

Assessment of Heavy Metal Contamination and Sediment Quality in the Urban River: A Case Of Ala River in Southwestern – Nigeria

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Abstract – Ala river is considered as one of the most important irrigation and drinking water resources in Akure, Nigeria. The distribution and accumulation of heavy metals: Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Lead (Pb) and Zinc (Zn) in sediment were investigated in this river during the raining season between August and September, 2012. The mean concentration of these metals were: 0.09 µg/g for Cd; 20.30 µg/g for Cr; 6.61 µg/g for Cu; 648.04 µg/g for Fe; 1.50 µg/g for Ni; 16.90 µg/g for Pb; 3.78 µg/g for Zn dry weight. The result showed that the average concentrations of heavy metals were ranked as: Fe > Cr > Pb > Zn > Ni > Cr > Cd. To assess metal contamination in sediment, United State environmental Protection Agency's (USEPA) Guidelines were applied. The concentrations of Cd in all the stations were moderately polluted. The metals contamination in the sediments were also evaluated by applying Index of geo-accumulation (I_{geo}), contamination factor (C_f) and Degree of contamination. On the basis of the mean values of I_{geo}, sediments are enriched with metals in the following order: Pb > Cd > Cr > Cu > Zn > Ni > Fe while according to contamination factor (C_f), Cd, Cr, Cu, Fe, Ni, Pb, Zn were at low contamination and in order of Pb > Cd > Cr > Cu > Zn > Ni > Fe. According to degree of contamination (C_d), site 4 has the highest amount of heavy metal contamination while site 9 has the lowest amount of heavy metal contamination. Pearson correlation indicates that Zn, Fe and Ni, Cr are highly significant (p < 0.01), suggesting that the anthropogenic sources of these metals are closely related in the sediment from Ala river.

Keywords – Ala river; sediment; heavy metal; contamination; contamination factor; geo-accumulation index;.

I. Introduction

Water is a vital resource to man. Its quantity and quality as well as its management contribute to its sustainability [1, 2]. Its usage constitutes a major criterion toward sustainable growth and development of a region and its economy [3, 4]. Water is one of the most important necessities of life that is required by man, animal and plant. Man uses water for domestic, industrial and agricultural purposes [5]. As noted by researcher, life on earth is impossible without water. It was argued that a man's most urgent need is drinking water [1]. Stating that, man may survive several weeks without food but will die within few days if deprived of water. The past decade has seen remarkable impact of man on the environment due to unprecedented increase in population and rapid rate of urbanization as well as the intensification of the use of fragile and marginal ecosystem [6]. This has led to progressive land and other vital resources degradation and continued desertification of marginal agricultural lands. Understanding and monitoring surface water quality of a region remains a better tool towards promoting sustainable development of water resources within the societal economic and conservational contextual need [7]. Also of importance is the assessment of the human activities that are capable of changing the quality of river water within an urban area [8]. This is necessary, since per capital water demand is increasing while accessibility to available fresh water availability is one that decreases [9, 10]. These have led to usage of polluted and contaminated water source. Globally, about 80% of all diseases and death in developing countries was caused by polluted water [11, 12].

Sediments are normally mixtures of several components including different mineral species as well as organic debris. Sediments represent one of the ultimate sinks for heavy metals discharge into the environment [13, 14, 15, and 16]. In the aquatic environment, sediment has a high storage capacity for contaminants. In the hydrological cycle, less than 0.1% of the metals are actually dissolved in the water and more than 99.9% are stored in sediments and soils [17, 18]. Sediments are frequently containing higher concentrations of pollutants. They act as carriers and possible sources of pollution due to the fact that heavy metals are not permanently fixed by them and can be released back to the water by changes in environmental conditions, therefore they may become sufficiently polluted to disrupt natural biological communities. Contaminated sediments are known to be responsible for degradation of water quality in the natural waters especially in the shallow and enclosed water systems [19, 20]. In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediment contamination have been introduced over the past 10 years [21, 22, and 23]

Heavy metals, such as arsenic (As), mercury (Hg), Cadmium (Cd), Lead (Pb) and Chromium(Cr), are commonly detected in lakes [24]. Like other aquatic system, heavy metals enter surface water like lakes and river through natural sources (e.g weathering, erosion) and anthropogenic sources (e.g mining, urban and industrial water waste [25, 26]. At present, heavy metal pollution has become a great environmental concern with their toxicity, persistence, bioaccumulation and biomagnifications in the food chain [27, 28]. Heavy metals contamination in aquatic environment is of critical concern, due to toxicity of metals and their accumulation in aquatic habitats. Trace metals in contrast to most pollutants are not bio-degradable, and they undergo a global ecological cycle in which natural waters are the main pathways. Of the chemical pollutants, heavy metals being non- biodegradable, they can be concentrated along the food chain, producing their toxic effect at points after far removed from the source of pollution [29]. Exposure to heavy metals has linked to several humans' disease such as development retardation or malformation, kidney damage, cancer, abortion, effect on intelligence and behavior, and even death in some cases of exposure to very high concentrations. For human beings, surface water is an important source of water and food. Thus heavy metals in surface water might ultimately have adverse biological effect on human health through drinking water and consuming aquatic products [30, 31]. For these reasons, it would be desirable and imperative to investigate their distribution in urban river like Ala which can provide valuable information of heavy metal pollution and help evaluate potential environmental risks. The aims of this of this study were to: investigate the contamination levels and distributions of heavy metals in surface sediment and evaluate the potential toxicity of the metal concentrations based on sediment quality guidelines.

II. Materials and Methods-

2.1 The study area:

Akure is the Capital City of Ondo State Nigeria and it is located in the Central Senatorial District of the State [32]. Akure falls between 739000 and 746000 Easting (i.e. between longitude 5°06'E and 5°38'E) and between 801500 and 807000 Northing (i . e . , between latitude 7° 07' N and 7 37' N) Fig 1.

Akure is bounded in the North by Ifedore local govt, in the west by Ile – Oluji Oke -Igbo local govt, in the South by Idanre local govt and East by Ore – Odigo Local govt. The study area experiences a frequent rainfall between April and July with a short break in August and continues between September and November, with the heaviest rainfall in July. The average daily temperature ranges from 22°C during harmattan (December – February) to 32°C in March which is the peak temperature. The vegetation is tropical rainforest [33, 34]. The population of the people residing in Akure is about 353,211 [35]

Geography of river Ala: River Ala and tributaries is one of the main tributaries of River Ogbese, South, western, Nigeria. River Ala with total length of about 57km has a length of about 14.81km with Akure Township (Fig 1). It took its source from north western part of Akure town and flows towards south eastern part of the town. Akure Township dominated the upstream of River Ala while rural towns such as Ilado, Ehinala, Ajegunle, Owode Aiyetoro and Araromi are located in downstream where the water is used for domestic purposes.

2.2 Samples Collection:

Sediment samples were collected from ten sites along Ala River (as shown in Fig 1) between the months of August and September 2012. The latitude and longitude for each site were illustrated in Table 1. The samples were carried by polythene bag and transported to the laboratory and stored at temperature of 4°C, after which the sediment samples were air – dried for 2 weeks in the Laboratory and sieved through a 1.7 µm mesh to remove the debris, then lightly ground in an agate mortar for homogenization and prepared for analysis of heavy metal.

2.3 Method of extraction

For heavy metals test, extraction of metals from sediment samples was by mixed acid digestion as described by [36, 37]. Briefly, the digestion was carried out with 20 mL of a mixture of Conc HClO₄ and HNO₃ at a 2:1 ratio (v/v) on a hot plate and the mixture heated to almost dryness, then 20 mL of 0.5M HNO₃ added was and the solution was filtered through Whatman N0 42 filter paper. The filtrate obtained was made up to 50 mL mark with distilled water in volumetric flask and the solution was analyzed for heavy metals content against those of the blank using a flame atomic absorption Spectrophotometer ,M series 600324 v1 .12. The blank was prepared by the method described above except that the sediment was not added.

2.4 Study area.

Table 1 Location of Sediment Sample Collection

Site No	Location	Latitude	Longitude
1	Aule	07°16.45'N	005°09.99'E
2	Ayedun	07°15.82'N	005°11.48'E
3	Araromi	07°15.67'N	005°11.67'E
4	Oke-Ijebu (Cocola deport	07°15.75'N	005°12.31'E
5	Oke- Ijebu (3- ages Hotel	07°16.44'N	005°12.44'E
6	Fiwasaye	07°15.33'N	005°13.23'E
7	Alagbaka	07°15.43'N	005°12.667'E
8	Odudu	07°19.16'N	005°14.31'E
9	Kojola- Ilado	07°11.60'N	005°17.58'E
10	Ehin- Ala	07°11.51'N	005°18.53'E

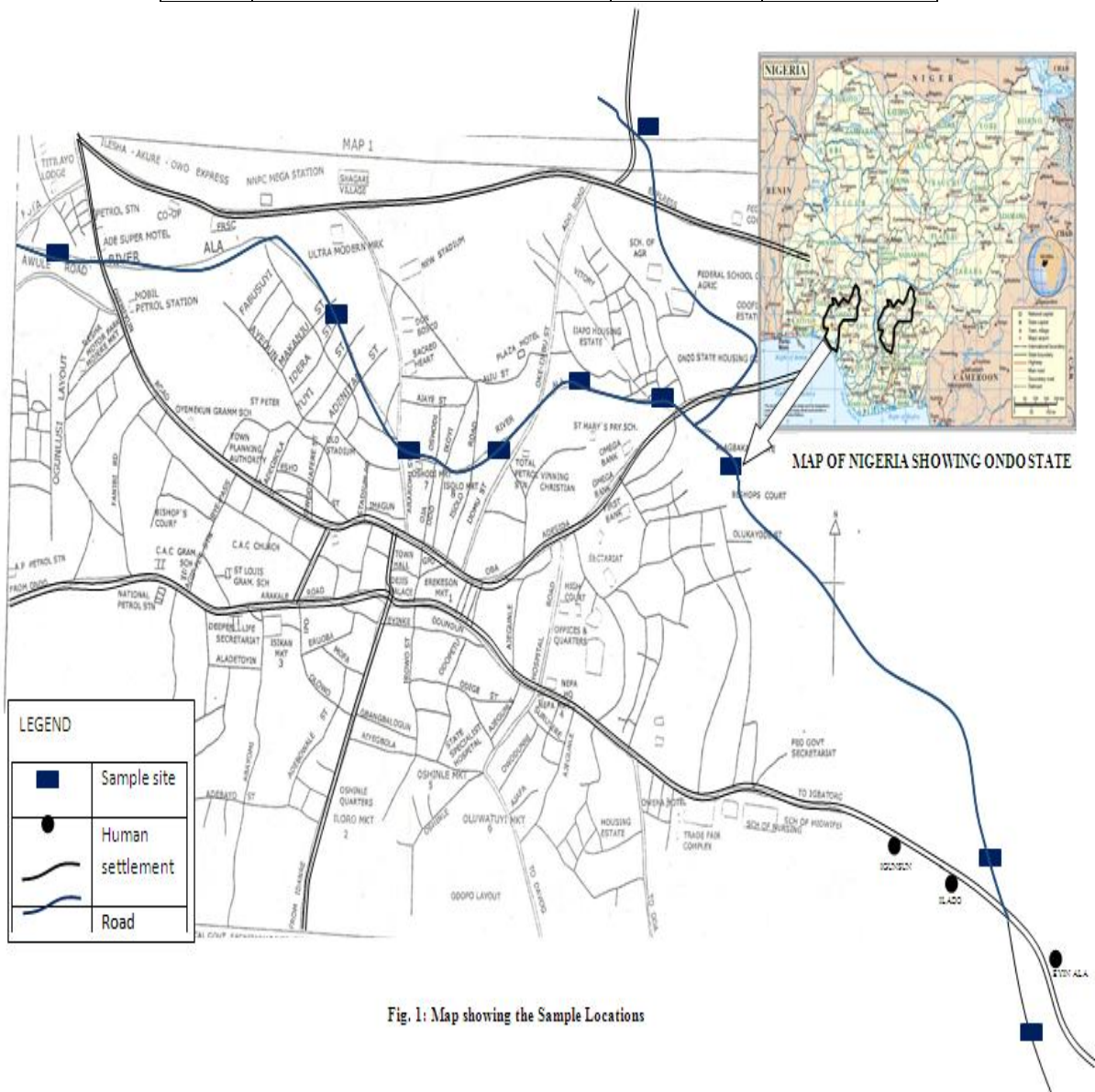


Fig. 1: Map showing the Sample Locations

III. Results And Discussion

3.1 Mean Concentration of Heavy Metals Concentration in Sediment (µg/g Dry Weight)

The total concentrations and average values for each site found in sediments in this study are shown in Table 2. Metal contents range over following intervals: Cd: 0.062 – 0.13 µg/g; Cr: 3.44 -38.05 µg/g; Cu: 0.62 - 27.92 µg/g; Fe: 475.20 -704.24 µg/g; Ni: 0.13 -2.83 µg/g; Pb: 3.11 -80.82 µg/g; Zn: 0.26 -6.58 µg/g dry weights. The mean metal contents of the ecosystem studied were: Cd 0.09 µg/g; Cr: 20.30 µg/g; Cu: 6.61 µg/g; Fe: 648.04 µg/g; Ni: 1.50 µg/g; Pb: 16.90 µg/g; Zn: 1.52 µg/g dry weights. The ranking of the mean metal contents in this area is as follows: Fe> Cr > Pb > Cu > Zn >Ni > Cd. The results obtained in this research indicated that metal contents of Ala River Sediment were lower when compared with sediments in Buriganga River, Bangladesh [38], Western part of Egyptian, Mediterranean Sea [39] and Wadi Al –Arab Dam, Jordan, Shadegan Wetland in Southwest of Iran [40]

The concentration of heavy metals in sediments can be a secondary source of water pollution, once environmental condition is changed [41, 42]. Therefore, an assessment of heavy metal contamination in sediments is an indispensable tool to assess the risk of an aquatic environment. To assess metal concentrations in sediment, Numerical Sediment Quality Guidelines (SQGs) were applied. SQGs include a threshold effect concentration (TEC) and a probable effect concentration (PEC) (Table2). If the metals in sediments are below the TEC, harmful effects are unlikely to be observed. If the metals are above the PEC, harmful effects are likely to be observed [39]. Previous researcher [43], noted in his studies that most of the TEC provide an accurate basis for predicting the absence of sediment toxicity, and most of the PECs, provide an accurate basis for predicting sediment toxicity. In this study, the concentrations of Cd, Cr, Cu, Ni, Pb and Zn in all sediment samples are lower than the proposed TECs, indicating that there are no harmful effects from these metals. On the other hand, the concentrations of Fe exceeded TEC in all samples indicated that these stations were in potential risk.

Table 2 Mean Concentrations of Heavy Metal in Sediment (µg/g Dry weight)

Site	Cd	Cr	Cu	Fe	Ni	Pb	Zn
1	0.12	25.55	8.10	684.33	2.83	7.90	4.41
2	0.08	22.14	8.58	672.05	1.07	6.85	4.33
3	0.06	19.21	27.92	698.87	2.68	37.89	6.58
4	0.09	22.33	4.89	689.65	0.87	80.82	4.40
5	0.13	26.16	3.64	704.24	2.83	6.05	5.37
6	0.10	23.95	4.52	653.31	1.55	6.75	4.65
7	0.06	38.05	4.16	662.16	2.04	10.93	5.52
8	0.11	4.85	2.19	655.37	0.86	5.10	0.72
9	0.06	3.44	0.62	475.20	0.15	3.59	0.26
10	0.09	17.36	1.43	576.23	0.13	3.11	1.52
Average	0.09	20.30	6.61	648.04	1.50	16.90	3.78
Max	0.13	38.05	8.58	704.24	2.83	80.82	6.58
Min	0.06	3.44	0.62	475.20	0.86	3.11	0.26
TEC	0.99	43.4	31.6	nd	22.7	35.8	121
PEC	4.98	111	149	nd	48.6	128	459

Note: Tec: Threshold Effect Concentration; PEC: Probable Effect Concentration

3.2 Assessment of Heavy Metal Concentration

3.2.1 Assessment According to United States Environment Protection Agency (USEPA)

The chemical Contamination in the sediments was evaluated by comparison with the sediment quality guideline proposed by USEPA. These criteria are shown in Table 3. Zn and Ni in all stations under investigation belong to unpolluted class. Site 1, 5 and 7 for Cr, station 2 for Cu, and station 4 for Pb were considered as moderately polluted. On the other hand Cd was all moderately polluted in all sites.

Table 3: EPA guide lines for sediments

Metal	Not Polluted	Moderately Polluted	Heavily Polluted	Present Study
Cd	>6	0.06-0.13
Cr	<25	25-27	>75	3.44-38.05
Cu	<25	25-50	>50	0.62-8.58
Ni	<20	20-25	>50	0.86-2.85
Pb	<40	40-60	>60	3.11-80.82
Zn	<90	90-200	>200	0.26-6.58

Source: [38].

Table 4: Muller’s Classification for the Geo- Accumulation Index.

Igeo	Class	Sediment Quality
≤0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
>6	6	Extremely polluted

3.2.2 Assessment According to Geo –accumulation Index (Igeo)

A common criterion to evaluate the heavy metal pollution in sediments is geo –accumulation index (Igeo), which was originally defined by a researcher to determine metals contamination in sediments, by comparing current concentrations with pre- industrial levels and can be calculated by the following equation [44]

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \quad (1)$$

Where, C_n is the concentration of element, B_n is world surface rock average [43]. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The geo -accumulation index (Igeo) scale consists of seven grades (0 – 6) ranging from unpolluted to extremely polluted (shown in Table 4).

Table 5: Geo –accumulation index for heavy metal in sediment of Ala river

Site	Cd	Cr	Cu	Fe	Ni	Pb	Zn
1	-1.91	-2.40	-3.06	-6.68	-5.17	-1.92	-5.01
2	-2.49	-2.61	-2.98	-6.70	-6.57	-2.13	-5.04
3	-2.91	-2.81	-1.27	-6.65	-5.25	0.34	-4.43
4	-2.32	-2.60	-3.79	-6.65	-6.87	1.43	-5.01
5	-1.79	-2.37	-4.21	-6.64	-5.17	-2.31	-4.73
6	-2.17	-2.49	-3.90	-6.74	-6.04	-2.15	-4.93
7	-2.91	-1.83	-4.02	-6.72	-5.64	-1.46	-4.69
8	-2.03	-4.80	-4.95	-6.74	-6.89	-2.56	-7.62
9	-2.91	-5.29	-6.77	-7.20	-9.41	-3.06	-9.09
10	-2.32	-2.96	-5.56	-6.93	-9.62	-3.27	-6.55
Mean	-2.37	-3.02	-4.05	-6.75	-6.66	-1.71	-5.71

According to the Muller scale, the calculated results of I_{geo} Values (shown in Table 5) indicate, for Pb sediment quality be considered as moderately polluted ($1 \leq I_{geo} < 2$) for site 4, but sediment quality ranges from unpolluted to moderately polluted ($0 \leq I_{geo} < 1$) for site 3 and unpolluted ($I_{geo} < 0$) for all other sites. Cd, Cr, Cu, Fe, Ni, Zn

were unpolluted in all the sites ($I_{geo} < 0$). On the basis of the mean values of I_{geo} , sediments are enriched for metals in the following order: $Pb > Cd > Cr > Cu > Zn > Ni > Fe$.

Table 6. Contamination factor (C_f) and Degree of contamination (C_d) for Ala River.

Site	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Degree of Contamination (C_d)
1	0.40	0.28	0.18	0.015	0.042	0.40	0.046	1.36
2	0.27	0.25	0.19	0.014	0.016	0.34	0.046	1.13
3	0.20	0.21	0.62	0.015	0.039	1.89	0.069	3.04
4	0.30	0.25	0.11	0.015	0.013	4.04	0.046	4.77
5	0.43	0.29	0.08	0.015	0.042	0.30	0.057	1.22
6	0.33	0.27	0.10	0.014	0.023	0.34	0.049	1.13
7	0.20	0.42	0.09	0.014	0.030	0.55	0.058	1.38
8	0.37	0.05	0.04	0.014	0.013	0.26	0.008	0.76
9	0.20	0.04	0.01	0.010	0.002	0.18	0.003	0.45
10	0.30	0.19	0.03	0.012	0.002	0.16	0.016	0.71
Mean	0.30	0.22	0.15	0.014	0.022	0.85	0.04	1.59

The contamination factors (C_f) or enrichment ratio (ER) and the degree of contamination (C_d) are used to determine the contamination status of sediment in the present study. (C_f) values for describing the contamination level are shown in Table 6. The contamination factors are calculated according to the eq. 2 and the degree of contamination (C_d) was defined as the sum of all contamination factors. Calculated contamination factor (C_f) and degree of contamination (C_d) for this study is shown in the Table 6.

$$C_f = \frac{\text{Measured concentration}}{\text{Background concentration}} \quad (2)$$

Where, Background value of the metal = world surface rock average [45]. In the present study, maximum contamination factor was found in the site 4 where the degree of contamination is 4.77. Contamination factor, $C_f > 4$ (indicates considerate contamination) is found in site 4 for Pb while in Site 3, $C_f > 1$ for Pb indicates moderately contamination. Site 4 and Site 3 are in the downstream of the river where dumping of refuse, agriculture wastes, industrial effluents and industrial activities are being channeled to. The remaining sites have a contamination factor (C_f) < 1 which indicates low contamination [46] in Table 7. On the basis of the mean value of C_f , sediment is enriched for metals in the following order: $Pb > Zn > Cd > Cr > Cu > Ni > Fe$.

Table 7: Contamination Factor and Level of Contamination (Hakanson 1980)

Contamination Factor (C_f)	Level of Contamination
$C_f < 1$	Low contamination
$1 \leq C_f < 3$	Moderate contamination
$3 < C_f < 6$	Considerate contamination
$C_f > 6$	Very high contamination

Table 8: Pearson's correlation coefficient among the selected heavy metals

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Cd	1						
Cr	0.0461	1					
Cu	-0.326	0.139	1				
Fe	0.406	0.601*	0.453	1			
Ni	0.309	0.602*	0.535*	0.7232*	1		
Pb	-0.176	0.125	0.359	0.359	0.013	1	
Zn	-0.012	0.804**	0.624*	0.781**	0.804**	0.344	1

Note : * is significant at $p < 0.05$; ** correlation is highly significant at the $p < 0.01$

Correlation Coefficient “ r ” is one of the most important statistical tests to evaluate the strength or weakness relationships among metals in this study. Significant correlations between the contaminants of Cr and Fe (0.601), Cr and Ni (0.602), Cu and Ni (0.535), Cu and Zn (0.624), Fe and Ni (0.723) at $p < 0.05$ and highly significant at $p < 0.01$ between Cr and Zn ($r = 0.8042$), Fe and Zn ($r = 0.7809$), Ni and Zn ($r = 0.8037$), could indicate the same or similar source input or similar enrichment mechanism [47], suggesting that the anthropogenic sources of these metals are closely related in the sediment from Ala river.

IV. Conclusions

The results of this study provide valuable information on metal contents of sediments from different sampling sites of Ala River. Moreover these results can also be used to test the chemical quality of the surface water sediment in order to evaluate the possible risk to the river of this area. The order of the mean concentration of tested heavy metals: Fe > Cr > Pb > Cu > Zn > Ni > Cd. USEPA guideline, Geo-accumulation Index, Contamination factor and degree of contamination, are successfully applied for the assessment of contamination. The result obtained from Igeo method emphasized that sediments are enriched with metals in the following order: Pb > Cd > Cr > Cu > Zn > Ni > Fe while according factor (C_f), Cd, Cr, Cu, Fe, Ni Zn were at low contamination. It could be concluded that both Igeo and C_f are powerful tools for the assessment of contamination of heavy metal. According to USEPA: for Cd, the sediment samples are moderately polluted; Considering all assessment criteria, only Cd is responsible for moderately amount of heavy metal contamination while Cr, Cu, Fe, Ni, Pb, Zn are responsible for low contaminations. According to degree of contamination, Site 4 has the highest amount of heavy contamination and Site 9 has the lowest amount of heavy metal contamination. This is plausible because site 4 is in the downstream area of river where dumping of refuse, agriculture wastes, industrial effluents and others industrial activities are channeled to while Site 9 is in the upstream of the river where there is little or no agricultural, domestic and industrial activities.

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