

## particle induced x-ray emission (pixe) assisted technique in the evaluation of potential ecological risks of heavy metals in surface sediments of Oba-Ile River, Ifelodun Local Government Area, Osun-State, Nigeria

Katherine Temitope Ogundele <sup>1,\*</sup>, John Adekunle Oyedele Oyekunle <sup>2</sup>, Emmanuel Ayodele Oluyemi <sup>2</sup>, Oladotun Wasiu Makinde <sup>1</sup> and Eusebius I. Obiajunwa <sup>1</sup>

<sup>1</sup> *Environmental and Earth Sciences Division, Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria.*

<sup>2</sup> *Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.*

World Journal of Advanced Research and Reviews, 2024, 24(02), 1139–1150

Publication history: Received on 08 November 2022; revised on 28 October 2024; accepted on 30 October 2024

Article DOI: <https://doi.org/10.30574/wjarr.2024.24.2.0840>

### Abstract

The seasonal evaluation of trace elements in the surface sediments collected from Oba-Ile River, using Particle Induced X-Ray Emission (PIXE) Spectroscopy had been carried out. This was done so as to provide information about the pollution status of the river during the rainy and dry seasons. The samples were subjected to trace metal profiling using a 2.5 MeV proton available at the Ion Beam Analysis (IBA)/accelerator laboratory, Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife. The facility is centered on a NEC 5SDH 1.7 MV Pelletron accelerator, equipped to provide proton and helium ions. A multi-elemental estuarine sediments referenced material (SRM 1646a purchased from NIST) was used for the determination of H-value which was subsequently used for analyzing the samples and assured the accuracy of the experimental procedure. The order of abundance of the 16 elements identified was Si > Fe > Al > K > Ca > Ti > Na > Mg > Zr > Mn > Sr > V > Cr > Zn > Pb > Cu. The contamination factor indicated that the metals presented a low contamination factor (LC<sub>f</sub>) to moderate contamination factor (MC<sub>f</sub>) except for Fe and Zr which presented a considerable contamination (CC<sub>f</sub>) and a very high contamination factor (VHC<sub>f</sub>) respectively. Other contamination indices indicated that Fe had either a moderate enrichment (ME) factor or a significant enrichment (SE) factor, thereby suggesting that Oba-Ile River sediment was particularly enriched in Fe

**Keywords:** River; Sediment; Oba-Ile; PIXE; Heavy metals; Pollution Indices

### 1. Introduction

The entrance of pollutants into the environment due to human and natural activities is one of the greatest problems facing the society today. This is as a result of increase in industrial and other anthropogenic activities of man (Shanbehzadeh *et al.*, 2014). Pollution in rivers happens through the introduction of compounds or elements that usually would not be found there without human action, or by variation in the normal concentration of the existing metals either an increase or decrease due to human action or natural disasters (Copaja, *et al.*, 2012). Some of these metals are potentially and in this category we have such metals (or metalloids) as Al, Sb, As, Cd, Cu, Cr, Fe, Hg, Mn, Ni, Pb, Se, and Zn. The influence of these metals to the aquatic body originates from numerous sources such as erosion, wet precipitation, aerial deposition, runoff from contaminated sites and so on, (Copaja, *et al.*, 2012). The introduction of agricultural, municipal and industrial wastes into the aquatic ecosystem is another route of environmental pollution by man.

\* Corresponding author: K.T. Ogundele

Water resources are among the most critical indispensable needs of man, animals and plants. The extent of water purity and usefulness is substantially determined by the water-sediment interface chemistry as impurities contained in the sediment can find their ways back into the water body depending on certain prevailing, physiochemical factors. As municipal, industrial, and agricultural waste find their way into water bodies, biological and chemical contaminants with heavy metals contained in the wastes similarly enter water body. Though some of these metals are very vital as micronutrients, but high concentrations or absence of these metals in food chain can cause harm, environmental effects, endanger aquatic ecosystems as well as their users (Prabu, 2009; Kane *et al.*, 2012).

Pollution of the aquatic environment with heavy metals has become a universal challenge lately since heavy metals are indestructible and many of them have harmful effects on organisms when they exceed certain threshold level (MacFarlane and Burchette, 2000). Though heavy metal contaminants are far less visible, but their consequence on the aquatic body is severe when compared with other forms of aquatic pollution, posing significant environmental threats and fears (Amisah *et al.*, 2009). These metals are frequently eroded into receiving bodies such as the sediment, soil and water bodies by run-offs, but, the aquatic ecosystem receives the bulk of the contaminants (Aladesanmi, 2014). Sediments serve as carriers and also probable sources of pollution since heavy metals are not permanent. They can be released into the water column due to various changes in environmental media such as pH, Eh, dissolved oxygen or the presence of organic compounds (Sigg *et al.*, 1987; Carignan, and Tessier, 1988; Biksham *et al.*, 1991; Copaja *et al.*, 2012). Around the world including Nigeria, there have been reports of elevated levels of heavy metals in several rivers, streams and ponds as a result of increased level of atmospheric deposit, agricultural release, rapid development of industrialization and anthropogenic activities around these water bodies. The corresponding increasing consciousness of the environmental hazards posed by toxic metals from the contributors mentioned above has attracted important attention in the study of levels and fate of heavy metals in the aquatic ecosystem (Aladesanmi, 2014). Thus, the investigating heavy metals in sediments could serve as a means of identifying contamination which may not be detected during water analysis and as such provide information about important aspects of an aquatic ecosystem (Förstner and Salomons, 1980; Belkin and Sparck, 1993; Chen *et al.*, 1996). Lately, diverse sediment quality pointers have been established, such as geo-accumulation index ( $I_{geo}$ ), contamination factor (CF), enrichment factor (EF) and pollution load index (PLI) for the determination of heavy metal contamination status by comparing calculated concentrations with pre-industrial levels (Guan *et al.*, 2018).

Oba-Ile aquatic ecosystem has not been previously subjected to any rigorous scientific investigation that involves profiling levels of heavy metals despite the fact that the water from the river serves very useful purposes ranging from drinking to fishing and other agricultural practices. The present study aimed at evaluating pollution status of Oba-Ile River sediment values of enrichment factor, geo-accumulation index, contamination factor and sediment quality guidelines.

---

## 2. Materials and method

### 2.1. Description of the Study Area

The study area lies between Latitude 7°57'0"N and Longitude 4° 35'30"E. Oba-Ile River traverses two states, namely: Oyo and Osun States in Nigeria. It is the main tributary of the Osun River and the people who live along its course practice farming and fishing. The area constitutes a part of the basement complex of Southwestern Nigeria and characteristically is underlain by crystalline igneous and metamorphic rocks. These rocks constitute the prominent outcrops and inselbergs that define the topographic highlands in the area. Although the rocks are essentially of granite-gneiss complex, they are largely monolithologic (Adeboye and Alatise, 2008). The study area is under Koppen's Af humid tropical rainforest climate. The mean annual rainfall is about 1400 mm with the rainy season covering eight months (April to November) which commences and ends with torrential rains and thunderstorms. The rainy season in the area is normally characterized by two maxima of rainfall usually in July and September. Temperatures are generally high and almost uniform (Iloeje, 1978).

#### 2.1.1. Sample Collection and Treatment

Twenty four sediment samples were collected from three sampling points along Oba-Ile River during the months of September and November, 2013 and January - June, 2014). The first sampling point was at the downstream, the second sampling point was at the middle, while the third point was at the upstream of the river. The study area apart from being close to residential area attracted such activities as fishing and planting of various crops. In each case, about 2 kg of the surface sediment samples were collected near the river bank with a hand trowel. The samples were air dried to constant weights and 2 mg of the dried samples were pulverized using agate mortar and pestle. Each sample was packed into a secure zi-lock water-tight polythene bag to prevent cross contamination.

### 2.1.2. Instrumental Analysis

From each sample, 1 mm thick pellets were produced using a 13 mm diameter die with Spec-caps by applying 12 ton pressure with hydraulic pelletizing machine. These pellets were subjected to PIXE analysis. Particle Induced X-ray Emission (PIXE) technique was employed for the determination of metals in the sediment samples. The experiments were performed using a 2.5 MeV proton available at the Ion Beam Analysis (IBA)/Accelerator laboratory at the Centre for Energy Research and Development (CERD) Obafemi Awolowo University, Ile-Ife. The facility is centered on a NEC 5SDH 1.7 MV Pelletron accelerator, equipped to provide proton and helium ions. The samples were placed on a ladder that can carry eleven 13 mm diameter pellets made from the samples. Estuarine sediments (SRM 1646a purchased from NIST) was used for the determination of H-value which was subsequently used for analyzing the samples and assured the accuracy of the experimental procedure. The measurements were carried out with a beam spot of 4 mm in diameter and a low beam current of 3-6 nA. The duration of the irradiation was for about 10-20 mins. A Canberra Si(Li) detector model ESLX 30-150, beryllium thickness of 25 mm, with full width half maximum (FWHM) 150 eV at 5.9keV, with the associated pulse processing electronics, and a Canberra Genie 2000 MCA card interfaced to a PC were used for the X-rays data acquisition. Comparison was made between experimental and certified values of metals in the standard reference materials.

## 2.2. Sediment Pollution Analysis

The concentrations of the metals in the sediment samples were subjected to various pollution indices such as contamination factor, geo-accumulation index, enrichment factor and pollution load index to evaluate metal pollution level.

### 2.2.1. Contamination Factor ( $C_f$ )

The contamination factor ( $C_f$ ) defined as:

$$C_f = C_{\text{metal}} / C_{\text{background}} \dots\dots\dots [1]$$

was used to determine the contamination status of sediment in the present study, where background value of the metals are as given by Turekian and Wedepohl (1961)

According to Ata *et al.* (2009),  $C_f$  is defined according to four categories as follows:

$C_f < 1$  = low contamination factor,  $1 < C_f < 3$  = moderate contamination factor,

$3 < C_f < 6$  = considerate contamination factor,  $C_f > 6$  = very high contamination factor

### 2.2.2. Index of Geo-Accumulation ( $I_{\text{geo}}$ )

Geo-accumulation index ( $I_{\text{geo}}$ ) was used to assess heavy metal pollution in the sediments of Oba-Ile River. The  $I_{\text{geo}}$  is a qualitative measure of pollution intensity of the samples and is classified as unpolluted ( $< 0$ ), unpolluted to moderately polluted ( $0 \leq I_{\text{geo}} \leq 1$ ), moderately polluted ( $1 \leq I_{\text{geo}} \leq 2$ ), moderately to strongly polluted ( $2 \leq I_{\text{geo}} \leq 3$ ), strongly polluted ( $3 \leq I_{\text{geo}} \leq 4$ ), strongly to extremely polluted ( $4 \leq I_{\text{geo}} \leq 5$ ) and extremely polluted ( $I_{\text{geo}} \geq 5$ ).

The  $I_{\text{geo}}$  formula used for the calculation is:

$$I_{\text{geo}} = \log_2 [C_s / 1.5 \times C_B] \dots\dots\dots [2]$$

$C_s$  is the calculated concentration of an element in the sample and  $C_B$ , is the geochemical background value in average shale (Turekian and Wedepohl, 1961) of element n. The geo-accumulation index ( $I_{\text{geo}}$ ) was earlier defined to measure quantitatively the pollution of aquatic sediments with metals. The concentration used as background is multiplied by a factor of 1.5 which takes care of natural fluctuations of the metal in the environment as well as other influences. The calculated  $I_{\text{geo}}$  values were compared with  $I_{\text{geo}}$  classification for sediment quality to know the extent of pollution of the sampled areas.

### 2.2.3. Enrichment Factor

Enrichment Factor (EF) was used to assess the degree of contamination and the possible anthropogenic impact on the sediment of Oba-Ile River. In this study, Ca was used as a conservative tracer to differentiate natural components from anthropogenic ones. Enrichment Factor was calculated using:

$$EF = (M/Ca)_{\text{sample}} / (M/Ca)_{\text{background}} \dots \dots \dots [3]$$

where  $(M/Ca)_{\text{sample}}$  is the ratio of metal and Ca concentration of the sample,  $(M/Ca)_{\text{background}}$  is the ratio of metal and Ca concentration of a background.

The background concentrations of the heavy metal study were taken from Turekian and Wedepohl (1961). There are five contamination categories recognized based on the EFs;  $EF < 2$  indicates depletion to minimal enrichment;  $EF = 2-5$  indicates moderate enrichment;  $EF = 5-20$  indicates significant enrichment;  $EF = 20-40$  indicates very high enrichment;  $EF > 40$  indicates extremely high enrichment.

#### 2.2.4. Statistical Treatment of Data

The data obtained were subjected to statistical analysis using appropriate up-to-date statistical package. Descriptive and inferential analysis was equally carried out and the results compared with environmental standard limits recommended by world regulatory bodies.

### 3. Results and discussion

#### 3.1. Validation of Results

The result of elemental analysis of IAEA Soil 7 reference material is presented in [Table 1](#). The results revealed a good agreement with certified concentration values of reference materials, except for the elements that were not detected in reference material. This validated the result obtained from the PIXE and its reliability.

**Table 1** Elemental analysis results of IAEA SOIL 7

Symbol	Conc. (mg/kg)	Cert. values
Mg	9043.0 ± 408.74	9040.0
Al	37,610.6 ± 285.84	37,600.0
Si	144,081.9 ± 360.20	144,000.0
K	9685.4 ± 80.39	9680.0
Ca	130,423.1 ± 182.59	130,400.0
Ti	2403.8 ± 36.78	2400.0
Cr	48.0 ± 3.40	48.0
Mn	503.0 ± 25.05	504.8
Fe	20,560.4 ± 84.30	20,560.0
Zn	83.6 ± 10.19	83.8
Ga	12.1 ± 7.39	8.0
As	26.7 ± 8.38	10.72
Rb	40.8 ± 13.42	40.8
Sr	86.3 ± 20.73	86.4
Zr	71.7 ± 31.55	148.0

#### 3.2. Levels of Heavy Metals Detected in Sediment Samples from Oba-Ile River

The result of the analysis of Oba-Ile sediment samples using Particle Induced X-ray Emission (PIXE) Spectrometry is presented and discussed below.

The concentration of metals detected in the order of abundance were  $Fe > Ti > Zr > Mn > Sr > V > Cr > Zn > Pb > Cu$ . Iron is an essential metal for living organisms as iron is necessary for respiratory pigments, proteins and many enzymes. The

mean concentrations of Fe in the sediments of Oba-Ile River were  $23596.08 \pm 69.03$  mg/kg,  $28789.53 \pm 66.27$  mg/kg and  $22176.48 \pm 67.90$  mg/kg for the first, second and third sampling locations respectively. These values were below the recommended limit of 50,000 mg/kg (WHO, 2004). Majority of heavy metals detected were believed to have been introduced into the study sites by the impact of agricultural wastes and other human activities taking place in the farms around the site in addition to run-offs and discharge from other streams and rivers that serve as tributaries to Oba-Ile River. Titanium was detected at levels ranging from  $1087.50 \pm 17.41$  mg/kg to  $17280.40 \pm 51.42$  with a mean value  $6172.18 \pm 41.87$  mg/kg at the first sampling location,  $1428.70 \pm 23.72$  to  $7694.80 \pm 54.63$  mg/kg with a mean value  $4504.75 \pm 39.83$  mg/kg at the second sampling point and  $2495.20 \pm 34.43$  to  $7145.90 \pm 39.54$  mg/kg with an average value  $4886.52 \pm 43.46$  mg/kg at the third location. There is no known biological role that suggests that Ti performs any essential role in human body (Oladebeye, 2017). Titanium is regarded as nontoxic, because of its poor penetration and retention in living organisms (Mertz, 1987).

Chromium is very toxic when inhaled and is a known human carcinogen (Mwangi, 2009). Breathing high levels of the element can cause irritation to the lining of the nose and breathing problems such as asthma, cough, shortness of breath, or wheezing where long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation (Mwangi, 2009). The mean Cr concentration in the sediment of Oba-Ile at the first sampling point was  $44.32 \pm 6.17$  mg/kg, at the second sampling point, the mean concentration was  $81.01 \pm 9.74$  mg/kg, while at the third point, value recorded was  $91.91 \pm 9.82$  mg/kg. Chromium concentrations obtained in this study sites indicated the river was highly enriched in Cr. The high mean Cr level detected in the sampling points could be due to agricultural wastes and sewage from the towns located within the catchment area. Chromium and its compounds are known to cause cancer of the lung, nasal cavity and suspected to cause cancer of the stomach and larynx. For Cr concentrations exceeding 37.5 mg/kg, a condition known as allergic dermatitis could also occur (EPA, 1999).

Manganese is known to be a very abundant element widely distributed in the earth's crust. It is used in manufacturing of dry cell batteries, glass, fertilizer and in the leather and textile industries. It is also released through agricultural and building activities and quarry processes (Ziemacki et al., 1989). The mean concentration of Mn at the first sampling point of Oba-Ile River was  $338.51 \pm 16.02$  mg/kg, the second sampling point recorded  $441.66 \pm 17.75$  mg/kg and the third point presented  $387.69 \pm 19.09$  mg/kg. Mean Mn concentrations observed in the sediments were lower than the recommended limit of 20 – 3,000 mg/kg for Mn in sediment (USEPA, 1992). With respect to Mn, the lower concentration obtained may probably be associated to a less quantity of discharge. Manganese is known to be a vital nutrient but exposure to high concentrations may pose adverse effects such as neurologic concentrations, death while at much lower concentrations, mild symptoms such as forgetfulness, anxiety, or insomnia may occur (Malcolm et al., 2012).

The average Cu content in the sediment ranged from  $7.70 \pm 1.67$  mg/kg at the first sampling point to  $13.14 \pm 3.02$  mg/kg at the third sampling point. These values were however, below the recommended value (25 mg/kg) of Cu in sediments (WHO, 2004). Copper finds their way into aquatic ecosystems from various sources such as Cu compounds used in fungicides, algacides, insecticides, wood preservatives, electroplating and azo dye manufacture (Akan et al., 2010). Copper compounds are also used in food additives and copper salts in water supply systems to control biological growths in reservoirs and distribution pipes (Nzeve et al., 2014).

Zinc is an essential nutrient utilized for the function of a large number of metalloenzymes and its deficiency has been associated with dermatitis, anorexia, growth retardation, poor wound healing, impaired immune function, and depressed mental function (Sipter, 2008). For Zn, the average concentrations recorded ranged between  $42.34 \pm 6.02$  mg/kg at the first sampling point and  $58.26 \pm 8.48$  mg/kg at the third sampling point. These values were found to be below the recommended limit of 123 mg/kg (USEPA, 1999). Zinc is a vital metal which plays enzymatic and regulatory roles in biological systems. High level of Zn can cause gastrointestinal problem, loose bowels, pancreatic harm, and feebleness, in both people and animals (Harendra et al., 2017).

The average concentration of Pb ranged from  $2.71 \pm 0.73$  mg/kg at the first sampling point to  $12.85 \pm 4.47$  mg/kg at the second sampling point. These values were nevertheless below the recommended limit of 35 mg/kg (WHO, 2004). Higher concentrations of Pb pose serious threat to aquatic animals, while, in plants, it originally enhance growth, but from a concentration of 5 mg/kg above, this is neutralized by severe growth retardation, discoloration, as well as morphological irregularities (Harendra et al., 2017). From this study, the Pb level might be destructive because of the increased activities around the river.

The mean concentration of Zr was ranged between  $330.72 \pm 21.53$  mg/kg at the first sampling point to  $646.43 \pm 21.23$  mg/kg at the third point. The mean values recorded in our samples were found to be higher than the background, showing a rise in its levels in relation to the Earth's crust. Vanadium mean concentration ranged from  $69.53 \pm 11.18$  mg/kg at the first sampling point to  $102.93 \pm 19.70$  mg/kg at the third point. The values obtained were lower than the

values reported by Gatti *et al.*, 1999 for lake sediment (155 mg/kg). However, the level of vanadium in food is directly dependent on the concentrations available in the soil and the vanadium concentration in water is mainly dependent on the geographical location and ranges. Industrial discharges in application of vanadium such as dyeing, ceramics, ink and catalyst manufacturers contribute to its presence in water supply (Tharakeswar *et al.*, 2014, APHA, 1995). Vanadium in soils at concentrations of 10 mg/kg or more is toxic for terrestrial plants (Arnon, 1956). Therefore, the determination of concentration of vanadium in the sediment of Oba-Ile is very useful in terms of environmental protection.

The mean concentration of Sr presented was  $151.98 \pm 13.06$  mg/kg at the first sampling point, the mean concentration of Sr in the second sampling point was  $111.80 \pm 17.02$  mg/kg and, the mean concentration of Sr at the third sampling point was  $174.21 \pm 11.87$  mg/kg. These values when compared with values obtained by Gatti *et al.*, 1999 (300 mg/kg), was observed to be lower. Metal pollutants and high concentrations are traceable to refuse dumps, farmlands, public gutter and effluents, manufacture, use and disposal of metal commodities, sewage sludges, fishing (Alloway, 1995).

**Table 2** Elemental analysis of the Sediment Samples

		Sep	Nov	Jan.	Feb.	Mar.	April	May	June	Mean
Fe	S 1	23524.3 $\pm 53.51$	9759.90 $\pm 61.49$	8806.70 $\pm 42.35$	50446.6 $\pm 62.72$	21328.3 $\pm 88.72$	37445.1 $\pm 96.08$	7498.80 $\pm 52.49$	29958.9 $\pm 94.86$	23596.0 $\pm 69.03$
	S 2	22708.7 $\pm 94.46$	16470.2 $\pm 77.41$	78512.2 $\pm 94.88$	36844.5 $\pm 44.51$	18212.4 $\pm 66.15$	12249.9 $\pm 46.15$	22151.4 $\pm 43.92$	23166.9 $\pm 62.67$	28789.5 $\pm 66.27$
	S 3	16545.5 $\pm 89.35$	24353.6 $\pm 94.98$	26317.4 $\pm 97.37$	4.30 $\pm 1.01$	14554.1 $\pm 63.54$	16373.1 $\pm 72.77$	45033.0 $\pm 58.09$	34230.8 $\pm 66.09$	22176.4 $\pm 67.90$
Ti	S 1	5895.12 $\pm 53.06$	4758.70 $\pm 44.26$	1087.50 $\pm 17.41$	17280.4 $\pm 51.42$	5438.30 $\pm 41.28$	9434.10 $\pm 60.38$	3104.00 $\pm 33.83$	2379.30 $\pm 33.31$	6172.18 $\pm 41.87$
	S 2	7551.70 $\pm 53.06$	1451.60 $\pm 29.47$	4376.20 $\pm 43.32$	5204.40 $\pm 45.12$	4958.30 $\pm 37.20$	1428.70 $\pm 23.72$	3372.30 $\pm 32.08$	7694.80 $\pm 54.63$	4504.75 $\pm 39.83$
	S 3	5408.15 $\pm 53.54$	5794.30 $\pm 47.51$	2495.20 $\pm 34.43$	5436.70 $\pm 42.74$	4553.50 $\pm 44.51$	4528.20 $\pm 42.35$	3730.20 $\pm 43.02$	7145.90 $\pm 39.54$	4886.52 $\pm 43.46$
Zr	S 1	716.30 $\pm 90.68$	569.60 $\pm 8.76$	194.20 $\pm 10.64$	ND	132.90 $\pm 10.32$	598.30 $\pm 28.07$	336.10 $\pm 14.77$	98.30 $\pm 9.02$	330.72 $\pm 21.53$
	S 2	780.30 $\pm 17.93$	214.00 $\pm 15.55$	1184.20 $\pm 90.49$	37.20 $\pm 7.78$	150.20 $\pm 8.99$	146.80 $\pm 43.51$	420.10 $\pm 27.16$	712.00 $\pm 99.89$	455.60 $\pm 38.91$
	S 3	820.01 $\pm 19.38$	637.90 $\pm 11.84$	574.60 $\pm 10.33$	ND	192.70 $\pm 10.11$	644.30 $\pm 24.13$	587.50 $\pm 18.33$	1714.40 $\pm 75.73$	646.43 $\pm 21.23$
Mn	S 1	293.10 $\pm 21.10$	213.70 $\pm 8.10$	117.30 $\pm 5.48$	533.80 $\pm 22.43$	184.30 $\pm 10.68$	766.60 $\pm 25.14$	181.60 $\pm 13.80$	417.70 $\pm 21.39$	338.51 $\pm 16.02$
	S 2	661.90 $\pm 27.01$	118.50 $\pm 11.40$	526.30 $\pm 19.00$	728.90 $\pm 21.09$	236.80 $\pm 10.01$	193.20 $\pm 13.68$	418.50 $\pm 13.02$	649.20 $\pm 26.75$	441.66 $\pm 17.75$
	S 3	353.00 $\pm 21.89$	325.40 $\pm 20.14$	194.70 $\pm 20.07$	127.30 $\pm 9.54$	417.90 $\pm 18.30$	402.90 $\pm 27.77$	739.50 $\pm 18.65$	540.80 $\pm 16.33$	387.69 $\pm 19.09$
Sr	S 1	271.80 $\pm 46.45$	95.20 $\pm 6.59$	49.30 $\pm 4.79$	289.30 $\pm 10.34$	83.60 $\pm 7.94$	170.90 $\pm 11.28$	201.50 $\pm 8.29$	54.20 $\pm 8.83$	151.98 $\pm 13.06$
	S 2	244.40 $\pm 10.32$	ND	92.60 $\pm 16.50$	14.20 $\pm 3.11$	127.50 $\pm 9.65$	72.10 $\pm 22.87$	153.70 $\pm 31.19$	189.90 $\pm 42.48$	111.80 $\pm 17.02$
	S 3	323.20 $\pm 8.22$	240.20 $\pm 6.97$	ND	144.10 $\pm 8.64$	186.60 $\pm 9.89$	91.90 $\pm 10.5$	175.90 $\pm 17.66$	231.80 $\pm 33.05$	174.21 $\pm 11.87$
V	S 1	43.13 $\pm 24.72$	48.10 $\pm 7.38$	61.3 $\pm 7.89$	1.90 $\pm 0.02$	0	153.90 $\pm 12.32$	85.20 $\pm 9.8$	162.70 $\pm 27.28$	69.53 $\pm 11.18$

	S 2	59.90 ± 9.38	89.50 ± 10.96	191.30 ± 21.44	2.10 ± 0.11	80.50 ± 8.20	34.80 ± 18.29	121.80 ± 16.66	137.10 ± 46.76	89.63 ±16.47
	S 3	82.07 ± 14.80	105.10 ± 23.42	64.40 ± 16.81	31.20 ± 4.98	146.40 ± 9.57	81.30 ± 34.10	190.20 ± 21.59	122.80 ± 32.35	102.93 ±19.70
Cr	S 1	60.06 ± 8.64	23.50 ± 7.66	12.70 ± 2.15	75.60 ± 8.07	20.20 ± 2.51	41.20 ± 9.95	ND	121.30 ± 10.41	44.32 ± 6.17
	S 2	34.40 ± 5.11	38.00 ± 7.24	137.30 ± 9.87	157.00 ± 11.87	38.10 ± 5.72	79.90 ± 9.31	32.60 ± 6.87	87.80 ± 21.91	81.01 ± 9.74
	S 3	108.14 ± 9.63	35.90 ± 7.78	50.60 ± 7.82	228.20 ± 10.02	49.80 ± 8.66	26.10 ± 16.84	67.80 ± 7.45	168.70 ± 10.35	91.91 ± 9.82
Zn	S 1	40.04 ± 7.39	28.10 ± 6.27	20.60 ± 5.14	19.60 ± 2.81	22.50 ± 4.22	87.80 ± 7.76	22.00 ± 3.95	98.10 ± 10.58	42.34 ± 6.02
	S 2	24.70 ± 5.90	27.00 ± 7.28	33.80 ± 6.96	60.70 ± 9.52	31.60 ± 4.72	22.40 ± 10.58	67.50 ± 4.01	95.70 ± 24.04	45.43 ± 9.13
	S 3	26.10 ± 6.39	44.00 ± 8.00	14.00 ± 3.35	32.20 ± 6.73	53.20 ± 6.55	27.00 ± 5.25	128.10 ± 8.50	141.50 ± 23.10	58.26 ± 8.48
Pb	S 1	ND	ND	ND	ND	ND	8.80 ± 2.27	ND	12.90 ± 3.54	2.71 ± 0.73
	S 2	ND	14.90 ± 4.1	22.60 ± 15.32	ND	ND	7.60 ± 4.35	12.00 ± 3.42	12.00 ± 2.07	8.64 ± 3.66
	S 3	16.03 ± 3.98	28.00 ± 4.42	ND	ND	8.00 ± 2.33	6.20 ± 1.19	12.00 ± 3.42	12.00 ± 2.07	10.28 ± 2.18
Cu	S 1	10.01 ± 2.94	5.10 ± 1.21	4.08 ± 1.08	14.40 ± 3.08	2.70 ± 0.09	7.90 ± 1.38	ND	16.70 ± 3.56	7.70 ± 1.67
	S 2	15.90 ± 3.41	6.90 ± 1.47	11.50 ± 1.91	16.00 ± 2.91	6.20 ± 1.21	6.70 ± 1.92	10.10 ± 0.78	19.70 ± 3.58	11.63 ± 2.15
	S 3	9.30 ± 2.60	6.10 ± 1.47	7.80 ± 1.61	26.30 ± 5.12	12.80 ± 2.02	4.00 ± 1.61	25.40 ± 5.14	13.40 ± 4.56	13.14 ± 3.02

ND: Not Detected

### 3.3. Sediment Pollution Evaluation

#### 3.3.1. Contamination Factor ( $C_f$ ) Assessment of Oba-Ile Sediment Samples

Contamination factor for describing the metal contamination level in Oba-Ile River sediment samples is shown in Table 3. The metals presented a low contamination factor ( $LC_f$ ) and moderate contamination factor ( $MC_f$ ) except for Fe and Zr which indicated very high contamination factor ( $VHC_f$ ) and considerable contamination factor ( $CC_f$ ) respectively.

#### 3.3.2. Pollution Assessment According to Geo-Accumulation Index ( $I_{geo}$ )

The calculated geo-accumulation index values are presented in Table 4. All the metals indicated an unpolluted (UP) geo-accumulation index to moderately polluted (MP) geo-accumulation index except Fe which indicated strongly polluted (SP) geo-accumulation index and strongly polluted to extremely polluted (SP-EP) geo-accumulation index.

#### 3.3.3. Pollution Assessment According to Enrichment Factor ( $EF$ )

Enrichment factor for the metals was determined to assess the degree of contamination and the possible anthropogenic impact on the sediments. The metals in all the sampling point presented deficiency to minimal enrichment (DME) except Fe which indicated a moderate enrichment (ME) factor and significant enrichment (SE) factor (Fig.1)

**Table 3** Contamination Factor ( $C_f$ ) Assessment of the Sediment Samples

		Sep.	Nov.	Jan.	Feb.	Mar.	Apr.	May	June
Ti	S1	1.28	1.03	0.24	3.76	1.18	2.05	0.67	0.52
	S2	1.64	0.32	0.95	1.13	1.08	0.31	0.73	1.67
	S3	1.18	1.26	0.54	1.18	0.99	0.98	0.81	1.55
V	S1	0.33	0.37	0.47	0.01	ND	1.18	0.66	1.25
	S2	0.46	0.69	1.47	0.02	0.62	0.27	0.94	1.05
	S3	0.63	0.81	0.50	0.24	1.13	0.63	1.46	0.94
Cr	S1	0.67	0.26	0.14	0.84	0.22	0.46	ND	1.35
	S2	0.38	0.42	1.53	1.74	0.42	0.89	0.36	0.98
	S3	1.20	0.40	0.56	2.54	0.55	0.29	0.75	1.87
Mn	S1	0.34	0.25	0.14	0.63	0.22	0.90	0.21	0.49
	S2	0.78	0.14	0.62	0.86	0.28	0.23	0.49	0.76
	S3	0.42	0.38	0.23	0.15	0.49	0.47	0.87	0.64
Fe	S1	4983.96	2067.78	1865.83	10687.84	4518.71	7933.28	1588.73	6347.22
	S2	4811.17	3489.45	16633.90	7806.04	3858.56	2595.32	4693.09	4908.24
	S3	3505.40	5159.66	5575.72	0.91	3083.50	3468.88	9540.89	7252.29
Cu	S1	0.22	0.11	0.11	0.33	0.06	0.18	ND	0.37
	S2	0.35	0.15	0.26	0.36	0.14	0.15	0.22	0.44
	S3	0.21	0.14	0.17	0.58	0.28	0.09	0.56	0.30
Zn	S1	0.42	0.30	0.22	0.21	0.24	0.92	0.23	1.03
	S2	0.26	0.28	0.36	0.64	0.33	0.24	0.71	1.01
	S3	0.27	0.46	0.15	0.34	0.56	0.28	1.35	3.59
Sr	S1	1.60	0.56	0.29	1.70	0.49	1.01	1.19	0.32
	S2	1.44	ND	0.54	0.08	0.75	0.42	0.90	1.12
	S3	1.90	1.41	ND	0.85	1.10	0.54	1.03	1.36
Zr	S1	4.48	3.56	1.21	ND	0.83	3.74	2.10	0.61
	S2	4.88	1.34	7.40	0.23	0.94	0.92	2.63	4.45
	S3	5.13	3.99	3.59	ND	6.83	4.03	3.67	10.72
Pb	S1	ND	ND	ND	ND	ND	0.44	ND	0.65
	S2	ND	0.75	1.13	ND	ND	0.38	0.32	ND
	S3	0.80	1.40	ND	ND	0.4	0.31	0.60	ND

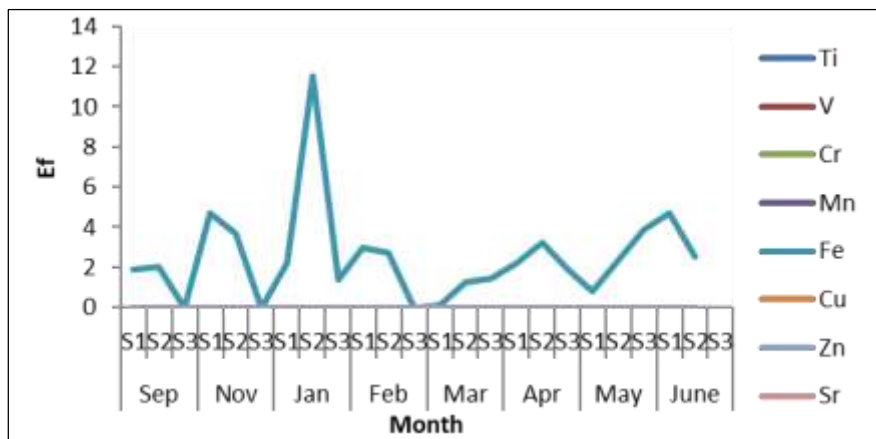
$C_f < 1$  = low contamination factor,  $1 < C_f < 3$  = moderate contamination factor;  $3 < C_f < 6$  = considerable contamination factor,  $C_f > 6$  = very high contamination factor



**Table 4** Geo-Accumulation Index (I-geo) of the Sediment Samples

		Ti	V	Cr	Mn	Fe	Cu	Zn	Sr	Zr	Pb
Sep.	S1	-0.07	-0.66	-0.35	-0.64	3.52	-0.83	-0.55	0.03	0.47	ND
	S2	0.04	-0.51	-0.59	-0.28	3.51	-0.63	-0.76	-0.02	0.51	ND
	S3	-0.11	-0.38	-0.1	-0.56	3.37	-0.86	-0.74	0.1	0.53	-0.27
Nov.	S1	-0.16	-0.61	-0.76	-0.78	3.14	-1.12	-0.71	-0.43	0.38	ND
	S2	-0.68	-0.34	-0.55	-1.03	3.37	-0.99	-0.72	ND	-0.05	-0.3
	S3	-0.08	-0.27	-0.58	-0.59	3.54	-1.04	-0.51	-0.03	0.42	-0.03
Jan.	S1	-0.8	-0.5	-1.03	-1.04	3.09	-1.15	-0.84	-0.71	-0.09	ND
	S2	-0.2	-0.01	0.01	-0.38	4.04	-0.77	-0.62	-0.44	0.69	-0.12
	S3	-0.44	-0.48	-0.43	-0.82	3.57	-0.94	-1.01	ND	0.38	ND
Feb.	S1	0.4	-2.01	-0.25	-0.38	3.85	-0.67	-0.86	0.05	ND	ND
	S2	-0.12	-1.97	0.07	-0.24	3.72	-0.63	-0.37	-1.25	-0.81	ND
	S3	-0.1	-0.8	0.23	-1	-0.22	-0.41	-0.65	-0.25	ND	ND
Mar.	S1	-0.1	ND	-0.82	-0.84	3.48	-1.4	-0.8	-0.48	-0.26	ND
	S2	-0.14	-0.38	-0.55	-0.73	3.41	-1.04	-0.65	-0.3	-0.2	ND
	S3	-0.19	-0.12	-0.43	-0.48	3.31	-0.72	-0.43	-0.14	-0.1	-0.57
Apr.	S1	0.14	-0.1	-0.52	-0.22	3.72	-0.93	-0.21	-0.17	0.4	-0.53
	S2	-0.68	-0.75	-0.23	-0.82	3.24	-1	-0.8	-0.55	-0.21	ND
	S3	-0.18	-0.38	-0.71	-0.5	3.36	-1.23	-0.72	-0.44	0.42	-0.68
May	S1	-0.35	-0.36	ND	-0.85	3.02	ND	-0.82	-0.1	0.15	ND
	S2	-0.31	-0.2	-0.62	-0.48	3.5	-0.82	-0.32	-0.22	0.24	-0.68
	S3	-0.27	-0.01	-0.3	-0.24	3.8	-0.42	-0.05	-0.16	0.39	-0.4
June	S1	-0.46	-0.08	-0.05	-0.48	3.63	-0.61	-0.16	-0.67	-0.39	-0.37
	S2	0.05	-0.15	-0.19	-0.29	3.51	-0.53	-0.17	-0.13	0.48	ND
	S3	0.02	-0.2	0.1	-0.37	3.68	-0.7	0.00	-0.04	0.85	ND

unpolluted (< 0), unpolluted to moderately polluted (0 ≤ I-geo ≤ 1), moderately polluted (1 ≤ I-geo ≤ 2), moderately to strongly polluted (2 ≤ I-geo ≤ 3), strongly polluted (3 ≤ I-geo ≤ 4), strongly to extremely polluted (4 ≤ I-geo ≤ 5) and extremely polluted (I-geo ≥ 5).



**Figure 1** Enrichment Factor (EF) of the Sediment Samples

### 3.4. Data Treatment

#### 3.4.1. Principal Component Analysis

Principal component analysis (PCA) of the results obtained from the Particle Induced X-ray Emission analysis of the sediment was carried out using unscramble X. Figure 2 shows the result which indicates that there were sixteen (16) variables, the first principal component explained 92%, second principal component explained 7% and the other five components took charge of the remaining 1%. From the score plot along the first principal component which explained 92% of the variance, Al had the largest contribution followed by Ti, Mg and K while along the second Si was the major contributor. The group that was close to origin showed the least variation. The loading plot showed two concentric ellipses. The elements (Sr, Fe, Mn, Cu, Cr, Zn, Na, Pb, Zr, V) within the first ellipse contributed little to the variance while the elements (Al, Ti, Mg, K, Si) formed within the second ellipse contributed greatly to the variance. From the plot, along the first principal component, aluminium had the highest contribution to the variances followed by titanium. Along the second principal component which accounted for 7% of the total loading, silicon was the highest contributor.

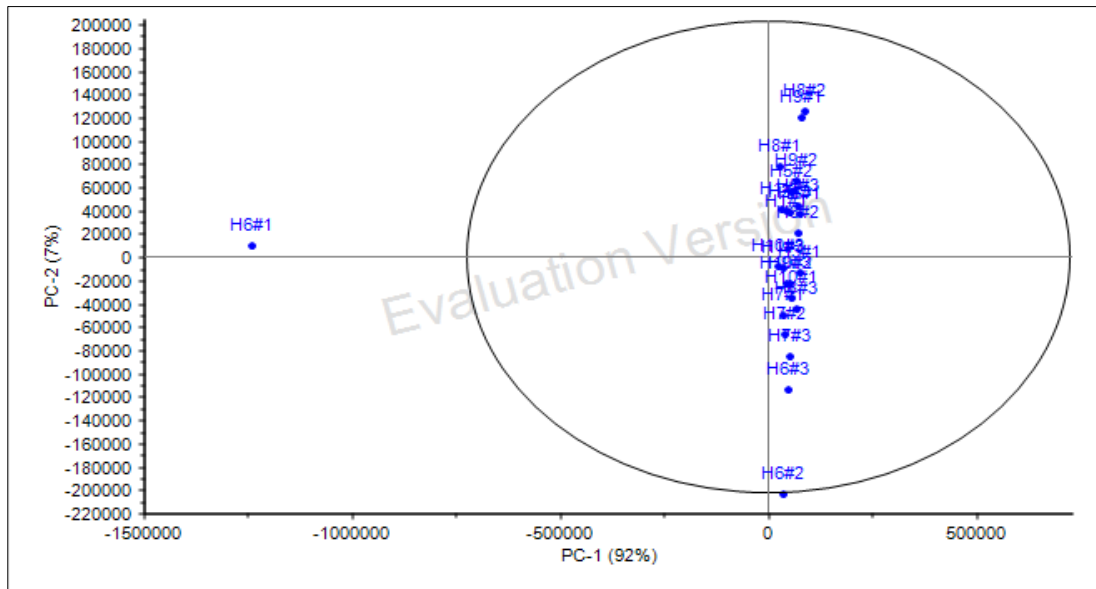


Figure 2a Principal Component Cluster Analysis

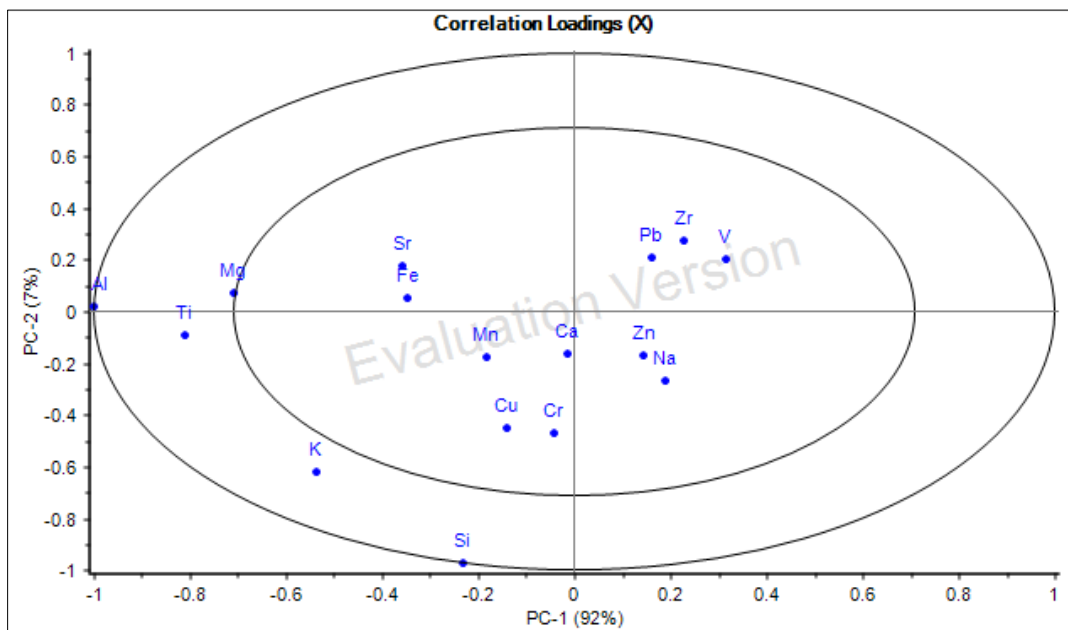


Figure 2b Principal Component Score plot Analysis

#### 4. Conclusion

The occurrence and concentrations of certain heavy metals in the sediment of Oba-Ile River has been established in this study. With the exception of Fe and Zr, the mean concentrations of heavy metals in the sediment samples were within the permissible values. In all the examined sediment samples, Fe and Zr were observed to have high values. This study indicated that certain amounts of untreated waste products were being discharged into Oba-Ile River from various sources many of which could be controlled if the aquatic life must not be unduly jeopardized in the nearest future.

#### Compliance with ethical standards

##### *Disclosure of conflict of interest*

The authors declare no conflict of interest on this work.

#### References

- [1] Adeboye, O. B. and Alatise, O.M. (2008). Surface Water Potential of the River Osun at Apoje Sub-basin Nigeria. *Soil & Water Research*, 3, (2): 74–79.
- [2] Aladesanmi<sup>1</sup>, O.T., Adeniyi, I.F. and Adesiyani, I. M. (2014). Comparative Assessment and Source Identification of Heavy Metals in Selected Fishpond Water, Sediment and Fish Tissues/Organs in Osun State, Nigeria. *J. Health Pollution*, 7: 42-53
- [3] Amisah, S., Adjei-Boateng, D., Obirikorang, K.A. and Quagraine, K.K. (2009). Effects of clam size on heavy metal accumulation in whole soft tissues of *Galatea paradoxa* from the Volta estuary, Ghana. *Int. J. Fish Aquaculture*, 1 (2), 14-21.
- [4] APHA (1995). Standard Methods for the Examination of Water and Wastewater. 19th Edition, American Public Health Association, Washington DC, 3-101.
- [5] Arnon, D.I. (1958). The Role of Micronutrients in Plant Nutrition with Special Reference to Photosynthesis and Nitrogen Assimilation. In: Lamb, C.A., Bentley, O.G. and Beattie, O.G., Eds., Trace Elements, Academic Press, New York, 1-32.
- [6] Belkin, H.E. and Sparck, H.M. (1993). Mercury, arsenic, antimony, and selenium contents of sediment from the Kuskokwim River, Bethel, Alaska, USA. *Geo. vol. 22*, pp.106–110
- [7] Biksham, G., Subramanian, V., Ramanathan, Al. and Van Greiken, R. (1991). Metal Pollution in the Aquatic Environment, *Springer Verlag, New York*, pp. 486.
- [8] Carignan, R. & Tessier, A. (1988). The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Quebec. *Geochim. Cosmochim. Acta* 52: 1179–1188.
- [9] Chen, W., Tan, S. K. & Tay, J.H. (1996). Distribution, fractional composition and release of sediment-bound heavy metals in tropical reservoirs. *Water Air Soil Pollution*, 92: 273-287.
- [10] Copaja, S.V., Díaz, G., Toro, R., Tessada, R., Miranda, P. and Morales, J.R. (2012). Determination of Mining Activity of River Sediments of Three Chilean Basins by Particle Induced X-Ray Emission (PIXE). *J. Chil. Chem. Soc.*, 57, No. 4, 1400-1403
- [11] Förstner, U. and Salomons, W. (1980). Trace metal analysis on polluted sediments. *Environmental Technology Letters*, vol. 1, issue 11, pp. 494-505
- [12] Gatti, L.V., Mozeto, A.A. and Artaxo, P. (1999). Trace elements in lake sediments measured by the PIXE technique. *Nuclear Instruments and Methods in Physics Research B*, 150
- [13] Guan, J., Jia, W., Pan, H., Yang, C., Qu, J., Lu, N., and Yuan, X. (2018). Heavy metals in Yinma River sediment in a major Phaeozems zone, Northeast China: Distribution, chemical fraction, contamination assessment and source apportionment. *Scientific reports*, vol.8 pp.12231.
- [14] Harendra, S., Ruby, P., Sudhir, K. S. and Shukla, D. N. (2017). Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India. *Appl. Water Sci.*, vol. 7, pp. 4133–4149
- [15] Iloeje, N.P. (1982). A New Geography of Nigeria. Fifth Edition. Ikeja: Longman Nigeria Plc.

- [16] Islam, M. A., Romic, M. A., and Romi ´ C, M. (2017). Trace Metals Accumulation in Soil Irrigated with Polluted Water and Assessment of Human Health Risk from Vegetable Consumption in Bangladesh. *Environ. Geochem. Health*, 40, 59–85.
- [17] Kane, S., Lazo, P. and A. Vlora, (2012). Assessment of heavy metals in some dumps of copper mining and plants in Mirdita Area, Albania,” in *Proceedings of the 5th International Scientific Conference on Water, Climate and Environment*, Eds., Ohrid, Macedonia
- [18] MacFarlane, G.R. and Burchette, M.D. (2000). Cellular distribution of copper, lead and zinc in the grey mangrove, Avicienna marina (Forsk) Vierh. *Aquatic Bot.*, 23, 68(1):45-59.
- [19] Malcolm,W., Daniel, G. T., Nickolette, R., Jewell, C., Charleton,, C., Peter, R. M., Joan D G., Kimberly, Z. and Mario, C.(2012). Toxicological Profile for Manganese, [Agency for Toxic Substances and Disease Registry \(US\)](#)
- [20] Mertz, W. (1987). Trace Elements in Human and Animal Nutrition. Science Direct, vol. 2, 5<sup>th</sup> Edition London: Academic Press.
- [21] Oladebeye, A.O. (2017). Assessment of Heavy Metals in Nigerian Vegetables and Soils in Owo and Edo Axes Using X-Ray Fluorescence (XRF) Technique. Department of Chemical Sciences, College of Natural and Applied Sciences Achievers University, Owo, Ondo State (B.Sc Thesis)
- [22] Prabu, P. C. (2009). Impact of heavy metal contamination of Akaki river of Ethiopia on soil and metal toxicity on cultivated vegetable crops,” *Electronic Journal of Environmental, Agricultural and Food Chemistry*, vol. 8, no. 9, pp. 818–827.
- [23] Shanbehzadeh, S., Dastjerdi, M.V., Hassanzadeh, A., and Kiyanzadeh, T. (2014). Heavy Metals in Water and Sediment: A Case Study of Tembi River. *Hindawi Publishing Corporation Journal of Environmental and Public Health*, vol. 2014, 5 pages
- [24] Sigg, L., Sturm, M. & Kistler, D. (1987). Vertical transport of heavy metals by settling particles in Lake Zurich. *Limnol. Oceanogr.* 32, 112–130.
- [25] Tharakeswar, Y., Kalyan, Y. and Ramakrishna, N. G. (2014). Determination and Quantification of Vanadium(V) in Environmental Samples Using Chemically Modified Chitosan Sorbent. *Journal of Encapsulation and Adsorption Sciences*, vol. 4, pp.53-61
- [26] Turekian, K.K., and Wedepohl, K.H. (1961). "Distribution of the elements in some major units of the earth's crust". *Geol. Soc. Am.*, 72, 175-192.
- [27] USEPA (1999). National recommended water quality criteria-correction-United State Environmental Protection Agency EPA 822-Z99-001, pp.25
- [28] World Health Organization (2004). Guidelines for drinking water quality: Recommendations 3rd Edn. World Health Organization, Geneva, pp. 516.