

Characterization and Evaluation of Heavy Metals Pollution in River Sediments from South Western Nigeria

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Abstract

Geochemistry, pollution load index (PLI) contamination factor (CF), geoaccumulation index (Igeo) and anthropogenic factors (AF) of sediment samples collected from Olonkoro river, South West, Nigeria has been conducted. Atomic absorption spectrometry (AAS), X-ray diffraction (XRD) and Fourier Transform infrared (FTIR) techniques were explored for sample analyses. Metals concentrations were varied therefore, the presences of these metals were entirely from non-crustal materials. The enrichment factor EF values in this site are in the decreasing order Cu > Pb > Mn > Zn > Cd. High Igeo was recorded for most of the metals; Zn belong to strongly contaminated while Pd was predominately extremely contaminated. Igeo values for Cu ranged from 5.44 to 6.98 with a mean value of 6.17 and most of the samples fell into class 6 of very strongly contaminated. This high index is caused mainly by industrial activities and agricultural activities taking place within the area. The PLI values from location P1 to P10 suggest deterioration of site sediment quality. The mineral phases were extracted from the XRD data. All the samples exhibited similar diffractographs, it is confirmed that the most dominant of all the minerals present is quartz. its absorption band appears around 455 to 450, 798 to 800. Pyrites are principally present at locations 1, 5, 7 and 10 its absorption frequency ranges from 700 to 800. This could be connected to the presence of iron (Fe) Thus, an immediate intervention to ameliorate pollution at sites is needed. The average AF of >1 was recorded for Fe, this suggest that it's enrichment was through anthropogenic source. Fe in the entire ten locations exhibit this characteristic while Mn, Cu, Zn, Pb, Cd reflect geogenic sources of these metals. Thus, the order of degrees of anthropogenic contamination in the sediment samples is: Fe > Cu > Zn > Pb > Mn > Cd. Geomineral analyses confirmed the presence of pyrite, quartz, Felspar, Goethite, chromites, calcite, and Kaolin as part of the sediment compositions.

Keywords: Geoaccumulation index; pollution index, contamination factor, anthropogenic factors, sediments, pollution

1. Introduction

The bottom sediment of river water serves as the carrier and ultimate sink for elements¹. They reflect pollution history and provide an adequate record of catchment inputs into aquatic environments. Understanding the concentration levels, and fate of elements is imperative in order to combat the adverse effect of elements in the environments². The chemical and mineralogical content of river sediments provide crucial information about their source and these can further be used to infer changes and as well the pollution source^{3, 4, 5, 6}.

Generally, contaminants in sediments have been widely known to have a negative impact on organisms once the concentration exceeds guideline limits^{7, 8}.

In the atmosphere, sediments have been confirmed to be the major carriers of trace elements and they have been used to

assess levels of contamination in the environment^{9, 10, 11, 12, 13,}

¹⁴. Due to chemical and geological conditions, heavy metals have been reported well in literatures to exist in various chemical forms such as soluble, exchangeable, bound to organic matter, occlusion in Mn/ or Fe oxides, as components of carbonates, phosphates, sulphur, or other secondary minerals or residual form as components of silicates^{15, 16, 17, 18}

Chemical leaching of bedrocks, water drainage basins and runoff from banks are the primary sources of heavy metals. Anthropogenic sources are attributed to mining operations, indiscriminate disposal of industrial and domestic wastes, and application of biocides for pests control among others^{19, 20}. The main source of heavy metals pollution in the Olonkoro River system is due to anthropogenic factors. For instance, there is a Shea butter industry situated along the river (Figure, 1), domestic wastes, farming and some industries that empty

partially untreated effluent into the river. Heavy metals from anthropogenic sources (Figure 1) enter the rivers as inorganic complexes, becoming easily adsorbed on the surface of sediment and forming labile fraction ^[21]. Environmental and ecosystems parameters such as water pH, turbulence, redox-potential and so on cause periodic remobilization of contaminated surface, thus, making the sediments a potential source for metal pollution ²².

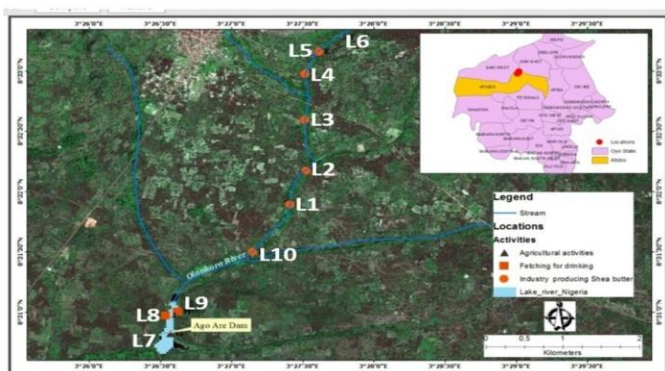


Figure 1: Map showing sampling locations and sampling points

Heavy metals pollution in the environment have been a serious concern globally due to their persistence, non-degradability and toxicity nature of these pollutants ^{23, 24, 25}. Previous studies have shown that 30-98% of heavy metals are transported in sediment form ²⁶. Increases in urbanization, industrialization, construction, agriculture, have made rivers situated in cities to receive heavy metals through natural and anthropogenic sources ^{1, 8, 18, 17, 27}.

To date many researchers, have conducted comprehensive surveys of heavy metals contamination in sediments of different regions ^{1, 8, 17, 18, 26, 27, 28, 29, 30, 31, 32, 33, 34}. Limited research has been undertaken to study distribution of heavy metals in Olukoro River sediments.

In this study, freshly collected bottom sediments from Olukoro River was analyzed for heavy metals to evaluate their concentration levels and possible mineral phases in the sediment samples. In particular, the main focus was to explore the possible anthropogenic and contamination factors *vis-à-vis* the geoaccumulation index and other sources of metal input into the river.

2. Methodology

2.1 Study area

The study area was Olukoro River in the Atisbbo Local Government Area of Oyo State which is located between

latitude 8° 33'36" N and 3° 28'30" E (Figure 1). This river empties into a popular Ago-Are Dam used by two indigenous communities with a population of about one hundred and twenty thousand for domestic purposes. The main sources of pollution in the river catchments are socio-economically related (Shea butter production). The natives also depend on the river for fishing and as a source of water for domestic purposes. They are also involved in commercial sand dredging. Some industrial concerns within the vicinity of the river catchments empty partially treated effluents into the river. Domestic waste discharges and makeshift latrines are evident in the river banks ³⁵. Coordinate of the Sampling Points and Figure showing sampling locations and points is shown in Table 1.0 and Figure 1.0 respectively.

2.3 Collection of Samples

Sediment and water samples that were used for the toxicity test and metal determination were collected between December 2015 and May 2016 at ten different locations along the Olukoro River. Surface sediments were collected at depths of 20–30 cm in the sediment core respectively. The sampler was inspected for possible cross-contamination and cleaned with ambient water for individual sample collection. The 10 sampling locations include 1 sample as control, 3 samples from the upper stream of the river, 2 samples from the middle stream, 1 sample from the point of discharge of Shea butter effluent into the river and 3 samples from the lower stream. The difference from one sampling point to another was approximately 100 m. The choice of locations was based on the ease of access to the River and the activities carried out along the River at such points. Water samples were collected in clean plastic containers, acidified with conc. HNO₃ to get rid of debris and unwanted particles. It was transported to the laboratory and refrigerated. The sediment samples were collected in a high-density polyethylene (HDPE) bottle, soaked in 3% HNO₃ and pre-rinsed with distilled water prior to sampling following the standard procedure described by America Public Health Association (1989) ³⁶ and the Department of Water Affairs and Forestry (1996) ³⁷ Pretoria, South Africa. Water and Sediment samples were tightly covered immediately after sampling in order to ensure that the degradation or alteration of the sample was avoided or minimized and transported to the laboratory on an ice chest for sample preparation and storage (refrigerated) prior to heavy metals analysis using AAS, FTIR and XRD.

2.4 Chemical and Reagents

All reagents were of analytical reagent grade. Double deionized water was used for all dilutions. Nitric acid, HNO₃ (65%) and hydrogen peroxide (30%), Bouins solution, 1% Eosine Y, Normal Saline, Formalin, Giemsa stain, May griwald stain, methanol were of ultrapure quality purchased

from Merck, Darmstadt, Germany. The element standard solutions from Merck Company to make the calibration were prepared by diluting the stock solutions of 1000 mg/L of each element³⁸

2.5 Elemental Analysis of Samples

Determination of Cadmium, Lead, Iron, Zinc, Copper and Tin was made directly on each final solution using Atomic Absorption spectroscopy (AAS) while the mineral phases were determined by XRD and FTIR.

2.6 Sample Preparation for XRD and FTIR Analysis

The FTIR and XRD were used to determine the solid/mineral phases of the dried sediment. 1g of the surface sediment sample was weighed. This sample was grounded to powder using mortar and pestle. Each powdered sample was sieved into selected mesh powder in order to remove sand particles, and the prepared sample was ready for XRD and FTIR analysis³⁹.

2.7 Assessment of sediment contamination with metals

2.7.1 Index of Geo-accumulation

The index of geo-accumulation (I_{geo}) was used for evaluating the level of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments; it will also be used to assess the soil contamination. It was computed using the Equation (1) as:

$$I_{geo} = \frac{\log_2 \frac{C_n}{1.5Bn}}{1.5}$$

Where C_n was the mean measured total concentration of the examined metal 'n' in the sediment; Bn was the average (crustal) geochemical background value for concentration of metal 'n' in fossil argillaceous sediment and sometimes referred to as 'average shale'; 1.5 was the background matrix correction factor due to lithogenic effect⁴⁰. Because we did not have the background values of metals of interest in the studied area, we will adopt the average crustal values for the metals (Fe, 46,700 µg/g; Pb, 20 µg/g; Zn, 95 µg/g; Mn, 850 µg/g; Cu, 45 µg/g; and Cd, 29 µg/g) for the calculations of EF and I_{geo} as commonly used^{41, 42, 43}.

2.7.2 Pollution Load Index (PLI)

To compare the total metal content at the different sampling stations, the metal pollution index (PLI) was used.

The PLI equation was as shown below:

$$PLI = (Cf1 \times Cf2 \times Cf3 \dots \dots \dots Cf_n)^{1/n}$$

Where $Cf1$ = concentration value of the first metal.

$Cf2$ = concentration value of the second metal.

Cf_n = concentration value of the nth metal in the sample⁴⁴.

2.7.3 Contamination Factors (CF)

CF was computed utilizing the metal content in sediment and coastal shale as the background value, to understand the contamination state of the metals in the sediment. PLI was computed (Tomlinson et al. 1980) as given below;

$$CF = C_i / C_n$$

Where C_i was Metal content in the sediment; C_n was background value of metal. According to Hakanson's (1980)⁴⁵ classification, $CF < 1$ refers to low contamination, $1 \leq CF \leq 3$ means moderate contamination, $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination.

2.7.4 Enrichment Factor (EF)

To differentiate between the metals originating from anthropogenic (non-crustal) and geogenic (crustal) sources, and to assess the degree of metal contamination, EF values was calculated for each metal of both the cores using Al as the reference element⁴⁶. The EFs for each element was calculated from the formula

$$EF = \left(\frac{C_n}{C_{Fe}} \right)_{\text{sediment}} / \left(\frac{C_n}{C_{Fe}} \right)_{\text{background}}$$

Where, (C_n/C_{Fe}) sample was the ratio of concentration of the element (C_n) to that of Iron (C_{Al}) in the sediment sample and (C_n/C_{Fe}) background was the same ratio with background value taken of average shale⁴⁷. The EF values are interpreted as: $EF < 1$ indicates depletion, $EF \geq 1$ indicates enrichment and $EF \geq 1.5$ was considered to indicate that an important proportion of trace metals was delivered from non-crustal materials or non-natural weathering processes, instead from biota and/or point and non-point pollution sources, $EF > 2$ means significantly enriched.

2.7.5 Anthropogenic Factor (AF)

AF was calculated with metal surface concentration and concentration at a depth which enables differentiation between geogenic and anthropogenic input of heavy metals, the results of which will indicate the extent of anthropogenic influence on metal deposition. AF was calculated⁴⁸, using the following formula,

$$AF = C_s / C_d$$

Where, C_s and C_d refer to the concentrations of the elements in the surface sediments and at depth in the sediment column. If AF was > 1 for a particular metal, it means contamination exists; otherwise, if AF was ≤ 1 , there was no metal enrichment of anthropogenic origin.

2.7.6 Quality Assurance

The extracts obtained from each step were analyzed for Pb, Cu, Zn, Sn, Cd, and Fe using AAS. The blank samples were analyzed after every 10 measurements. Major and trace elements were analyzed by AAS. For quantification of the element of interest, the instrument was calibrated daily using NWAIST traceable standards. A quality control standard was analyzed prior to the samples to verify the accuracy of the calibration standards, while control standards were used throughout the analysis to monitor accuracy and instrument drift. On the AAS, internal standards were introduced continuously with the samples and standards to correct for drift due to high matrix load. In order to check for the accuracy of the sequential extraction procedure, reference sediment materials (for trace elements) were extracted using the above procedure and analyzed in triplicates.

3. Results and Discussion

3.1 Enrichment factor (EF)

A common approach to estimating anthropogenic impact on water and sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels. The EF measured in heavy metal content with respect to a reference metal such as Fe or Al. due to the lack of geochemical background values of the study area, an alternative of the average crustal concentrations as reference material^{43, 49}. Deely and Fergusson (1994)⁵⁰ proposed Fe as an acceptable normalization element to be used in the calculation of the EF since they consider the Fe distribution which was not related to other heavy metals.

EF close to unity point show crustal origins while those greater than one is related to non-crustal source (Table 26). In this study the EFs obtained for all heavy metals are greater than unity that reveals these elements are depleted in some of the phases relative to non-crustal abundance in the study area. Enrichment factor categories proposed by Sutherland et al. (2000) ^[51] were used as follows: $EF < 2$ = deficiently to minimal enrichment, $2 \leq EF < 5$ = moderate enrichment, $5 \leq EF < 20$ = significant enrichment, $20 \leq EF < 40$ = very high enrichment and $EF \geq 40$ = extremely high enrichment. The EF values for the trace metals are presented in Table 2.0

Table 2.0: EF values calculated from the concentration of heavy metals in sediment of Olonkoro River.

Sites	Mn	Cu	Zn	Pb	Cd
P1	2.65	18.59	6.7	19.70	ND
P2	2.25	13.83	2.45	4.75	ND
P3	4.57	27.48	7.93	11.35	ND
P4	2.56	1.29	6.76	6.55	ND
P5	1.23	21.27	3.32	3.48	ND
P6	10.25	34.68	4.23	5.20	ND
P7	1.75	20.28	4.19	5.33	ND

P8	4.49	33.09	8.60	4.61	ND
P9	2.28	15.82	3.05	0.61	ND
P10	4.67	51.65	5.64	0.14	ND

From the result presented in Table 2.0, it is evident that copper at location P10 (Figure 2.0) showed the highest value for enrichment which falls in extremely high enrichment. Manganese, lead, zinc has a very significant enrichment while cadmium is deficiently to minimal enrichment. This implies that it has anthropogenic enrichment. Therefore, the presences of these metals were entirely from non-crustal materials ⁴³. However, the major source of this metal is anthropogenic. The EF values in this site are in the decreasing order $Cu > Pb > Mn > Zn > Cd$.

Copper showed a variation in EF across the location, at P4 it falls deficiently to minimal enrichment, P1, P2, P5, P9 all fall on significant enrichment while P3, P6, P7, P8 have very high enrichment. However, P10 showed to be extremely high enrichment indicating that copper is highly enrichment in all the 10 locations and may be due to anthropogenic enrichment Table 2.0 ⁵². The enrichment of manganese in location P6 is extremely high indicating that it has low enrichment from the crustal materials; all other locations are moderately enriched showing values less than 5 and greater than 2. Zinc and lead have a significant enrichment factor and cadmium has low enrichment in all locations. The majority of the metals in the locations are enriched from anthropogenic sources except for Cd in all the locations and Cd in location P9 and P10 indicated that there was no anthropogenic enrichment. Therefore, the presence of these trace metals were entirely from crustal materials or natural weathering processes ⁴⁹. Mn showed a similar pattern of enrichment (moderate enrichment) in all the locations except for P6 that is significantly enriched. The application of the established pollution indices to our data gave an insight to the degrees and various sources of the heavy metals input into the river. The EF values for the metals are presented in Table 2.0 Most of the heavy metals (Mn, Zn, Pb and Cu) in Olonkoro River originated from non-crustal materials or anthropogenic sources. It is only Cd that originated from crustal materials or natural weathering processes ²⁸

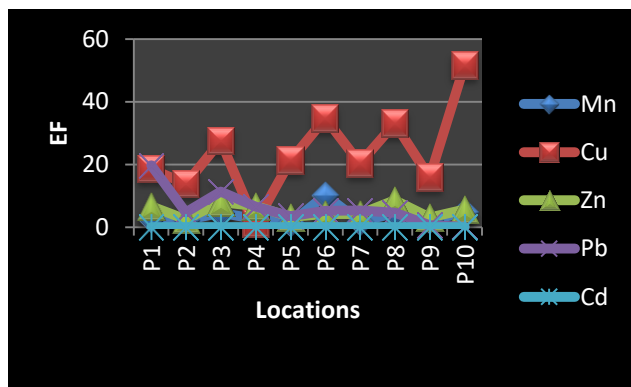
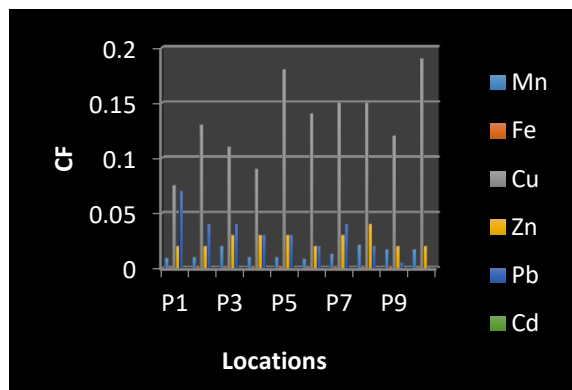


Figure 2.0: The Enrichment factor of sediments samples from Olonkoro River

Table 3.0: Contamination factor and pollution load index calculated from the concentration of heavy metals in sediment of Olonkoro River.

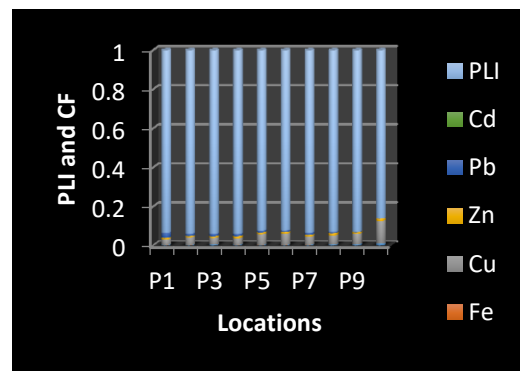
Sites	Mn	Fe	Cu	Zn	Pb	Cd	PLI
P1	0.0093	0.00070	0.075	0.02	0.0700	-	2.49
P2	0.0100	0.00180	0.130	0.02	0.0400	-	3.11
P3	0.0200	0.00077	0.110	0.03	0.0400	-	3.16
P4	0.0100	0.00090	0.090	0.03	0.0300	-	2.55
P5	0.0100	0.00170	0.180	0.03	0.0300	-	3.03
P6	0.0085	0.00083	0.140	0.02	0.0200	-	2.25
P7	0.0130	0.00150	0.150	0.03	0.0400	-	3.34
P8	0.0210	0.00093	0.150	0.04	0.0200	-	3.10
P9	0.0170	0.00150	0.120	0.02	0.0050	-	2.15
P10	0.0170	0.00073	0.190	0.02	0.0005	-	1.42

The contamination factor from the Table 3.0 indicates that various sampling location has low contamination degree of heavy metals because their values are far less than 1 (Figure 3.0).

**Figure 3.0:** Contamination factor of sediment sample of Olonkoro River.

3.2 Pollution load index

The PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. A $PLI < 1$ denote perfection; $PLI = 1$ present that only baseline levels of pollutants are present and $PLI > 1$ would indicate deterioration of site quality⁴⁴. If the PLI value of ≥ 1 indicates an immediate intervention to ameliorate pollution; $0.5 \leq PLI < 1$ suggests that more detailed study is needed to monitor the site, whilst a value of < 0.5 indicates that there is no need for drastic rectification measures to be taken. From the present study, the PLI values from location P1 to P10 suggest deterioration of site quality (Figure 4.0). Thus, an immediate intervention to ameliorate pollution at sites is needed.

**Figure 4.0:** Pollution load index with Contamination factor of sediment of Olonkoro River.

3.3 Index of Geo-accumulation

The index of geo-accumulation (I_{geo}) was used for evaluating the level of contamination by comparing the current and pre-industrial concentrations originally used with bottom sediments; it was also used to assess the soil contamination.

Table 4.0: Geo-accumulation Index (I_{geo}) calculated from the concentration of heavy metals in sediment of Olonkoro River.

Sites	Mn	Fe	Cu	Zn	Pb	Cd
P1	-0.69	-1.10	5.44	3.40	5.52	0
P2	-0.29	0.27	6.38	3.89	4.84	0
P3	0.22	-0.33	6.13	4.34	4.86	0
P4	-0.38	-0.74	5.86	4.34	4.30	0
P5	-0.57	0.13	6.86	4.18	4.25	0
P6	-0.82	-0.86	6.58		3.84	0
P7	-0.17	0.02	6.68	3.54	4.75	0
P8	0.48	-0.68	6.69	4.74	3.84	0
P9	0.18	-0.02	6.24	3.92	1.58	0
P10	0.19	-1.04	6.98	3.78	-1.58	0

Average I_{geo} and contamination levels of different metals in soil are given in Table 4.0 while Table 5.0 represents the sampling point wise I_{geo} value. I_{geo} is distinctly variable and suggests that soil around Tede ranged from uncontaminated to strongly/extremely contaminated with respect to the analyzed metals. I_{geo} revealed that all the samples examined, Fe and Mn fell into class 0—uncontaminated to moderately contaminated. In the case of Cu in seasons, all the sampling points fell in class 6 and the average I_{geo} was 6.98 indicating very strongly contaminated. I_{geo} for Zn belong to strongly contaminated while Pd was predominately extremely contaminated. This high index is caused mainly by industrial activities and agricultural activities within the area; hence its content in the areas affected by industrial activity may be

elevated. Igeo values for Cu ranged from 5.44 to 6.98 with a mean value of 6.17 and most of the samples fell into class 6 of very strongly contaminated. Igeo of Zn was 3.40 and belongs to Igeo class 5. Fe showed uncontaminated/moderately contaminated in some locations. A similar trend to Cu was also found for Pb, but different for Cd. Mn followed uncontaminated/moderately contaminated index.

Table 5.0: Representation of Igeo of metals at different sampling points

SP	Mn	Fe	Cu	Zn	Pb	Cd
P1						
P2		•				
P3	•					
P4						
P5		•				
P6						
P7		•				
P8	•					
P9	•				•	
P10	•					

KEY	
I	0 < Igeo < 1 Uncontaminated/moderately contaminated
ii	1 < Igeo < 2 Moderately contaminated
iii	2 < Igeo < 3 Moderately/strongly contaminated
iv	3 < Igeo < 4 Strongly contaminated
v	4 < Igeo < 5 Strongly/extremely contaminated
vi	> 5 Very strongly polluted

SP: Sampling points

3.4 Anthropogenic Factor (AF)

AF will be calculated with metal surface concentration and concentration at a depth which enables differentiation between geogenic and anthropogenic input of heavy metals, the results

of which will indicate the extent of anthropogenic influence on metal deposition.

Table 6.0: Anthropogenic factor calculated from the concentration of heavy metals in sediment of Olonkoro River.

Sites	Mn	Fe	Cu	Zn	Pb	Cd
P1	0.033	1.378	0.122	0.093	0.058	-
P2	0.042	3.42	0.226	0.084	0.034	-
P3	0.062	2.341	0.198	0.120	0.036	-
P4	0.038	1.635	0.150	0.111	0.023	-
P5	0.034	3.096	0.314	0.104	0.023	-
P6	0.031	1.697	0.280	0.072	0.019	-
P7	0.049	3.121	0.3017	0.132	0.035	-
P8	0.081	2.002	0.316	0.173	0.020	-
P9	0.072	3.501	0.255	0.108	0.005	-
P10	0.058	1.380	0.340	0.078	0.001	-

The average AF of >1 for Fe (Figure 5.0), suggest that it is enrichment through anthropogenic source. Fe in the entire ten locations exhibit this characteristic while Mn, Cu, Zn, Pb, Cd in all locations reflect geogenic sources of these metals Figure 5.0⁴⁸. Thus, the order of degrees of anthropogenic contamination in the sediment samples is: Fe > Cu > Zn > Pb > Mn > Cd for location P1, Fe > Cu > Zn > Mn > Pb > Cd for location P2 to P10. Therefore, Fe is enrichment of anthropogenic origin while all other metals are of geogenic or non-anthropogenic source.

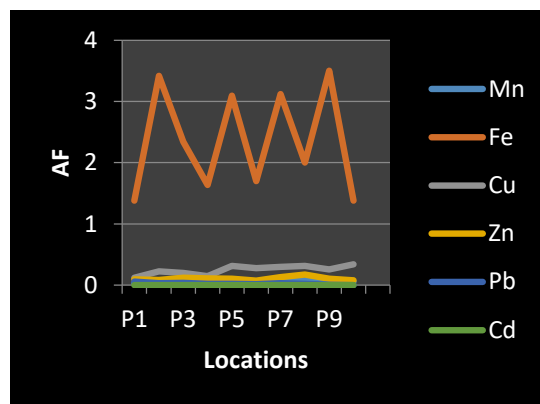
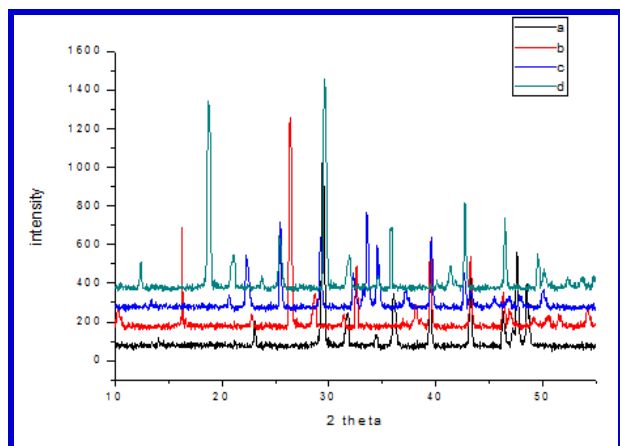


Figure 5.0: The anthropogenic factor for sediments samples from Olonkoro River.



Key:
Locations
a. P1
b. P5
c. P7
d. P10

Figure 6.0: X-ray Diffractographs of sediments samples collected from Location P1, P5, P7 and P10 in Olonkoro River

Table 7.0: Major mineral phases in Olonkoro River sediments (extracted from XRD)

Locations	Quartz	Feldspar	Goethite	Pyrite	Chromite	Calcite	Kaolinite
P1	❖		❖	❖	❖		
P5	❖		❖	❖			
P7	❖	❖		❖			
P10	❖	❖	❖	❖			

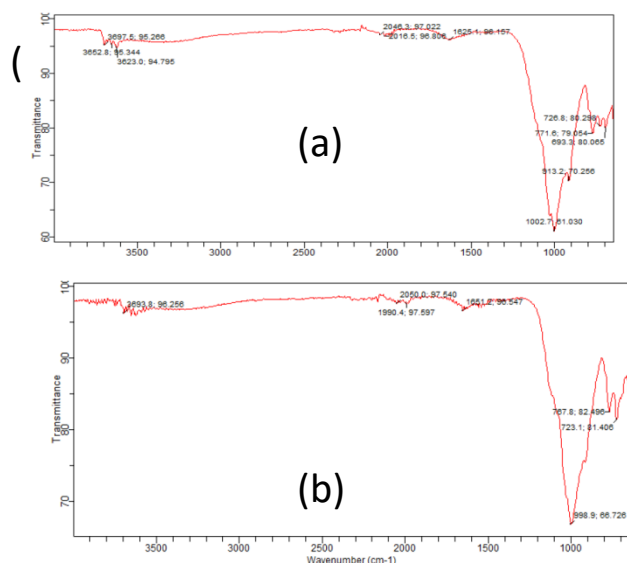
All the major mineral phases identified at the four locations are summarized in Table 7.0. The mineral phases were extracted from the XRD data. All the samples exhibited similar diffractographs, these are shown in Figure 7.0 respectively. By comparing the observed frequencies with available literature, the minerals such as pyrite, quartz, Feldspar, Goethite, chromites, calcite, and Kaolin have been identified^{53, 54}. Quartz, this particular mineral, present principally across all locations, could be as a result of deposition of shell of dead plank tonic life settle on the sediment^{16, 55}.

Feldspar was only present in location P7 and P10 while kaolinite was only present in location P1. All the major mineral phases from the XRD results showed that, the sediments of Olonkoro River contained predominantly quartz,

pyrite and calcite. The iron present in locations 1,5 and 7 is mainly present as amorphous iron oxide since the presence of Fe in other form different from crystalline goethite is not detectable by XRD^{56, 57}. Pyrites are principally present at locations 1, 5, 7 and 10. It can be observed from Table 34 that IR absorption frequency for pyrite ranges from 700 to 800. This was similar to results recorded in literature^{16, 39, 58, 59, 60, 61, 62}. Infrared Spectroscopy was used to complement these findings. The IR spectra data of major peaks

Table 8.0: Observed IR absorption frequencies of sediment samples of Olonkoro River and their assignment

P1	P5	P7	P10	Assignment
3667,	3697,	3690	3690	OH-Stretching
3652	3619	3623	3623	frequency of
3623	-	-	-	H ₂ O
-	-	2322	2322	Free surface
-	2918	1632	1632	OH-stretching
1625	1610	-	-	frequency
-	-	-	-	Intra molecular
1002	-	998,	998, 913	OH stretching
913	-	913	767, 723	frequency
771,	-	767,723	-	OH of lattice
726	-	-	-	H ₂ O
693	-	-	-	Intra molecular
				H ₂ O bending
				frequency
				Fe – OH
				bending mode
				Si – O bending
				mode
				Fe – OH
				stretching
				frequency
				OH
				deformation
				frequency



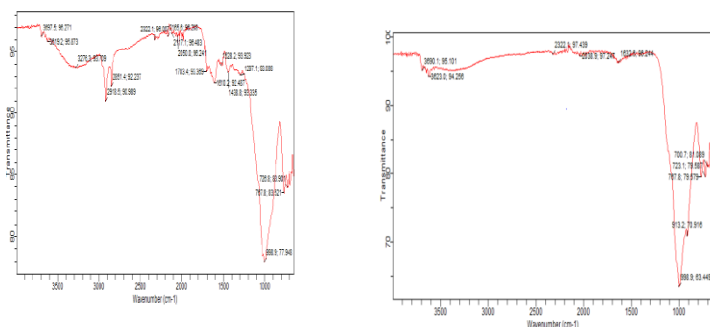


Figure 7: The FTIR spectra of sediment in Location P10 of Olonkoro River

Table 8.0: summarizes the absorption frequencies of the peaks in each of the spectra. The following minerals were confirmed when the observed frequencies were compared with the literature. They are: quartz, pyrite, calcite, feldspar and kaolinite. Quartz was reported in literature to be the second most dominant of all the minerals in the earth crust⁵⁵. The chemical representation of quartz is SiO₂. Quartz forms the major constituent of metamorphic, sedimentary, granite, limestone, etc. In the present study, it is confirmed that the most dominant of all the minerals present is quartz and from Table 8.0 its absorption band appears around 455 to 450, 798 to 800. This was similar to results recorded in literature^{58, 59, 60, 61, 62}. Pyrites are principally present at locations 1, 5, 7 and 10. It can be observed from Table 8.0 that IR absorption frequency for pyrite ranges from 700 to 800. This could be connected to the presence of Fe at these locations; the source could be that the pond was receiving effluent from industry. It can be observed from the Table 8.0 that IR absorption bands appearing at or around 455- 450, 510-505, 695-690, 780-775 and 800-795 cm⁻¹ suggests the presence of quartz in the samples^{58, 59, 60, 61, 62}.

Conclusions

A detailed study of the geochemical evaluation of Olonkoro River has been conducted. The geochemical data has been carefully studied to predict the levels of heavy metals contamination in the sediment samples. Copper showed the highest value for enrichment which falls in extremely high enrichment, Manganese, lead, zinc has a very significant enrichment while cadmium is deficiently to minimal enrichment. According to the patterns of elements enrichments recorded, anthropogenic source predominates the huge source of contamination. This implies that it has anthropogenic enrichment. The FTIR and XRD analyses indicate the presence of quartz, pyrite, calcite and carrolite in the river sediments. The exploration of the two techniques justified that they are useful techniques for mineral analysis. Igeo is distinctly variable and suggests that soil around Tede ranged from uncontaminated to strongly contaminated with respect to the analyzed metals. The contamination factor data reveals

that various sampling locations have a low contamination degree of heavy metals because their values are far less than 1. Apparently, it is possible that concentrated polluted sediments transported through industrial effluents that empty into the river could be transported regionally.

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