
LF13	-2.78	-2.09	-2.46	-3.09	-2.27	-2.55	-3.05	-3.50
LF14	-3.55	-2.51	-2.55	-2.82	-2.31	-2.72	-3.78	-4.02
LF15	-3.61	-2.57	-2.34	-3.18	-2.55	-2.45	-3.91	-4.16
LF16	-2.99	-2.66	-1.69	-3.25	-2.49	-1.62	-3.75	-4.19
LF17	-3.29	-2.07	-2.44	-2.82	-2.08	-2.61	-3.62	-3.62
LF18	-3.23	-2.51	-2.71	-2.97	-2.57	-2.93	-3.63	-4.04
LF19	-4.30	-4.25	-4.59	-3.29	-2.57	-3.61	-4.86	-6.19
LF20	-4.33	-4.57	-4.44	-4.42	-3.84	-3.48	-4.89	-5.91
LF21	-3.09	-3.83	-4.02	-4.65	-3.36	-3.58	-4.15	-4.87
LF22	-3.71	-4.35	-4.02	-3.88	-3.70	-2.28	-4.27	-5.75
LF23	-3.55	-3.45	-3.55	-4.25	-3.22	-2.72	-3.76	-4.67
LF24	-3.02	-3.57	-3.48	-3.65	-3.43	-1.93	-3.55	-5.09
LF25	-0.41	-1.75	-2.38	-3.73	-2.04	-1.80	-1.01	-3.17
LF26	-3.39	-3.63	-3.74	-2.16	-3.59	-3.05	-4.15	-4.91
LF27	-3.15	-2.83	-3.22	-3.94	-2.81	-2.35	-3.53	-4.32
LF28	-2.77	-2.83	-3.31	-3.16	-2.84	-3.02	-3.56	-4.38
LF29	-2.11	-1.15	-2.42	-3.19	-1.04	-1.94	-2.59	-3.25
LF30	-2.68	-2.49	-2.70	-2.04	-2.36	-2.37	-3.24	-4.02

SUMMARY AND CONCLUSION

From the foregoing discussion, the assessment of the pollution of the stream sediments of the study area reveals that the analyzed elements are widely distributed in the study area with the order of the mean values of the concentrations being Fe>Mn>Cr>Zn>Cu>Ni>Pb>Co. The correlational analysis reveals that strong positive correlation exists between the pairs of Fe-Ni, Fe-Co, Mn-Co, Cu-Zn etc. These strong positive correlations between Cu/Zn could be probably due to natural mineralization in form of sulphides found in association with gold mineralization while the correlation between Fe-Ni, Mn-Co could be due to the scavenging action of both Fe- and Mn- oxides on these metals.

Assessment of the stream sediments by comparing the mean concentration values of the analyzed heavy metals with the USEPA, 1995 sediment quality guidelines reveals that the sediments are unpolluted by Cu, Co, Cr, Fe, Pb, Zn and Ni except for Mn. The Enrichment Factor values (EF) indicates that the sediments were largely unpolluted except for the moderate enrichment by Cu, Cr, Mn and Pb at sites LF 01, 03, 04, 13, 17, 20, 21, 23, 25 and 26. The sources of the moderate enrichment by Pb could be as a result of natural mineralization in form of sulphides, Pb also substitutes for K, hence it is concentrated in felsic rocks, probably granite and pegmatite. It also occur in trace amounts in minerals like amphibole and micas (Krauskopf., 1979). Most parts of the study area are cultivated; hence Mn, Cu and Pb which are components of soil fertilizer could have been applied to the cultivated fields. Both the Pollution load Index (PLI) and the Geo- accumulation Index (Igeo) assessments indicate that the Oyi sediments are practically not polluted by the heavy metals.

REFERENCES

Adebowale, O., Agunbiade, F. O., and Olu-owolabi. 2009. Trace metal concentration, site variations and partitioning pattern in water and bottom sediments from coastal area: A case study of Ondo Coast, Nigeria. *Environmental Research Journal*, 3(2), 46-59.

Adedoyin, A. D., Adekeye, J. I. D. And Alao, D. A. 2006. Trace element geochemistry of selected pegmatites from southwestern Nigeria. *Nig. Jour. Pure and Appli. Sci.*, 21: 2023 – 2035.

Adekoya, J.A. 1991. The geology of the banded iron – formation in the Precambrian Basement Complex of northern Nigeria. *Unpubl. Ph.D. Thesis. University of Ibadan, Nigeria.* 395pp.

Adekoya, J.A., Kehinde-Phillips, O.O. and Odukoya, A.M. 2003. Geological distribution of mineral resources in southwestern Nigeria. In: *Prospects for investment in mineral resources of southwestern Nigeria.* A. A. Elueze (ed.):1-13.

Ajibade, A.C. Woakes, M. and Rahaman, M.A. 1987. Proterozoic crustal development in the Pan-African regime of Nigeria. In: Kroner, A. (ed.), *Proterozoic Crustal Evolution. American Geophysical Union .Geodynamic Series* 17: 259-271.

Awofolu, O. R.; Mbolekwa, Z.; Mtshemla, V; Fatoki, O. S. 2005. Levels of trace metals in water and sediments from Tyume River and its effects on an irrigated farmland. *Water SA.*,3(1).87 – 94.

Chakravarty, M., Patgiri, A. D. 2009. Metal pollution assessment in sediments of the Dekrong River, NE India. *J. Hum. Ecol.*, 27(1), 63-67.

Estifanos, S. 2013.Heavy metal assessment by Partial Geochemical Extraction technique. Momona *Ethiopian Journal of Science*, vol. 5(1): 71 – 88.

Grant, N. K. 1970. Geochemistry of Precambrian Basement Rocks from Ibadan, southwestern Nigeria. *Earth and Planetary Science Letters.*10: 29-38.

Hernandez, L., Probst, A. and Ulrich, E. 2003. Heavy metal distribution in some French forest soils: Evidencefor Atmospheric Contamination. *The Science of Total Environment.*312, 195-210.

Horsnail, R.F. and Elliot, I.L. 1971. Some environmental influences on the secondary dispersion of molybdenum and copper in western Canada. *Geochemical Exploration. CIM. Spec.* 11:166-175.

Kamaruzzaman, M. C., Ong, M. S., Noor, A., Shahbudin, S., Jalal, K. C. A. 2008. Geochemistry of sediment in the major estuarine mangrove forest of Terengganu region, Malaysia. *Am. J. Appl. Sci.*, 5(12), 1707-1712 (6 pages)

Krauskopf, K. B. 1979. Introduction to geochemistry.(second edition). McGraw Hill Book Company. 617pp.

Ladigbolu, I. A. and Balogun, K. J. 2011. Distribution of heavy metals in sediments of selected streams of Ibadan Metropolis, Nigeria. *Int. Journ. Envi. Sci.*, vol. 1, No. 6, 1186 – 1191.

Lecomte, P. and Sondag, F. (1980): Regional geochemical reconnaissance in the Belgian Ardennes: Secondary dispersion patterns in stream sediments. *Mineralium Deposita (Berl.)* 15, 47-60.

Libes, S. M. 2009. Introduction to Marine Biogeochemistry. 2nd ed., *Elsevier Inc., Amsterdam.* 515 – 524.

Loska, K., Wiechula, D., Barska, B., Cebula, E.,Chojnecka, A.2003. Assessment of arsenic enrichment of cultivated soils in southern Polland. *Pol. J. Environ. Stud.,* 12(2), 187-192.

Malomo, S. 2012. Solid Mineral as the Base for Sustainable Development in Nigeria.87pp.

McCurry, P. and Wright, J. B. 1971. On Place and Time in Orogenic Granite Plutonism. *Geological Society America Bulletin* 82:1713-1776.

McCurry, P. 1976. The geology of the Precambrian to Lower Paleozoic rocks of northern Nigeria – A review. In: C.A. Kogbe (ed.), Geology of Nigeria. (1st Edition). *Elizabeth publishing Company*, Lagos. 15-40.

Megwara, J. U. and Udensi, E. E. 2014. Structural Analysis Using Aeromagnetic Data: Case Study of Parts of Southern Bida Basin, Nigeria and Surrounding Basement Rocks. *Earth Science Research.* Vol. 3(2): 27-42

Muller, G. 1981. The heavy metal pollution of the sediments of Neckars and its tributary. A stocktaking. *Chem. Zenith.*, 105: 157-164.

Muwanga, A. 1997. Environmental impact of copper mining at Kilembe, Uganda : A geochemical investigation of heavy metal pollution of drainage waters, stream sediments and soils in the Kilembe valley in relation to mine waste disposal. *Ph.D. dissertation. Universitat Braunschweig, Germany.*

Mwiganga, M. and Kansiime, F. 2005. Impact of Mpererwe Landfill in Kampala Uganda, on the surrounding environment. *Phys. Chem. Earth*, 30 (11 -16). 744 – 750.

Nyangababo, J. T., Henry, E., Omutange, E. 2005a. Lead, cadmium, copper, manganese and zinc in wetland waters of Victoria Late Basin, East Africa. *Bull. Environ. Contam. Toxicol.*, 74(5), 1003-1010 (8 pages)

NGSA 2006. Geological Map of Nigeria. *Nigeria Geological Survey Agency.*

Obaje, N. G. 2009.Geology and Mineral Resources of Nigeria. Lecture notes in Earth Sciences series. *Springer*, Vol. 120, 221pp.

Odeyemi, I.B. 1981. A review of the orogenic events in the Precambrian Basement of Nigeria, West Africa. *Geologische Rundschau*, 70(3): 879-909.

Okafor, E. C. and Opuene, K. 2007. Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. *Int. Jour. Environ. Sci. Tech.*, 4(2), 233 – 240.

Oyawoye, M.O. 1972. The Basement Complex of Nigeria. In African Geology, Ibadan 1970. Eds. Dessauvagie and Whiteman. Geology Department, University of Ibadan. 67-99.

Oyinloye, A.O. and Steed, G.M. 1996. Geology and geochemistry of Iperindo primary gold deposit, Ilesha schist belt, southwestern Nigeria. *Trans. Inst. Min. Metall.*,105: B74-B81.

Priju, C. P. and Narayana, A. C. 2006. Spatial and temporal variability of trace element concentrations in a tropical lagoon, southwest coast of India: Environmental Implications. *Journal of Coastal Research*, Vol. 39, p. 1053 – 1057.

Rabee, A. M., Al-Fatlawy, Y. F., Abdown, A. N. And Nameer, M. 2011. Using Pollution Load Index (PLI) and geoaccumulation index (I-Geo) for the assessment of heavy metals pollution in Tigris river sediment in Baghdad region. *Jour. Al-Nahrain Univ.*, 14: 106-114.

Rahaman, M. A. 1976. Review of the Basement Geology of Southwestern Nigeria. In: *Geology of Nigeria*, C. A. Kogbe (Editor). Elizabethan Publication Company, Lagos. 41-58.

Rahaman, M. A. 1988. Recent advances in the study of the Basement Complex of Nigeria. In: Oluyide, P.O., W.C. Mbonu, A.E. Ogezi, I.G. Egbuniwe, A.C. Ajibade, and A.C. Umeji (editors), *Pre-Cambrian Geology of Nigeria*. Publ. Geological Survey of Nigeria. 11-41.

Rose, A. W. Hawkes, H. E. and Webb, J. S. 1979. *Geochemistry in Mineral Exploration*, 2nd edition, Academic Press, London, England, 657pp.

Seshan, B.R.R., Natesan, U., deepthi, K. 2010. Geochemical and statistical approach for evaluation of heavy metal pollution in core sediments in southeast coast of Indian. *Int. J. Environ. Sci. Tech.*, 7(2), 291-306 (16 pages)

Soares, H. M., Boaventura, R. A. R. And Esteves da Silva, J. 1999. Sediments as monitors of heavy metal contamination in the Ave River Basin (Portugal): Multivariate Analysis of Data. *Environmental Pollution,* Vol. 105, p. 311 – 323.

Sutherland, R. A.2000. Bed sediment associated trace metals in an urban stream Oahu. Hawaii Environ. *Geo.*, 39(6), 611-627 (17 pages).

Thompson, I.1986. Exploration geochemistry: Design and interpretation of soil surveys. Rev. *Econ. Geol.* 3, 1-18.

Tomilson, D. C., Wilson, D. J., Harris, C. R., Jeffery, D. W. 1980. Problems in assessment of heavy metals in estuarine and the formation of pollution index. Helgoland Wiss. Meeresun Iter 33(1-4), 566-575(10 pages)

Turekian, K. K. and Wedepohl, K. H. 1961. Distribution of the elements in some major units of the earth's crust. *Geo. Soc. Am. Bull.*, 72(2), 175-192.(13pages)

USEPA.1999. "US Environmental Protection Agency: Screening level ecological risk assessment protocol for hazardous waste combustion facilities," Appendix E: Toxicity Reference Values, vol. 3.

Zhang, J. and Liu, C. L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China – Weathering features, anthropogenic impact and chemical fluxes. *Estuar. Coast. Shelf S.*, 54: 1051 – 1070.

Zvinowanda, C. M.; Okonkwo, J. O.; Shabalala, P. N.; Agyei, N. M. 2009. A novel adsorbent for heavy metal remediation in aqueous environments. *Int. Jour. Environ. Sci. Tech.*, 6(3), 425 – 434 (10 pages).