

Geochemistry of terrigenous sediments in surface water from ore and okitipupa southwest, Nigeria

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ABSTRACT

Elements pollution in water bodies and sediment have becoming increasingly a catholic focus. The knowledge of hydrogeochemical processes affecting water quality is necessary in order to assess the potential changes that occur and identify possible abatement strategy. Fifteen elements were analyzed in the sediment using AMPTEX (R), X-ray fluorescence method. The highest average concentration was recorded for Fe with an average value of 19650 ppm and the lowest average concentration was recorded for Cu with an average value of 10.86 ppm. The average concentration values recorded in this study fell with the purview of the available regulatory limits. The highest enrichment value and geo-accumulation value was recorded for Se and the highest pollution index was recorded for Fe, Mn, K, and Ca correlated well with Ni. The Enrichment values when Titanium (Ti) was used as reference element Se > Zr > As > Zn > V > Ni > Fe > Mn > Cu ≥ Sr > Cr > Rb > K > Ca. For Iron Se > Zr > As > Zn > V > Ni > Ti > Mn > Cu ≥ Sr > Cr > Rb > K > Ca. For Manganese (Mn) was Se > Zr > As > Zn > V > Ni > Ti > Fe > Cu ≥ Sr > Cr > Rb > K > Ca. For Copper Se > Zr > As > Zn > V > Ni > Ti > Fe > Mn > Sr > Cr > Rb > K > Ca.

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Introduction

Sediments have been described by many authors as the reservoir of numerous chemicals and also a pivotal influence in water contamination (Mil-Homens, *et al.*, 2013; Yu *et al.*, 2001; Sakan *et al.*, 2009; Wepener, and Vermeulen, 2005; Mil-Homens *et al.*, 2007; Shakeri and Moore, 2010; Yang *et al.*, 2009). The upsurge of industrialization and population have engendered harmful chemicals and elemental pollutants that are always injected into the soils and sediments through numerous anthropogenic activities which preclude: atmospheric deposition, industrialization, agricultural activities and riparian anthropogenic activities, where chemicals and metals are produced. Trace metals are often housed by soil which are repeatedly leached into the environment (Peizhong *et al.*, 2015; Uwumarongie *et al.*, 2008; Banat *et al.*, 2005; Rafael *et al.*, 2016), materials beneath surface water serve as barometer to survey the pollutant level in aquatic ecosystem (Yang *et al.*, 2009; Safaa,

2015; Pekey *et al.*, 2004). The chemistry of aquatic ecosystem towards the level of pollutants varies, where the amount and nature of pollutant in the seabed will quantify the degree of pollution (Edward *et al.*, 2013; Abida *et al.*, 2009; Verep *et al.*, 2012; Marchand *et al.*, 2016). Therefore, sediment quality data provide essential information for evaluating ambient environmental quality conditions in aquatic ecosystem. Elements from incoming tidal water and freshwater sources are rapidly removed from the water body and are deposited onto the sediments (Wei *et al.*, 2015; Guzman and Garcia, 2002). The toxicity and mobility of the metals in sediments vary among different chemical forms. Sediments consist of various forms of insidious trace elements which move from one location to another as a result of their physicochemical situation (Agnieszka *et al.*, 2012; Varol and Sen, 2012; Cuong and Obbard, 2006; Yu *et al.*, 2010; Burton, 1991).

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Recently, plethora of researchers have placed emphasis on the pitfalls of elements in the environment (Verep *et al.*, 2012; Marchand *et al.*, 2016; Mouvet *et al.*, 1993; Erno and Gyula, 2003) due to their deleterious effect and capacity to concentrate in the food chain (Safaa, 2015; Agnieszka *et al.*, 2012; Adams *et al.*, 1992; Nsenga *et al.*, 2016). A lot of elements have been fingered as essential elements to the health of both human beings and organisms at minute quantities but harmful at higher quantities. Just to mention, a few, lead, cadmium, and arsenic had been fingered as detrimental elements in the environment and are mirrored among the most decimating substances according to US Environmental Protection Agency (EPA, 1999). Contamination of ecosystem by trace elements is a burning issue because metal remains in the bottom sediments for decades and remain non-biodegradable which are detrimental to living materials, when the standard of the trace elements is violated (Eduardo *et al.* 2015; Guangming *et al.*, 2016). Heavy metal concentration in sediment and aquatic organism had been reported by Davies *et al.* (2006). Furthermore, sediments have high physical-chemical stability and their characteristics usually represent the average condition of the system, often being representative of the average water quality (Turkemen, *et al.*, 2005; Forstner, 1981). The indiscriminate disposal of industrial, domestic and agricultural wastewater without treatment to comply with the safe and standard disposal regulatory limit on agricultural lands, into rivers, stream and lakes are the obvious pollution type that are of serious concern due to the negative effect of elements in water and soil (Hong *et al.*, 2014). The pH is a pivotal barometer for controlling heavy metal transfer behavior in sediment. Decrease in pH decreases the adsorption abilities and bioavailability of the metals, and then increases the mobility of heavy metal in the sediment and water bodies (Gundersen and Steinnes, 2003). The influences of other factors, such as organic compounds are more is also sacrosanct. In sediment, there exists a limit pH controlling heavy metal mobility. And the trace metal would be released only as they reaching such pH value. The limit pH differs from one metal to another (Vale'rie, and Jiska, 2004). The objectives of this study are: to provide information on the concentrations and distribution of selected elements sediments from Ore and Okitipupa using X-ray fluorescence, to compute the enrichment factor, Geo-accumulation index and a contamination/pollution index of elements sediments of the creek under study.

Materials and method

The study area

Ore lies between Latitude 6.7615°N Longitude 4.86204°E and Latitude 6.7373°N Longitude 4.8806°E. It is the headquarters of Odigbo Local Government Area of Ondo State, Nigeria. It has an area of 1,818 km² and a population of

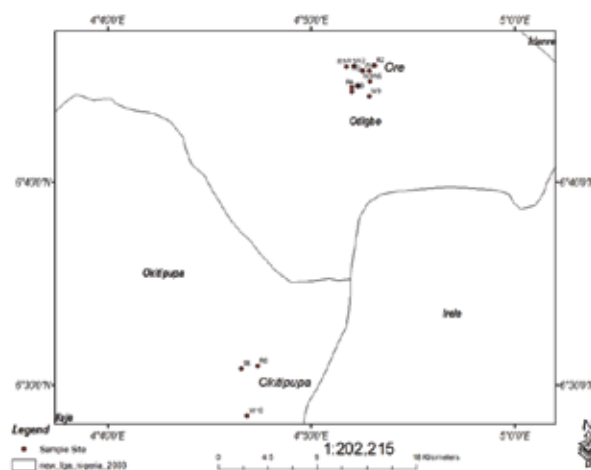


Fig. 1. Sampling area in Ore and Okitipupa

230,351 at 2006 census. It is situated along Lagos Benin express way where travelers from the South-South and South Eastern part of the country used to stop and take a rest after travelling for hours. Okitipupa town lies between Latitude 5.125°N Longitude 4.008°E and Latitude 8.042°N Longitude 6.011°E. It is the headquarters of Okitipupa local government of Ondo State, Nigeria. It has an area of 63 square kilometers and a population of 233,565 at 2006 census. It is bounded in the North by Odigbo Local government, East by Irele Local government, and South by Ilaje Ese Odo Local government and West by Ogun State.

Sediment sample preparation and measurement using X-ray Florescence

Sediment samples were collected in triplicate from ore and Okitipupa using a stainless steel dredge. The sample was kept in a polyethylene bags well labeled and sealed. Thereafter, the sediments were dried in an oven at 50°C for 2 days and sieved through a 20- μ m sieve. It was crushed in an agate mortar into fine powder. A CARVER model manual pelletizing machine was used to form a pellet at a pressure of 6-8 Torr. The pelletized sample was inserted into the sample holder of the XRF system and was bombarded by X-ray fluorescence spectrometer with a silver (Ag) anode at a voltage of 25kV and current of 50 μ A for 1000 counts or approximately 18 minutes in an external chamber set up. Analysis were carried out at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria.

Data analysis

Data generated were subjected to statistical analysis Pearson correlation, enrichment factor method, toxicity risk, geo-accumulation, and pollution index. During this study the

enrichment factor was computed using Iron, Manganese and Chromium as reference element. In previous study, Aluminum, Iron, Chromium and Manganese were used as reference element (Loska *et al.*, 1997; Gary *et al.*, 1995). The reference crustal ratio was taken from Wedepohl (Wedepohl, 1961). An enrichment factor less than one suggests no enrichment, enrichment factor less than three suggests minor enrichment, three to ten is moderate enrichment, ten to twenty-five severe enrichment, twenty-five to fifty is severely enrichment and greater than fifty is extremely enrichment (Chen *et al.*, 2007).

The enrichment factor was computed using this formula:

$$\frac{\left(\frac{Q_1}{Q_{Fe}}\right)_{sediment}}{\left(\frac{Q_1}{Q_{Fe}}\right)_{crust}}$$

where the concentration of the element is considered in the sediment of the crust and is the concentration of the reference element (Fe). The quality criteria are very useful as it allows to take an easy decision of the sediment toxicity risk in a short time. The measured metal concentrations (C_{mi}) are used to determine Sediment Quality (Q_{Si}) w.r.t to permissible limit in sediment quality criteria (SQ_{Ci}) prescribed by CCME (CCME, 2001), and then is used to calculate the mean quality in sediment (Q_{Sm}). Q_{Sm}<0.1: toxicity risk is negligible. 0.1<Q_{Sm}<0.5: risk is low, but the non-hazardous of sediments must be checked. Q_{Sm}>0.5: risk is non-negligible and its possible hazard for aquatic life.

$$Q_{si} = \frac{C_{mi}}{SQ_{Ci}}$$

$$Q_{sm} = \sum Q_{st}/n$$

Geo-accumulation Index (I_{geo})

$$I_{geo} = \log_2 \left(C_m / 1.5B_m \right)$$

- Grade 0: I-geo ≤ 0: unpolluted
- Grade 1: I-geo ≤ 1: slightly polluted
- Grade 2: I-geo ≤ 2: moderately polluted
- Grade 3: I-geo ≤ 3: moderately severely polluted
- Grade 4: I-geo ≤ 4: severely polluted
- Grade 5: I-geo ≤ 5: severely extremely polluted
- Grade 6: I-geo > 5: extremely polluted

Pollution index (PI) is a simple, comparative tools for assessing the level of heavy metal pollution. The pollution

load index (PLI) is classified as; (PLI <1), moderate (PLI < 2), heavy (PLI < 3), or (PLI >3) the pollution extremely heavy (Mashiatullah *et al.*, 2013; Muller, 1969).

Results and discussion

Table I shows the minimum, maximum and mean of pH, conductivity and heavy metal concentrations, Table II shows the Duncan Multiple Range Test of metals, Table III shows the Enrichment factor using Titanium, Iron, Manganese and Copper as reference element, geo-accumulation sediment quality and pollution index while Table IV shows the Pearson correlation of trace metal in the sediment. The pH ranged between 8.1–11.5 with the mean value of 9.36±1.02 while the conductivity ranged between 198.3–1382 μSCm⁻¹ with a mean of 1023±369 μSCm⁻¹ (Table I). The alkaline pH and high conductivity indicate the presence of charged ion. K concentration in sediment samples ranged from 1550–3220

Table I. Range of pH, conductivity (μSCm⁻¹) and trace elements (ppm) in sediment samples

	Min	Max	Mean±SD
pH	8.1	11.5	9.36±1.02
Conductivity	198.3	1382	1023±369
K	1550	3200	2140±0.05
Ca	630	1270	1020±0.024
Ti	1002	3220	2210±0.045
Mn	160.9	491	309±88.5
Fe	12900	28100	19650±0.44
Ni	26.1	128	59.07±31.3
Zn	50	141	111.8±29.3
Cr	5	34	18.8±10.6
As	8.2	32	15.9±6.92
Rb	19.2	32.4	26.1±4.38
Sr	49	105	71.9±16.6
Se	10.9	35	27.3±7.64
Zr	122	635.2	400±147
V	0.001	223	135.5±65.2
Cu	5	18.01	10.86±4.82

ppm with the mean value of 2140 ± 0.05 ppm while the Ca concentration ranged from 630 – 1270 ppm with the mean value of 1020 ± 0.024 ppm. Higher concentration values of K and Ca were reported in previous study (Edward *et al.*, 2013; Akpan and Thompson, 2013; Ediagbonya, 2016). Ti concentration ranged from 1002 – 3220 ppm with a mean concentration of 2210 ± 0.045 ppm while Mn concentration ranged from 160.9 – 491 ppm and the mean was 309 ± 88.9 ppm. The Fe concentration ranged from 12900 – 28100 ppm and this value 19650 ± 0.44 ppm was recorded as the mean while Ni concentration ranged from 50 – 141 ppm whose mean value was 59.07 ± 31.3 ppm. The concentration of Ni obtained in this study was higher than the Hungarian regulatory limit for Ni in the sediment (40 ppm) (Hungarian Ministry for Environment, 2000; 1999) and higher than (12.4 – 30.9 ppm) reported in sediments samples collected from Kumasi area of Ghana (Kodom *et al.*, 2012).

Zn concentration ranged from 0.1002–0.322 ppm with an average value of 111.8 ± 29.3 ppm (Davies *et al.*, 2006) reported Zn concentration of 148.8 ppm in sediment samples of Calabar, Southeast Nigeria. Cr concentration ranged from 5 – 34 ppm while of 18.8 ± 10.6 ppm was recorded as the mean. The results of Cr from the present study is similar to results obtained in west Guangdong coastal region of China (Guangming *et al.*, 2016). Arsenic (As) concentration ranged

from 8.2 – 32 ppm (15.9 ± 6.92 ppm) while Rb concentration ranged from 19.2 – 32.4 ppm (26.1 ± 4.38 ppm). Sr concentration ranged from 49 – 105 ppm (71.9 ± 16.6 ppm) while Se concentration ranged from 10.9 – 35 ppm and the mean value was 27.3 ± 7.64 ppm. Zr concentration ranged from 122 – 635.2 ppm (400 ± 147 ppm) while V concentration ranged from 0.001 – 223 ppm (135.5 ± 65.2 ppm). Cu concentration ranged from 5 – 18.01 ppm with the mean value of 10.86 ± 4.82 ppm.

There was a great variation in the concentration of all the elements from sediments collected from Ore ($S_1 - S_4$) and Okitipupa ($S_5 - S_7$) (Table II). Significantly high value ($P \leq 0.05$) of K (0.292 ± 0.023 ppm), Mn (482 ± 5.21 ppm), Fe (2.49 ± 0.293 ppm), Ni (67.7 ± 1.185 ppm), Cr (33.7 ± 0.285 ppm), As (31.57 ± 0.296 ppm), Sr (102.7 ± 1.48 ppm), and V (220 ± 1.73 ppm) were recorded in sediment samples collected from Ore. However, significantly high value ($P < 0.05$) of Ca (0.126 ± 0.00 ppm), Ti (0.307 ± 0.007 ppm), Zn (140.7 ± 0.145 ppm), Rb (31.5 ± 0.742 ppm), Se (33.7 ± 0.44 ppm) and Zr (627 ± 3.99 ppm) were recorded in Okitipupa. Means with the same subscript down the column are not significantly different according to Duncan's Multiple Range Test ($P \leq 0.05$).

The sources of trace elements in the environment can be guessed using Enrichment factors (EFs) (Reimann and de

Table II. Duncan Multiple Range Test of trace elements in sediment samples (n=3)

	K	Ca	Ti	Mn	Fe	Ni	Zn	Cr
S1	$2830 \pm 0.004d$	$912 \pm 0.002c$	$1630 \pm 0.0315a$	$329 \pm 10.3e$	$24900 \pm 0.293d$	$48.33 \pm 0.882c$	$52 \pm 1.527a$	$28.7 \pm 0.882e$
S2	$2920 \pm 0.023d$	$727 \pm 0.003b$	$1980 \pm 0.009ab$	$482 \pm 5.21f$	$23200 \pm 0.0115cd$	$29 \pm 1.13b$	$86 \pm 1.527b$	$6.467 \pm 0.291a$
S3	$1680 \pm 0.0001ab$	$1150 \pm 0.001d$	$2160 \pm 0.001bc$	$289.7 \pm 0.907c$	$14890 \pm 0.004a$	$67.7 \pm 1.185f$	$126.3 \pm 2.33d$	$26.4 \pm 0.722d$
S4	$1950 \pm 0.002bc$	$1220 \pm 0.00de$	$2510 \pm 0.00c$	$318.1 \pm 0.968de$	$13110 \pm 0.0121a$	$55.7 \pm 0.371d$	$134.7 \pm 0.882e$	$33.7 \pm 0.285f$
S5	$1570 \pm 0.001a$	$1260 \pm 0.00e$	$3070 \pm 0.007d$	$266.7 \pm 0.318b$	$18540 \pm 0.048b$	$58.8 \pm 0.24e$	$122.6 \pm 0.306cd$	$21.3 \pm 0.285c$
S6	$2210 \pm 0.003c$	$650 \pm 0.001a$	$1940 \pm 0.001ab$	$313 \pm 1.155d$	$22860 \pm 0.007cd$	$26.4 \pm 0.173a$	$120 \pm 0.24c$	$6.67 \pm 0.882a$
S7	$1790 \pm 0.011ab$	$1210 \pm 0.00de$	$2128 \pm 0.002bc$	$161.3 \pm 0.351a$	$19950 \pm 0.001bc$	$127 \pm 0.291g$	$140.7 \pm 0.145f$	$8.6 \pm 0.252b$

	As	Rb	Sr	Se	Zr	V	Cu
S1(n=3)	$8.53 \pm 0.202a$	$27.26 \pm 0.371c$	$76 \pm 2.65d$	$31.3 \pm 1.86cd$	$399.7 \pm 25.8c$	$197.6 \pm 3.38e$	$9.47 \pm 0.318c$
S2(n=3)	$11 \pm 0.577b$	$20.1 \pm 0.521a$	$102.7 \pm 1.48f$	$11.3 \pm 0.338a$	$388.3 \pm 3.84c$	$141.3 \pm 0.882d$	$6.84 \pm 0.145b$
S3(n=3)	$17.4 \pm 0.306e$	$24.5 \pm 0.26b$	$54.7 \pm 0.351b$	$21.3 \pm 0.29b$	$505.3 \pm 3.844e$	$220 \pm 1.73f$	$5.23 \pm 0.1201a$
S4(n=3)	$31.57 \pm 0.296f$	$29.6 \pm 0.296d$	$49.4 \pm 0.29a$	$30.1 \pm 0.208c$	$122.5 \pm 0.288a$	$0.0117 \pm 0.006a$	$17.7 \pm 0.252f$
S5(n=3)	$15.36 \pm 0.233d$	$20.03 \pm 0.23a$	$74.6 \pm 0.153d$	$33.7 \pm 0.317d$	$446.5 \pm 2.42d$	$118.5 \pm 0.265b$	$17.97 \pm 0.035f$
S6(n=3)	$14.7 \pm 0.296d$	$29.8 \pm 0.38d$	$63.8 \pm 0.6c$	$30.27 \pm 0.218c$	$311.7 \pm 1.202b$	$132.3 \pm 0.651c$	$7.1 \pm 0.115b$
S7(n=3)	$13.4 \pm 0.218c$	$31.5 \pm 0.742e$	$81.9 \pm 0.585e$	$33.7 \pm 0.44d$	$627 \pm 3.99f$	$133.3 \pm 0.458c$	$11.7 \pm 0.436e$

Caritat, 2000; Blaser *et al.*, 2000). Few studies had in water (Loska *et al.*, 1997; Wedephol, 1961; Birth, 2003). Scandium (Sc) and Titanium (Ti) Aluminum (Al), Zirconium (Zr) and Iron (Fe) are often used in computing enrichment factor (Ediagbonya, 2016; Hosseini *et al.*, 2015) while some studies had used Manganese (Mn) and Chromium (Cr) for the computation of enrichment factor (Loska *et al.*, 1997, Valerie, and Jiska, 2004; Zhang *et al.*, 2003). From the enrichment values as shown in Table III, it was observed that there was a steady increase in the enrichment values from Ti,

decreasing trend of; Se> Zr> As> Zn> V> Ni> Ti> Mn> Cu \geq Sr> Cr> Rb> K> Ca.

When Manganese (Mn) was used as reference element in the sediment sample had a decreasing trend of; Se>Zr>As>Zn>V>Ni>Ti>Fe>Cu \geq Sr>Cr>Rb>K>Ca. Finally, when Copper was used as reference element in the sediment sample had a decreasing trend of; Se >Zr>As>Zn>V>Ni>Ti>Fe>Mn >Sr>Cr>Rb>K>Ca. The decreasing pattern of the enrichment value from Selenium (Se) to Calcium (Ca) were similar when the different

Table III. Enrichment factor using Titanium, Iron, Manganese and Copper as reference element, geo-accumulation and pollution index

Metals	Mean	Ti	Fe	Mn	Cu	Igeo	Qs	Pollution Index	Qsm
K	2139	0.17	0.19	0.22	0.33	0.00			
Ca	1020	0.10	0.11	0.13	0.19	0.00			
Ti	2120	1.00	1.11	1.27	1.91	0.00			
Mn	309	0.79	0.87	1.00	1.51	0.00	0.761	0.71	0.109
Fe	19650	0.90	1.00	1.15	1.73	0.00	0.9825	3.93	0.140
Ni	59.07	1.88	2.09	2.39	3.60	0.02	3.69	1.69	0.528
Zn	111.8	2.55	2.83	3.24	4.88	0.02	0.909	0.80	0.13
Cr	18.8	0.45	0.50	0.57	0.87	0.01	0.504	0.19	0.072
As	15.9	2.65	2.94	3.36	5.07	0.08	2.695	0.55	0.385
Rb	26.1	0.40	0.45	0.51	0.77	0.01			
Sr	71.9	0.52	0.58	0.66	0.99	0.00			
Se	27.3	98.73	109.29	125.16	188.54	1.93			
Zr	400	5.42	6.01	6.88	10.36	0.01			
V	135.5	2.26	2.50	2.87	4.32	0.01			
Cu	10.86	0.52	0.58	0.66	1.00	0.02	0.304	0.30	0.0435

Fe, Mn to Cu when these elements were used as a reference element. This steady increase of enrichment values from Ti to Cu could be adduced to the speed in which these elements are being emitted by human activities. Enrichment values when Titanium (Ti) was used as reference element in the sediment sample had a decreasing trend of; Se> Zr> As> Zn> V> Ni> Fe> Mn> Cu \geq Sr> Cr> Rb> K> Ca. Iron (Fe) gave a

reference elements were used. From the result as shown in Table III, Selenium (Se) was extremely and highly enriched while Zirconium (Zr), Arsenic (As), Vanadium (V) and Zinc are moderately enriched. Other elements such as Calcium (Ca), Potassium (K), Rhodium (Rb), Chromium (Cr), Strontium (Sr), Manganese (Mn), Titanium (Ti) and Nickel (Ni) were not enriched (Ghrefat *et al.*, 2011). Enrichment

Table IV. Pearson Correlation of trace elements in sediment samples

	K	Ca	Ti	Mn	Fe	Ni	Zn	Cr	As	Rb	Sr	Se	Zr	V	Cu
K	1														
Ca	-.722**	1													
Ti	-.606**	.606**	1												
Mn	.714**	-.638**	-.247	1											
Fe	.667**	-.691**	-.388	.294	1										
Ni	-.522*	.680**	.148	-.816**	-.273	1									
Zn	-.812**	.524*	.540*	-.574**	-.665**	.493*	1								
Cr	-.199	.557**	.212	-.089	-.520*	-.008	-.086	1							
As	-.442*	.477*	.453*	-.117	-.800**	.042	.606**	.531*	1						
Rb	-.112	.042	-.325	-.544*	-.069	.411	.296	.038	.279	1					
Sr	.543*	-.381	-.235	.374	.628**	-.021	-.449*	.640**	-.429	.708**	1				
Se	-.467*	.445*	.210	-.791**	-.131	.424	.269	.261	.163	.554**	-.408	1			
Zr	-.219	.200	-.064	-.470*	.239	.640**	.060	-.397	-.645**	-.100	.414	.024	1		
V	.185	-.251	-.457*	.012	.414	.021	-.449*	-.166	-.779**	-.245	.265	-.242	.674**	1	
Cu	-.422	.655**	.713**	-.332	-.392	.230	.335	.420	.549**	.028	-.224	.576**	-.320	-.738**	1

*Correlation is significant at the 0.05 level (2 -tailed)

**. Correlation is significant at the 0.01 level (2 -tailed)

values from 0.5-1.5 is an indication of crustal material and natural origin while enrichment value greater than or equal to 1.5 is an indication of anthropogenic source (Ghrefat *et al.*, 2011). The highest Geo-accumulation value was recorded in Selenium (Se) followed by Arsenic (As). Calcium (Ca), Potassium (K), Iron (Fe), Strontium (Sr), Manganese (Mn), and Titanium (Ti) were unpolluted. Zirconium (Zr), Arsenic (As), Copper (Cu), Zinc (Zn), Vanadium (V), Rhodium (Rb), Nickel (Ni), and Chromium (Cr) were slightly polluted and Selenium (Se) was moderately contaminated. The Geo-accumulation values show similar pattern with the enrichment values, this observation is in agreement with a study done by Chen *et al.* (2007). The highest pollution index value as shown in Table III was recorded in Iron (Fe) followed by Nickel (Ni). The lowest pollution index value was recorded in Chromium (Cr). From the pollution index, Zinc (Zn), Manganese (Mn), Arsenic (As), Copper (Cu) and Chromium (Cr) were moderately polluted while Nickel (Ni) was heavily polluted and Iron (Fe) was extremely polluted. Table III also shows the toxicity risk values of the sediment, the interim sediment guideline and the Ontario provincial sediment quality guideline were used for the computation for the toxicity risk. The toxicity risk for Chromium (Cr) and Copper (Cu) were negligible, Arsenic (As), Iron (Fe), Zinc (Zn) and Manganese (Mn) shown low risk but non-hazardous while Nickel (Ni) shown risk possibility that be insidious to aquatic life. From Table IV, there was a strong positive and negative relationship between the trace metals a significant level of 0.05 and 0.01.

At significant level of $P < 0.01$, Positive correlation was recorded between K, Mn and Fe while at significant level of $P < 0.05$, there was a positive correlation between K and Sr. Zn and Ti were positively correlated at significant level of $P < 0.05$. There was a positive correlation between As and Zn (0.01 level) and also between As and Cr (0.05 level). Sr and Fe were positively correlated (0.01 level), Se and Rb were positively correlated (0.01 level). There was also a positive correlation between Zr, Ni and V (0.01 level). Finally, there was a positive relationship between Ca, Ni, Ti Cr (0.01 level) and Zn (0.05 level). Negative relationship was recorded between Ca, Mn and Fe (0.01 level) A significant negative relationship was showed between Ni and Mn (0.05 level) and between Ni and K (0.01 level). There was a significant negative correlation between Zn, K, Mn and Fe (0.01 level). Fe correlated well with Zn (0.01 level) and Cr (0.05 level). Mn correlated negatively with Rb (0.01 level) and Se (0.05 level). As correlated negatively well with Fe, Cr, Sr, Zr and V (0.01 level) (Table IV).

Those elements that are positively correlated means that their concentration increases in the same manner which may be as

a result of originating from the same source. However, those that are negatively correlated, show inverse concentration relationship which may be attributed to different source of origin. These correlations obtained are not in agreement with Mashiattullah *et al.*, (2013).

Conclusion

The present study shows geochemical distribution of elements in sediment samples from the area varies widely. The highest enrichment value and geo-accumulation value was recorded in Se. The activities in these areas should be checked in order to forestall the vulnerability of the living things as a result of riparian heavy metal contamination. From the toxicity risk computation, Nickel (Ni) showed a possible risk in the sediment which was further corroborated by the pollution index computation.

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