Geochemical Evaluation of Heavy Metal Impact on the Stream Sediments of Ajakanga Area, Ibadan, Southwestern Nigeria

ROLAND ANTHONY ISIBOR[1], JOSEPH AYOFE ADEROGBIN[2], ODUNAYO JUMOKE OYEBODE[3]
[1, 2, 3] Department of Earth Sciences, Faculty of Natural Sciences, Ajayi Crowther University, Oyo, Oyo state, Nigeria

Abstract- Ten sediment samples were collected from Ajakanga stream in Ibadan in order to determine concentration, spatial distribution and assess the pollution status of the heavy metals, Zn, Cr, Co, Pb, Cu and Ni.The samples were analyzed using the Inductively Couple Plasma Mass Spectrometer. The mean concentrations are 66.750ppm for Zn, 37.833ppm for Cr, 23.083ppm for Co, 18.750ppm for Pb, 14.583ppm for Cu and 12.000ppm for Ni. To assess pollution in the sediments, sediment quality guideline were applied. The mean concentrations of Pb, Cu, Ni and Zn were below the USEPA guideline, while that for Cr exceeded that of the guideline. Based on evaluation using geoaccumulation index, all the metals have low to moderate contamination, while the enrichment factor showed that the entire content of Ni and Cr in the stream sediments were derived from natural sources.Pb, Zn, Cu and Co concentrations in the sediments have anthropogenic input.Ni and Cr are deficient to minimally enriched in the sediments. Cu and Co are moderately enriched, while Pb and Zn are significantly enriched.The contamination factor for Cu, Ni, Pb, Co and Cr is low, while that of Zn is moderate. Contamination degree calculated for the stream sediments also indicated a low degree of contamination. The ecological risk index and potential ecological risk index is low,indicating that the risk of potential contamination of Ajakanga stream sediments with the current concentration of Cu, Ni, Pb, Zn, Co and Cr is low.

Indexed Terms- Stream sediment, Pollution, Ajakanga, Geoaccumulation index, Enrichment factor, Ecological risk index

I. INTRODUCTION

Sediments are considered to be the most important sinks for the heavy metals in the aquatic environment [1]. As a result these metals commonly have higher concentration in the sediments than in the water column [2, 3, 4, 5, 6].

These metals can be derived from both natural and anthropogenic sources. Natural processes include chemical leaching of bedrocks, stream and river basins, and runoff from banks [7], while anthropogenic sources include mining operations, disposal of industrial and domestic wastes and application of biocides for pest control [8].

Recent studies have shown that contaminants such as heavy metals pose substantial risks to humans and benthic communities [9,10, 11, 12, 13, 14, 15].

Heavy metal pollution of sediments is of major concern because of their toxicity, ability to accumulate in aquatic biota and their non-degradable nature [4, 10, 16, 17, 18].

The effect of anthropogenic activities on the aquatic environment is that it alters the physical and chemical properties of both water and sediment. This may lead to a potentially dangerous concentration of the metals in the media. Consequently, this work will assess the pollution of the aquatic environment of Ajakanga stream, Ibadan, Southwestern Nigeria by potentially toxic heavy metals such as Cu, Pb, Zn, Co, Ni and Cr, using pollution indices such as Geoaccumulation index, Enrichment factor, Contamination Factor, Contamination Degree, and ecological risk indices such as Ecological risk index and Potential ecological risk index.

II. MATERIALS AND METHODS

2.1 Description of the Study Area

Ajakanga and environs lies between N7^{0}17'30.5", E3^{0}49'29.15" and 7°19'59.0", 3°50'38.8" on Ibadan sheet No 59 (Figure 1)[19].

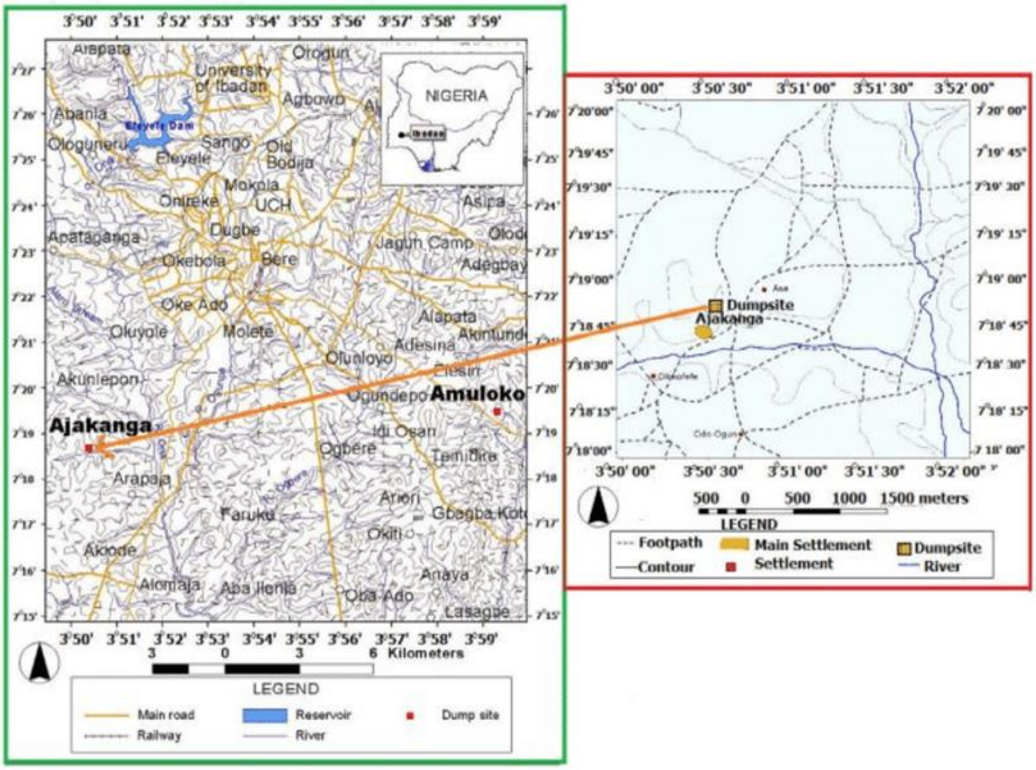

Figure 1: Ajakangaand environ (Extracted from Nigeria Geological Survey Agency, Ibadan Sheet No.59, 1980)

Ibadan is naturally drained by four rivers with many tributaries: Ona River in the North and West; Ogbere River towards the East; Ogunpa River flowing through the city and Kudeti River in the Central part of the metropolis. Ogunpa River, a third-order stream with a channel length of 12.76 km and a catchment area of 54.92 km^2. Lake Eleyele is located at the northwestern part of the city, while the Osun River and the Asejire Lake bounds the city to the east.The drainage pattern is mainly dendritic.

Ibadan has a tropical wet and dry climate with a lengthy wet season and relatively constant temperatures throughout the course of the year. Ibadan's wet season runs from March through October, though August sees somewhat of a lull in precipitation. This lull nearly divides the wet season into two different wet seasons. November to February forms the city's dry season, during which Ibadan experiences the typical West African harmattan. The mean total rainfall for Ibadan is 1420.06 mm, falling in approximately 109 days. There are two peaks for rainfall, June and September. The mean maximum temperature is 26.46 C, minimum 21.42 C and the relative humidity is 74.55%.

- GEOLOGIC SETTING

Nigeria lies in an extensive Pan-African mobile belt which separates the West African and Congo cratons (Figure 2). The belt is interpreted to have evolved from the continental collision between the West African craton and the Pan-African belt. The latter part of the Pan-African orogeny was characterized by brittle deformation which resulted in a very consistent conjugate strike-slip fault system consisting of faults trending Northeast-Southwest.

The surface area of Nigeria 923,768 square kilometers is covered, almost in equal proportions, by the crystalline rocks of the Basement Complex [20] and sedimentary rocks. The sediments are mainly Upper Cretaceous to Recent in age, while the Basement Complex rocks are considered to be Precambrian.

The crystalline rocks are further divided into three main groups, viz; the Basement Complex, the Younger Granites, and the Tertiary–Recent volcanics. The Basement Complex rocks include the undifferentiated metamorphic and igneous rocks, and their in-situ weathering products. On the other hand, the sedimentary rocks are divided into eight main basins. These include Lower Benue Trough (Anambra Basin), Middle Benue Trough, Upper Benue Trough, Borno Basin (Chad Basin), Bida Basin, Niger-Delta Basin, Benin Basin and Sokoto Basin.

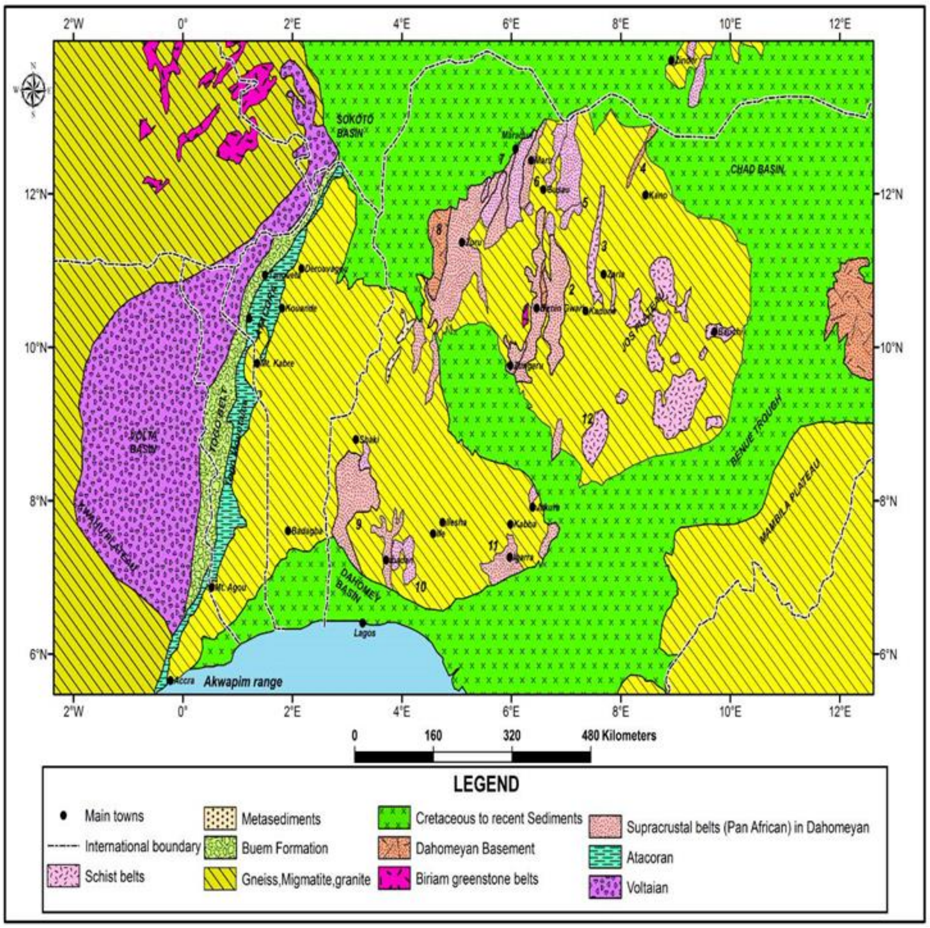

Figure 2: Basement Complex of Nigeria within the framework of the geology of West Africa (adapted from Wright, 1985)

Major rock types in Ajakanga area are; quartzites, banded gneiss, with pegmatites and quartzo-feldspartic intrusions. Essentially, the quartzites are composed of interlocking, medium grained quartz. Quartz is the dominant mineral, while muscovite, Biotite, and iron oxides are found in minor amounts.The banded gneisses are rarely found as outcrops. Most often they are strongly weathered and are found to dot the landscape. The gneisses are strongly foliated with a general strike of NNW-SSE direction. Usually, the bands are few centimeters in width, and the grains are predominantly medium sized. Pegmatite and quartz veins occur as concordant bodies within the major rock types. They vary both in length and width. Generally the pegmatites are pale-pink in color, while the quartz veins are white or grey.

III. METHODOLOGY

3.1 Sampling, Sample Preparation and Laboratory Analysis

Sediments samples were collected at 10 different locations within the stream. The samples were collected at reasonably distance from one another (Figure 3).Samples were collected and kept in tagged sample bag and GPS coordinates of each sample locations were recorded (Table 1).

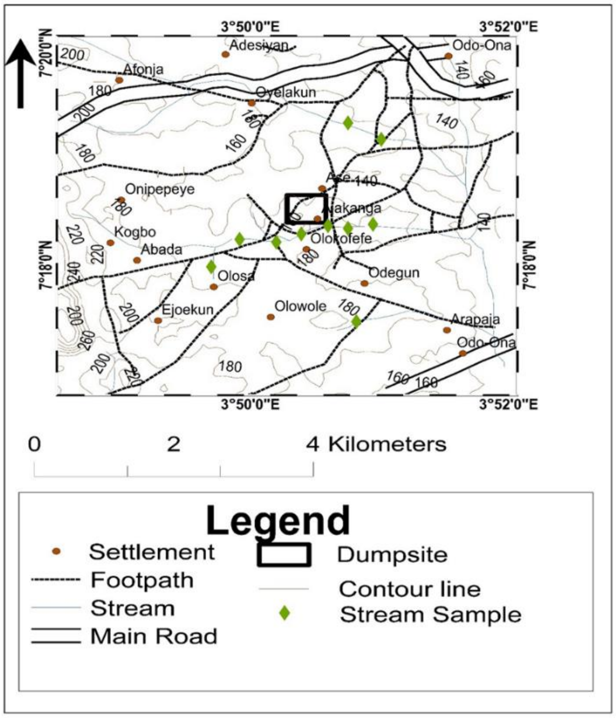

Figure 3: Stream sediment sample locations

TABLE 1: Stream Sediment Sample Location Coordinates.

Sample ID	Northings	Easting	Elevation (m)
L1	7° 18' 33.5"	3° 50' 20.4"	144
L2	7° 18' 35.8"	3° 50' 23.0"	152
L3	7° 18' 38.3"	3° 50' 32.4"	144
L4	7° 18' 43.3"	3° 50' 33.3"	142
L5	7° 18' 25.4"	3 ° 50' 15.1"	154
L6	7° 18' 08.2"	3° 50' 13.8"	172
L7	7° 17' 49.7"	3° 50' 47.8"	155
L8	7° 18' 06.2"	3° 49' 48.1"	168
L9	7° 19' 17.6"	3° 50' 53.7"	155
L10	7° 19' 21.7"	3° 50' 57.6"	155

The sediments were air dried in the laboratory. And sieved through a <0.075mm sieve to obtain fine grained samples for chemical analysis. To prevent contamination, after a sample from a location was sieved, the sieve and the pan were thoroughly brushed out and cleaned with acetone before another sample was put in for sieving and this was done all through the sample preparation. The shaking was done by a mechanical sieve shaker and then the sieved portion (<0.075mm) was collected and fraction packed into air tight polythene bag which was later sent to ACME laboratories, Vancouver, Canada for geochemical analysis. Inductively coupled plasma–mass spectrometry (ICP-MS) was used to measure the concentration of each metal in the sample.

3.2 Statistical Analysis

The range, mean, and standard deviation calculation were carried out using Microsoft excel 2013 Program.

3.3 Pollution and Ecological Risk Indices

The index of geo-accumulation (Igeo) enable the assessment of contamination by comparing the current and pre-industrial concentration originally used with bottom sediment [21]; it can also be applied to the assessment of soil contamination. The method assesses the degree of metal pollution in term of enrichment classes (Table 2) based on the increasing numerical values of the index. It is computed using the equation below.

$Igeo = \log_2 Cn/1.5Bn$

Where:

Cn is the measured concentration of the element in the politic sediment fraction (<2mm) and Bn is the geochemical background value/average shale concentration. The constant 1.5 allows for analysis of natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences.

Table 2:Class of Index of Geo-accumulation (Igeo)

I geo Class	I geo Value	Contaminated Level
0	I geo≤0	Uncontaminated
1	0<Igeo≤1	Uncontaminated or moderately Contaminated
2	1<Igeo≤2	Moderately Contaminated
3	2<Igeo≤3	Moderately or Strongly Contaminated
4	3<Igeo≤4	Strongly Contaminated

5.	$4<Igeo\leq5$	Strongly or Extremely Contaminated
6	$Igeo>5$	Extremely Contaminated

The enrichment factor was calculated using the formula:

$$EF = \frac{(Cx/Cref)}{(Bx / Bref)}$$

where:
Cx = content of the examined element in the examined environment,
Cref = content of the examined element in the reference environment,
Bx = content of the reference element in the examined environment and
Bref= content of the reference element in the reference environment.
Enrichment Factor is categories into five classes [22] (Table 3).

Table 3:Categories of Enrichment Factor

EF < 2	deficiency to minimal enrichment
EF 2-5	moderate enrichment
EF 5-20	significant enrichment
EF 20-40	very high enrichment
EF > 40	extremely high enrichment

The assessment of soil contamination was also carried out using the contamination factor (C^i_f) and the degree of contamination (C_d) (Tables 4 and 5). The (C^i_f) is the single element index; the sum of contamination factors for all elements examined represents the C_d of the environments and all four classes are recognized [23]. Table 3 shows the different contamination factors class and level. The equation is shown below:

$C^i_f=C^i_0/C^i_n$

Where C^i_0 is the mean content of metals from at least five sampling sites and C^i_n is the pre-industrial concentration of the individual's metal.

Table 4: Class of Contamination Factor (C^i_f) [23]

C^i_fClass	Contamination factor Level
$C^i_f< 1$	Low contamination factor indicating low contamination
$1<C^i_f< 3$	Moderate Contamination factor
$3 <C^i_f< 6$	Considerable Contamination factor
$6 <C^i_f$	Very High Contamination factor

The C_d is defined as the sum of $\mathbf{C^i_f}$ species specified by Hakanson L. (1980)
The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular sampling site. The C_d was divided into four groups as given in Table 4.

Table 5: Class of contamination degree(C_d) [23]

C_d Class	Contamination factor Level
$C_d< 8$	Low degree of contamination
$8 < C_d< 16$	Moderate degree of contamination
$16 < C_d< 32$	Considerable degree of contamination
$32 > C_d< 8$	Very High degree of Contamination

The ecological risk index (E_r^i) evaluates the toxicity of trace elements in sediment and has been extensively applied to soils [24].

$E_r^i = T_r^i \times C_f^i$

Where, $T_r^i$is toxicity coefficient, and has the following values; Cd = 30, As = 10, Co = 5, Cu = 5, Ni = 5, Pb = 5, Cr = 2, Zn = 1. [23].
$C_f^i$is contamination factor.

The potential ecological risk index (RI) reflects the general status of pollution as a result of the combined presence of the total heavy metal analyzed.

IV. RESULTS AND DISCUSSION

4.1 Concentration of Heavy metals in Ajakanga Stream sediments

The concentrations and statistical summary of the heavy metals concentrations are presented in Table 6.

Table 6: Heavy Metal Concentration in the Sediments of Ajakanga Stream

	Cu(ppm)	Ni(ppm)	Pb(ppm)	Zn(ppm)	Co(ppm)	Cr(ppm)
L1	16	16	18	63	36	39
L2	13	12	12	38	11	30
L3	17	17	20	64	29	58
L4	12	13	11	57	14	26
L5	12	10	13	83	21	39
L6	20	11	43	63	34	49
L7	18	16	23	75	36	58

L8	7	9	6	27	13	22
L9	16	11	19	130	20	30
L10	17	6	11	44	16	23
Max	20	17	43	130	36	58
Min	7	6	6	27	11	22
Mean	14.58	12.00	18.75	66.75	23.08	37.83
Total	148	121	176	644	230	374
C^i_f	0.265	0.218	0.341	1.213	0.419	0.688
Eri	1.326	1.091	1.705	6.068	2.098	3.439
R.I.	15.727					
C_d	3.145					

Results showed that Cu ranged from 7.00 to 20.00 ppm with mean value of 14.58ppm (Figure 4). Zn ranged from 27.00 to 130.00 ppm, with a mean value of 66.75ppm(Figure 5). Co ranged from 11.00 to 36.00 ppm, with a mean of 23.08ppm (Figure 6). Cr ranged from 22.00 to 58.00 ppm with a mean value of 37.83 ppm (Figure 7).

Pb ranged from 6.00 to 43.00 ppm, with a mean value of 18.75 ppm (Figure 8). Ni ranged from 6.00 to 16.00ppm, with a mean value of 12.00 ppm (Figure 9).

The concentration of the heavy metals in the soil is of the order Zn>Cr>Co>Pb>Cu>Ni.

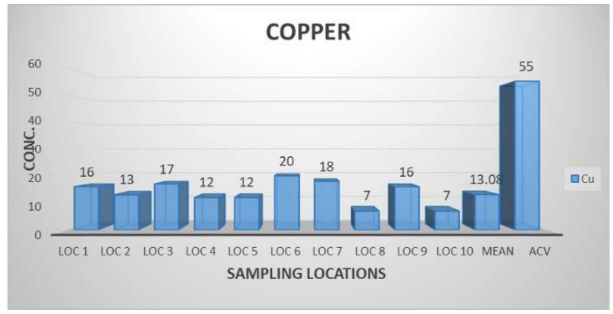

Figure 4: Concentration of copper (ppm).

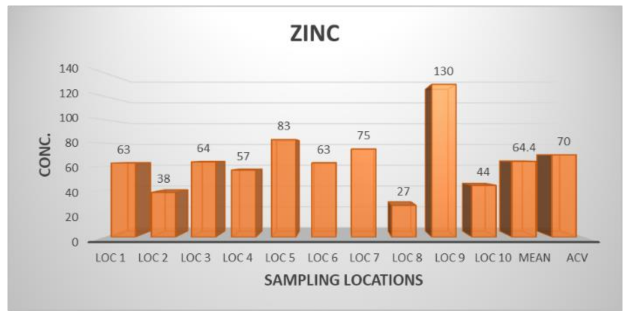

Figure 5: concentration of Zn (ppm)

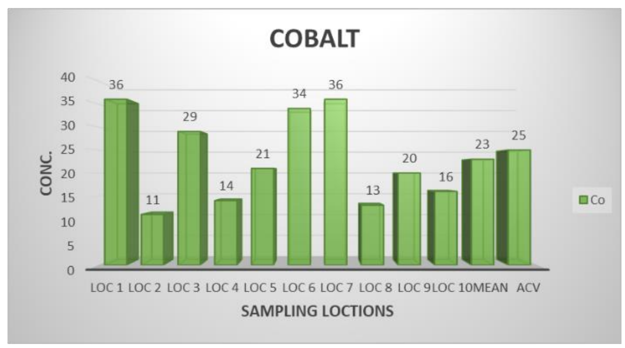

Figure 6: concentration of cobalt (ppm)

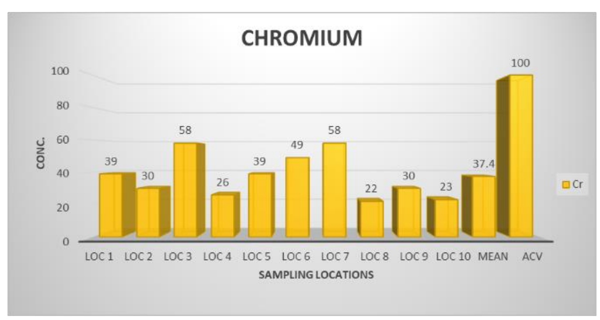

Figure 7: concentration of chromium (ppm)

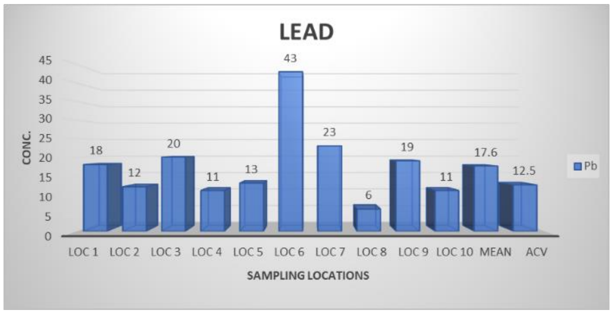

Figure 8: concentration of lead (ppm)

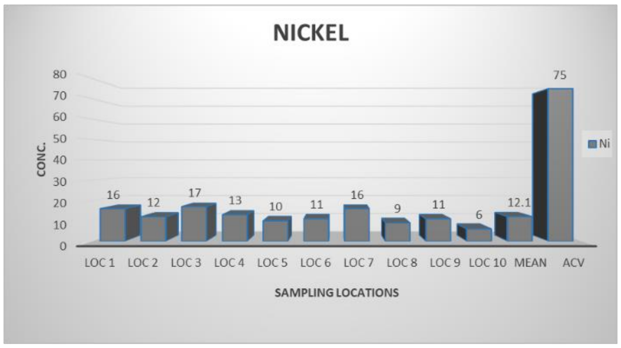

Figure 9: concentration of nickel (ppm)

Compared to the U.S. Environmental Protection Agency's (EPA) Sediment Quality Guidelines (SQGs), the concentrations of Pb in nine locations are <40, and >40<60 in one location (Table 7). This indicated that 90%, and 10% of the sediments is non-polluted and moderately polluted respectively by Pb. Cr concentration in two locations are <25 and >25<75 in eight locations, indicating that 20% and 80% of the sediments is non-polluted and moderately polluted respectively by Cr. Concentration of Cu in all locations is <25, indicating that the sediments are not polluted at all by Cu. Also Ni concentrations in all locations is <20, indicating that the sediments are not polluted at all by Ni. Only in one location is the concentration of Zn < 90. In all other location Zn range from >90<200, indicating that 10% and 90% of the sediments is non-polluted and moderately polluted respectively by Zn. In general, compared with the USEPA Sediment Quality Guidelines [25] , the sediments are non – moderately polluted by the analyzed heavy metals

Table 7: USEPA Sediment Quality Guidelines (SQG)

Metal (ppm)	Non Polluted	Moderately Polluted	Heavily Polluted	Current Study Range(ppm)	Current Study Mean (ppm)
Pb	<40	40 - 60	>60	6 - 43	18.750
Cr	<25	25 - 75	>75	22 - 58	37.833
Cu	<25	25 - 50	>50	7 - 20	14.583
Ni	<20	20 - 50	>50	6 - 17	12.000
Zn	<90	90 - 200	>200	27 - 130	66.750
Co	-	-	-	11 - 36	23.083

4.2 Assessment of metal pollution in the soil

The following pollution and ecological risk indices were employed in assessing the soil pollution status. The index of geoaccumulation, enrichment factor, contamination factor, contamination degree, ecological risk index, and potential ecological risk index.

4.2.1 Geoaccumulation Index

Geoaccumulation index allows the assessment of soil contamination with heavy metals compared with its content in the A or O horizons [26] referenced to a specific geochemical background [21]. It is considered as an accurate index in the evaluation of the degree of contamination of environmental media [26, 27, 28, 29, 30]. The calculated index of geoaccumulation for the heavy metals in Ajakanga stream sediment is presented in Table 8.

Table 8: Index of Geoaccumulation for the sediments of Ajakanga stream

	Igeo Cu	Igeo Ni	IgeoPb	Igeo Zn	Igeo Co	Igeo Cr
L1	0.058	0.043	0.289	0.181	0.289	0.078
L2	0.047	0.032	0.193	0.109	0.088	0.060

L3	0.062	0.045	0.321	0.183	0.233	0.116
L4	0.044	0.035	0.177	0.163	0.112	0.052
L5	0.044	0.027	0.209	0.238	0.169	0.078
L6	0.073	0.029	0.690	0.181	0.273	0.098
L7	0.066	0.043	0.369	0.215	0.289	0.116
L8	0.026	0.024	0.096	0.077	0.104	0.044
L9	0.058	0.029	0.305	0.373	0.161	0.060
L10	0.062	0.016	0.177	0.126	0.128	0.046
Max	0.073	0.045	0.690	0.373	0.289	0.116
Min	0.026	0.016	0.096	0.077	0.088	0.044
Mean	0.054	0.032	0.283	0.185	0.185	0.075
Total	0.540	0.324	2.825	1.846	1.846	0.750

All the values of Igeo for all heavy metals analyzed in the sediments including Cu, Ni, Pb, Zn, Co and Cr, are in the class 0<Igeo≤1: uncontaminated to moderately contaminated. This means that the pollution effect of the heavy metals on the stream sediments of Ajakanga Stream range from uncontaminated to moderately contaminated.

- Enrichment Factor (EF)

Enrichment Factor (EF) measures the impact of anthropogenic activities on soil heavy metal concentrations. An EF ranging from 0.5 to 1.5 indicates enrichment was by natural processes. Whereas, an EF greater than 1.5 indicate anthropogenic contributions [31, 32, 33, 34]. The result of the enrichment factor is presented in Table 9.

Table 9: Enrichment factor for the sediments of Ajakanga Stream

	EF Cu	EF Ni	EF Pb	EF Zn	EF Co	EF Cr
L1	0.50	0.37	2.46	1.54	2.50	0.67
L2	0.90	0.59	3.56	2.01	1.63	1.11
L3	0.51	0.37	2.63	1.51	1.91	0.95
L4	0.53	0.42	2.13	1.97	1.53	0.63
L5	0.60	0.34	2.69	3.06	2.17	1.01
L6	0.81	0.33	7.62	1.99	3.01	1.09
L7	0.55	0.36	3.08	1.80	2.41	0.97
L8	2.16	0.52	2.09	1.68	2.27	0.96
L9	0.92	0.46	4.81	5.87	2.53	0.95
L10	1.30	0.34	3.69	2.64	2.69	0.97
Max	2.16	0.59	7.62	5.87	3.01	1.11
Min	0.50	0.33	2.09	1.51	1.53	0.63

The entire content of Ni and Cr in the stream sediments were derived from natural sources as indicated by EF value of <1.5 for the entire area. Cu contents is mostly from natural sources as shown by EF value of <1.5 in all locations except one location, Location 8. All the other elements including Pb, Zn, and Co Enrichment factor >1.5, which indicated that some of these metals were derived from anthropogenic sources. Ni and Cr have deficient to minimal enrichment in the sediments, Cu and Co are moderately enriched, while Pb and Zn are significantly enriched.

- Contamination Factor (C_f^i), and Contamination Degree (Cd)

The contamination factor (C^i_f) for the heavy metals in the soil of Ajakanga and environs range from 0.218 to 1.213 (Table 6). The Contamination Factor (C^i_f) for Cu, Ni, Pb, Co and Cr is <1, while that of Zn is >1<3. This indicted that the contamination effect of Cu, Ni, Pb, Co and Cr is low, while that of Zn is moderate.
Contamination degree calculated for the stream sediments is 3.145, which indicates a low degree of contamination (Table 6).

- Assessment of Potential Ecological risk

The ecological risk index (E_r^i) and the potential ecological risk index (RI) were employed to determine the potential risk of the concentration of the heavy metals to the ecological system of Ajakangastream as a whole (Table 6).

The calculated ecological risk index (E_r^i) showed that all the heavy metal analyzed in the stream sediments fall below 40 (E_r^i<40). This shows that the contamination of Ajakanga stream sediments by Cu, Ni, Pb, Zn, Co and Cr is low.

The potential ecological risk index (RI) for the area is 15.727 (Table 6), indicating that the risk of potential contamination of Ajakanga stream sediments with the current concentration of Cu, Ni, Pb, Zn, Co and Cr is low.

4.3 Spatial Distribution of the Metals in the Soil of Ajakanga and environs

The graphical representation of the spatial distribution of the metals in the studied area is shown in figure 10 to figure 15.Cu spatial distribution map shows that Copper has its highest concentration of 20ppm in L6, and the minimum concentration of 7ppm in L8.Zn spatial distribution map shows that Zinc has its highest concentration of 130ppm in L9 and the minimum concentration 27ppm in L8. Co spatial distribution map shows that Cobalt has its highest concentration of 36ppm in L1 and the minimum concentration of 11ppm in L2. Cr spatial distribution map shows that Chromium has its highest concentration of 58ppm in L3 and the minimum concentration of 22ppm in, L8.Pb spatial distribution map shows that Lead has its highest concentration of 43ppm in L6, and the least concentration 6ppm in L8. Ni spatial distribution map shows that Nickel has its highest concentration of 17ppm in L3 and the minimum concentration of 6ppm in L10.

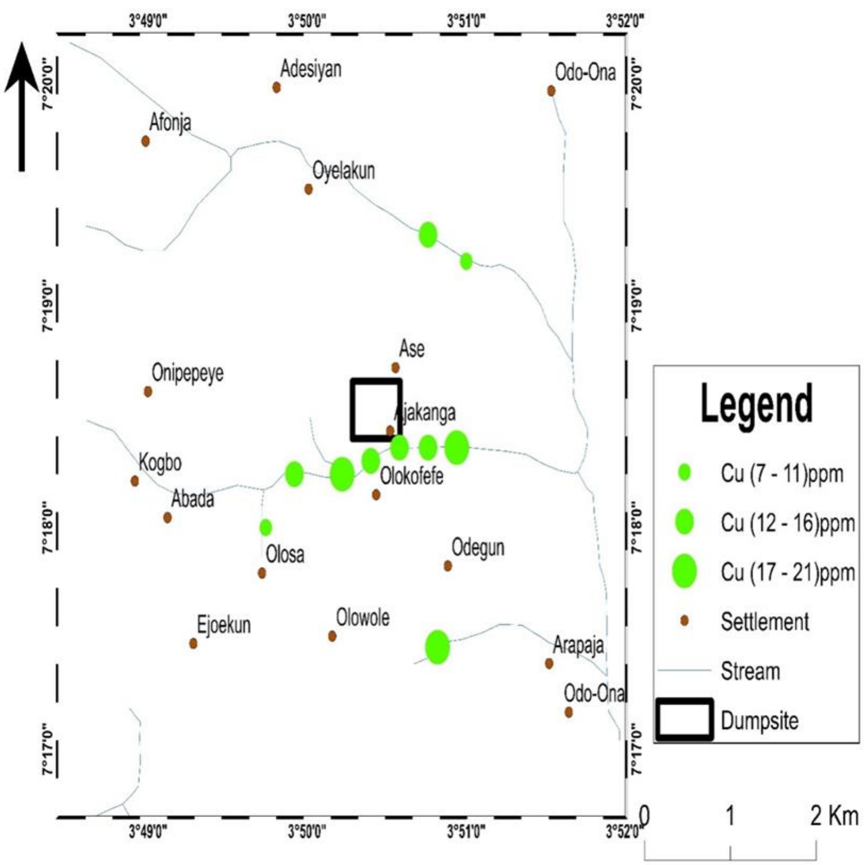

Figure 10: Cu distribution in the sediment of Ajakanga stream

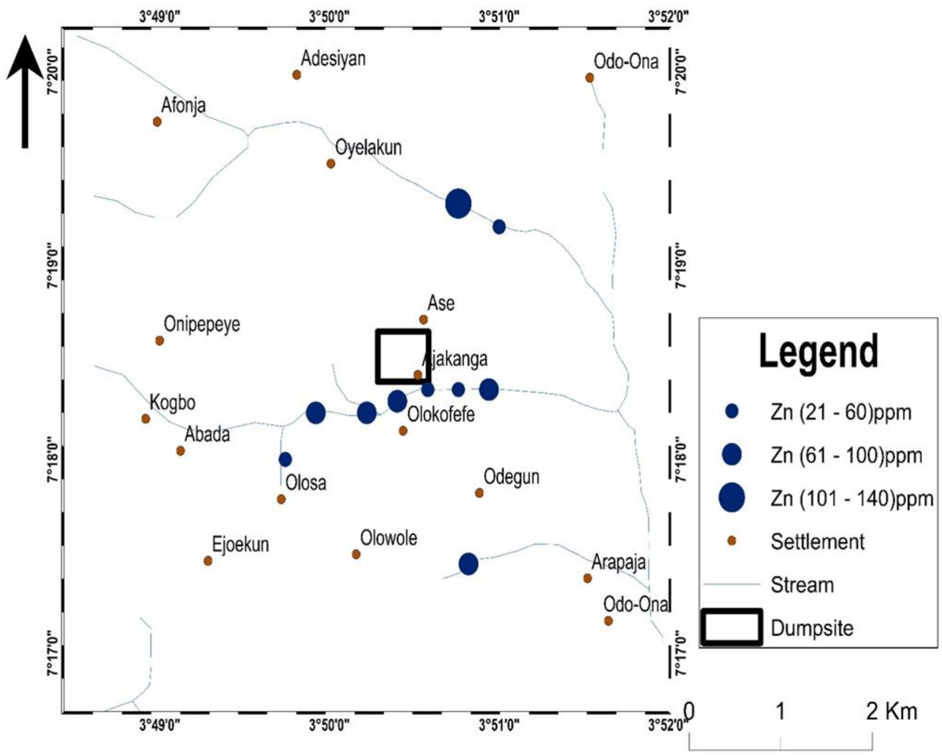

Figure 11: Zndistribution in the sediment of Ajakanga stream

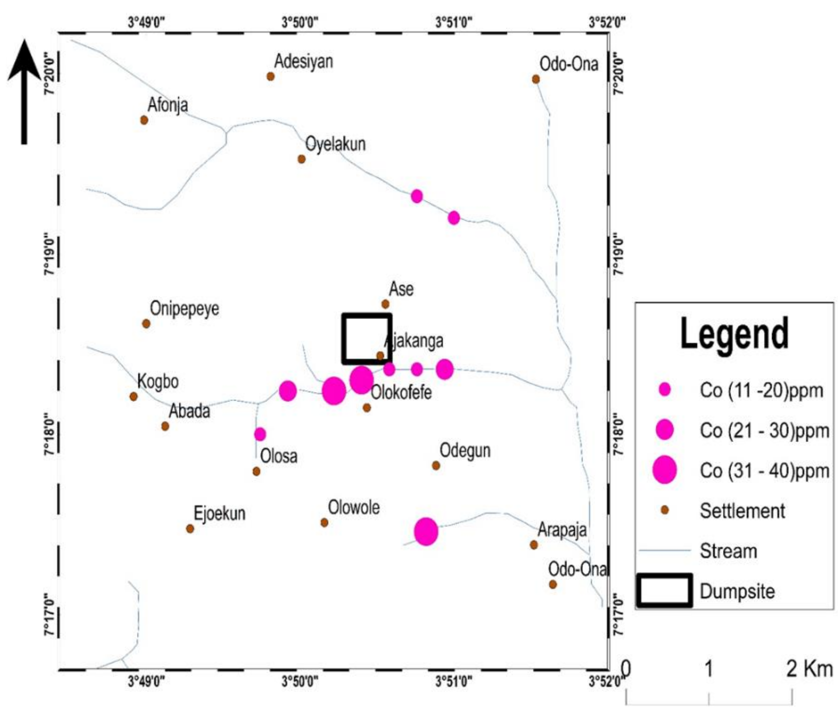

Figure 12: Co distribution in the sediment of Ajakanga stream

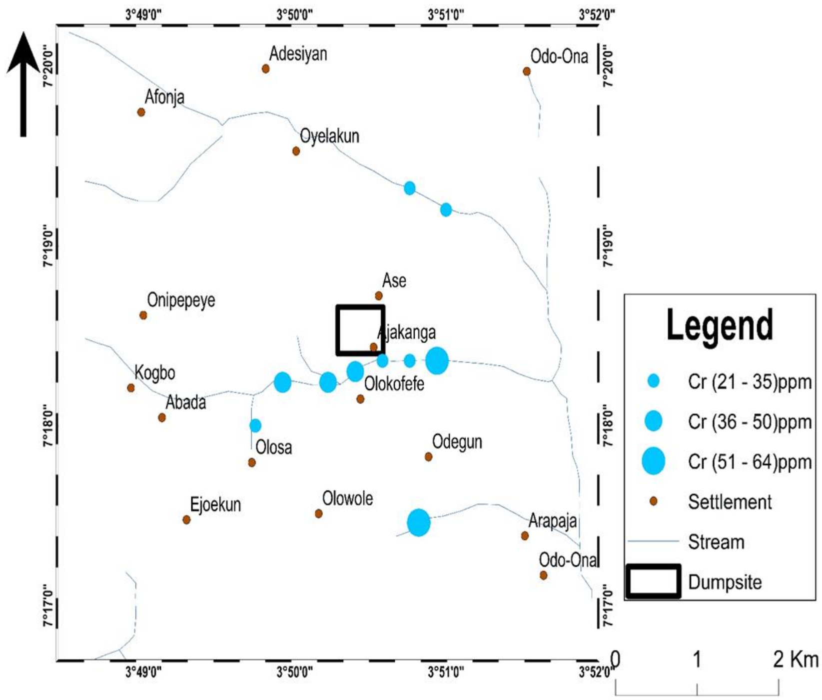

Figure 13: Cr distribution in the sediment of Ajakanga stream

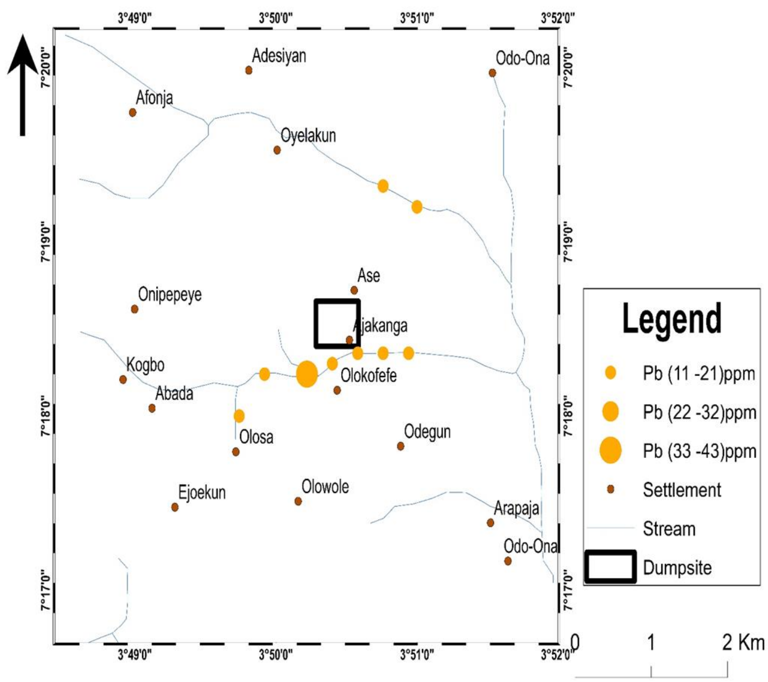

Figure 14: Pb distribution in the sediments of Ajakanga stream

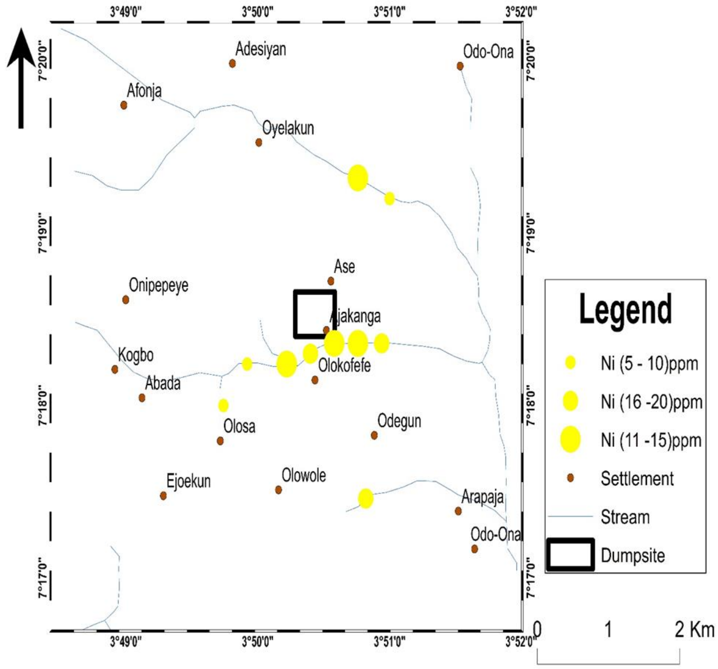

Figure 15: Ni distribution in the sediment of Ajakanga stream

CONCLUSION

Analysis of the geochemical results of the Ajakanga stream sediments samples showed that the average concentration of the heavy metals varied significantly and decrease in the order ofZn>Cr>Co>Pb>Cu>Ni.

In general, compared with the United States Environmental Protection Agency's (EPA) Sediment Quality Guidelines (SQGs), the sediments are non to moderately polluted by the analyzed heavy metals.The result of the geoaccumulation index showed that the pollution effect of the heavy metals on the stream sediments of Ajakanga stream range from uncontaminated to moderately contaminated, while the enrichment factor showed that the entire content of Ni and Cr in the stream sediments were derived from natural sources. Cu contents are mainly from natural sources a very low percentage are from anthropogenic source. The enrichment factor for all the other metals which includePb, Zn, and Co indicated a major contribution from anthropogenic sources. Moreover, the enrichment factor showed that Ni and Cr have deficient to minimal enrichment in the sediments, Cu and Co are moderately enriched, while Pb and Zn are significantly enriched.

The calculated ecological risk index (E_r^i) showed that all the heavy metal analyzed in the stream sediments fall below 40 (E_r^i<40). This shows that the contamination of Ajakanga stream sediments by Cu, Ni, Pb, Zn, Co and Cr is low, which is in agreement with the potential ecological risk index (RI) for the area which indicated that the risk of potential contamination of Ajakanga stream sediments with the current concentration of Cd, Cu, Ni, Pb, Zn, As, Co and Cr is low.

REFERENCES

[1] Bettinentti,R. C. Giarei and A. Provini, "A Chemical Analysis and Sediment Toxicity Bioassays to Assess the Contamination of River Lambro (Northern Italy)," *Archives of Environmental Contamination and Toxicology*, Vol. 45, No. 1, 2003, pp. 72-78.

[2] Li, X., Shen, Z., Wai, O.W., Li, Y.S., 2001. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River estuary. Mar. Pollut. Bull. 42, 215–223.

[3] Xia, P., Meng, X., Yin, P., Cao, Z., Wang, X., 2011. Eighty-year sedimentary record of heavy metal inputs in the intertidal sediments from the

Nanliu River estuary, Beibu gulf of south China Sea. Environ. Pollut. 159, 92–99.

[4] Wang, Y., Hu, J., Xiong, K., Huang, X., Duan, S., 2012. Distribution of heavy metals in core sediments from Baihua Lake. Procedia Environ. Sci. 16, 51–58.

[5] Mashiatullah, A., Chaudhary, M., Ahmad, N., Ahmad, N., Javed, T., Ghaffar, A., 2015. Geochemical assessment of metal pollution and ecotoxicology in sediment cores along Karachi coast, Pakitstan. Environ. Monit. Assess. 187.

[6] Jahan S, and Strezov V, 2018. Comparison of pollution indices for the assessment of heavy metals in the sediments of seaports of NSW, Australia. Marine Pollution Bulletin 128 (2018) 295–306.

[7] Raju,K. V. R. Somashekar and K. Prakash, "Heavy Metal Status of Sediment in River Cauvery, Karnataka," *Environmental Monitoring and Assessment*, Vol. 184, No. 1, 2012, pp. 361-373. doi:10.1007/s10661-011-1973-2

[8] Chakravarty, M. and Patgiri, A. "Metal Pollution Assessment in Sediments of the Dikrong River, N. E. India," *Journal of Human Ecology*, Vol. 27, No. 1, 2009, pp. 63-67.

[9] Benson, N.U., Asuquo, F.E., Williams, A.B., Essien, J.P., Ekong, C.I., Akpabio, O., Olajire, A.A., 2016a. Source evaluation and trace metal contamination in benthic sediments from equatorial ecosystems using multivariate statistical techniques. PLoS ONE, 11(6), 1-19.

[10] Benson, N.U., Anake, W.U., Essien, J.P. Enyong, P.A., Olajire, A.A., 2016b. Distribution and risk assessment of trace metals in *Leptodiusexarata*, surface water and sediments from Douglas Creek, Qua Iboe estuary. J. Taibah University for Science, 11 (3), 434 – 449.

[11] Lin, Y.C., Chang-Chien, G.P., Chiang, P.C., Chen, W.H., Lin, Y.C., 2013. Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan. Mar. Pollut. Bull., 76(1-2), 266-275.

[12] Liu, J., Wu, H., Feng, J., Li, Z., Lin, G., 2014. Heavy metal contamination and ecological risk assessments in sediments and zoobenthos of selected mangrove ecosystems, South China. Catena, 119, 136-142.

[13] Maanan, M., Saddik, M., Maanan, M., Chaibi, M., Assobhei, O., Zourarah, B., 205. Environmental and ecological risk assessment of heavy metals in sediments of nador lagoon, Morocco. Ecol. Indic., 48, 616-626.

[14] Saleem, M., Iqbal. J., Shah. M.H., 2015 Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments – A case study from Mangla lake, Pakistan. Environ. Nanotechnol. Monit. Manage., 4, 27-36.

[15] Tornero, V., Anas, A.M., Blasco, J., 2014. Trace element contamination in the Guadalquivir River Estuary Ten years after the Aznacollar mine spill. Mar. Pollut. Bull, 86(1-2), 349-360.

[16] Diaz-de Alba, M., Galindo-Riano, M.D., Casanueva-Marenco, M.J., Garcia-Vargas, M., Kosore, C.M., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. J. Hazard Mater., 190, 177-187.

[17] Pejman, A., Bidhendi, N.G., Ardestani, M., Saeedi, M., Baghvand, A., 2015. A new index for assessing heavy metals contamination in sediments: A case study, Ecol. Indic., 58, 365-373.

[18] Zhang, W., Lin. X., Cheng, H., Zeng, E.Y., 2012. Heavy metal pollution insediments of typical mariculture zone in South China. Mar. Pollut. Bull. 64, 712-720.

[19] Nigerian Geological Survey Agency, 1980.

[20] Wright, J.B. (1985). *Geology and mineral resources of West Africa.*, London: George Allen & Unwin.

[21] Muller G. 1969: Index of geoaccumulation in sediments of the Rhine River Geol. J. 2(3): 108-118.

[22] Sutherland RA (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environmental Geology 39: 611-637.

[23] Hakanson, L. 1980, "An ecological risk index for the aquatic pollution control, a

sedimentologicalapproach". Water Res. 14, 975 – 165.

[24] Liang, J., Liu, J.Y., Yuan, X.Z., Zeng, G.M., Lai, X., Li, X.D., Wu, H.P., Yuan, Y.J., Li, F. 2015. Spatial and temporal variation of heavy metal risk and source in sediments of Dongting lake wetland, mid – south China. J. Environ. Sci. Health, 50, 100 – 108.

[25] U.S. Environmental Protection Agency (USEPA) Guideline for the Pollutional Classification of Great Lakes Harbor Sediments, Region V, Chicago Illinois (1977).

[26] Kowalska, J., Mazurek, R., Gasiorek, M. and Zaleski, T. 2018. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination – A review. Environ Geochem Health, 40: 2395 – 2420.

[27] Begum, K., Mohiuddin, K.M., Zakir, H.M., Moshfigur Rahman, M., and NazmulHasan, M. 2014. Heavy metal pollution and major nutrient elements assessment in the soils of Bogra city in Bangladesh. Canadian Chemical Transactions, 3, 316 – 326.

[28] Karim, Z., Qureshi, B.A. and Mumtaz, M. 2015. Geochemical baseline determination and pollution assessment of heavy metals in urban soils of Karachi, Pakistan. Ecological Indicators, 48, 358 – 364.

[29] Li, M.S., and Yang, S.X. 2008. Heavy metal contamination in soils and phytoaccumulation in sediments and macrobenthos in coastal wetlands induced by freshwater releases: A case study in the Yellow River Delta, China. Marine Pollution Bulletin, 103, 227 – 239.

[30] Sayadi, M.H., Shabani, M. and Ahmadpour, N. 2015. Pollution index and ecological risk of heavy metals in the surface soils of Amir – Ad Area in Birjand City, Iran. Health Scope, 4, 121 – 137.

[31] Elias, P., and Gbadegesin, A. 2011. Spatial relationships in urban land use, soils and heavy metal concentrations in Lagos Mainland area. Journal of Applied Sciences and Environmental Management, 15, 391 – 399.

[32] Zhang, J., and Liu, C.L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China: Weathering features, anthropogenic impact and chemical fluxes. Estuarine Coastal Shelf Science, 54, 1051 – 1070.

[33] Dung, T.T.T., Cappuyns, V., Swennen, R., and Phung, N.K. 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Reviews in environmental Science and Biotechnology, 12, 335 – 353.

[34] Kowalska, J., Mazurek, R., Gsiorek, M., Setlak, M., Zaleski, T. and Waroszewski, J. 2016. Soil pollution indices conditioned by medieval metallurgical activity: A case study from Krakow (Poland). Environmental Pollution, 218, 1023 - 1036.