Bull. Chem. Soc. Ethiop. **2016**, 30(2), 199-208. ISSN 1011-3924
Printed in Ethiopia

DOI: http://dx.doi.org/10.4314/bcse.v30i2.4

SPECIATION AND DETERMINATION OF PRIORITY METALS IN SEDIMENTS OF OYUN RIVER, ILORIN, KWARA, NIGERIA

Hussein K. Okoro[1*] and Hadizat A. Jimoh[2]

[1]Environmental-Analytical Research Laboratory, Department of Industrial Chemistry, Faculty of Physical Sciences, P.M.B. 1515, University of Ilorin, Ilorin, Nigeria
[2]Department of Chemistry, Faculty of Physical Sciences, P.M.B. 1515, University of Ilorin, Ilorin, Nigeria

(Received September 30, 2014; revised April 14, 2016)

ABSTRACT. This work was carried out to determine the concentrations, bioavailability and mobility of priority metals in sediments of Oyun River, Sango, Ilorin, Nigeria. The river sediments were sampled at six selected locations and the samples were analyzed for some certain priority metals to determine the concentration, speciation and distribution pattern of the metals. The sediments were obtained specifically at upstream, middle-stream and downstream of the river. In general, the total metal concentrations was in the order: Mn > Pb > Cu > Cd in sediment samples and for Tessier's sequential fractionation, manganese was found to be more in the exchangeable phase, while Pb was higher in the residual form and Cu was found to be more concentrated in the organic phase. Total priority metal bio-availability and mobility of Pb, Mn, Cu and Cd in the samples varied between 0-83.61 mg/kg, 93.01-96.65 mg/kg, 23.53-45.88 mg/kg and 0-100 mg/kg, respectively. This clearly indicates that with the exception of Cu, the metals are highly bioavailable leading to it having a higher impact on its target system, subsequently leading to contamination of the water. The high percent bioavailability is an indication of poor retention in the residual geochemical form partly due to saturation of the sediment (river). The pH value was found to be basic but within the WHO standards throughout all locations. The high percentage of Mn, Cd and Pb in the bioavailable forms suggested the need to keep close surveillance on these metals because of their high toxicity.

KEY WORDS: Speciation, Mobility, Priority metals, Sediments, Bioavailability, Pearson correlation, Principal component analysis

INTRODUCTION

Water and land, the vital resources of life are increasingly being overstressed as a result of contamination in the wake of population growth, poor land and water use system, agricultural activities and industrialization [1]. Heavy metals in the surface water systems can be from natural or anthropogenic sources. Excess metal levels in surface and ground water may pose a health risk to humans and the environment either directly if the polluted water is consumed or indirectly if it is used to irrigate agricultural fields [2]. Heavy metals have continued to receive regular attention due to their toxicity and accumulative behavior [3].

Moreover, they are not biodegradable and undergo a global ecological cycle in which natural waters are their main pathways. The river sediments existing at the bottom of the water table plays an important role in predicting the pollution scheme of the river systems by priority metals. Water can transport both dissolved metals and adsorbed metals to the sediment particles [3]. The analysis of heavy metals in sediments enables one to assess the level of pollution [4].

Priority metals are of high ecological importance since they are not removed from water as a result of self-purification, but accumulate in reservoir and enter the food chain [5]. The elevation of metal levels in a water body is shown mainly by an increase in their concentrations in bottom sediment. Their occurrence in the environment results primarily from anthropogenic activities

---

*Corresponding author. Present address: Analytical/Environmental Chemistry Research Group, Department of Applied Chemistry, Faculty of Science, Doornfontein Campus P.O Box 17011, Doornfontein 2028, University of Johannesburg, Auckland, South Africa.
E-mail: okoroowo@yahoo.com; hkoadeola@gmail.com

[6]. Moreover, the natural process, such as weathering of rocks and volcanic activities plays a noticeable role in enriching the water reservoirs with heavy metals [7, 8].

In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediments contamination have been introduced, since the determination of total concentration of heavy metals are not the best indicator of their mobility, bioavailability and toxicity [9, 10]. Sediments are normally mixtures of several components, including different mineral species as well as organic debris [6]. Sediment can act as both a sink and a source for contaminants. It reflects the quality of surface water as well as provides information on the transportation and fate of the pollutant [11, 12]. The uses of the hydrosphere by the living organisms (biosphere) of the environment have been found to be numerous and this has brought about the need for the practice of chemical speciation [13].

Over the years, the greater demand for chemical speciation comes from the need to immobilize the metals released to the environment and partially lost through human technological and industrial activities [14]. In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediments contamination have been introduced, since the determination of total concentration of heavy metals are not the best indicator of their mobility, bioavailability and toxicity [9, 10]. Speciation is the determination of the species or the physico-chemical forms of an element which together comprise its total concentration in a given sample [15]. Speciation can further be defined as the identification and quantification of the different species, forms, or phases present in a material [3, 10].

Specifically, this study involved determination of heavy metal distribution and speciation in the sediments. The relative mobility of Pb, Cu, Cd and Mn in the river sediments was also evaluated. Principal component analysis and Pearson correlation coefficient were used to further explain the binding behavior of these metals.

EXPERIMENTAL

The study area

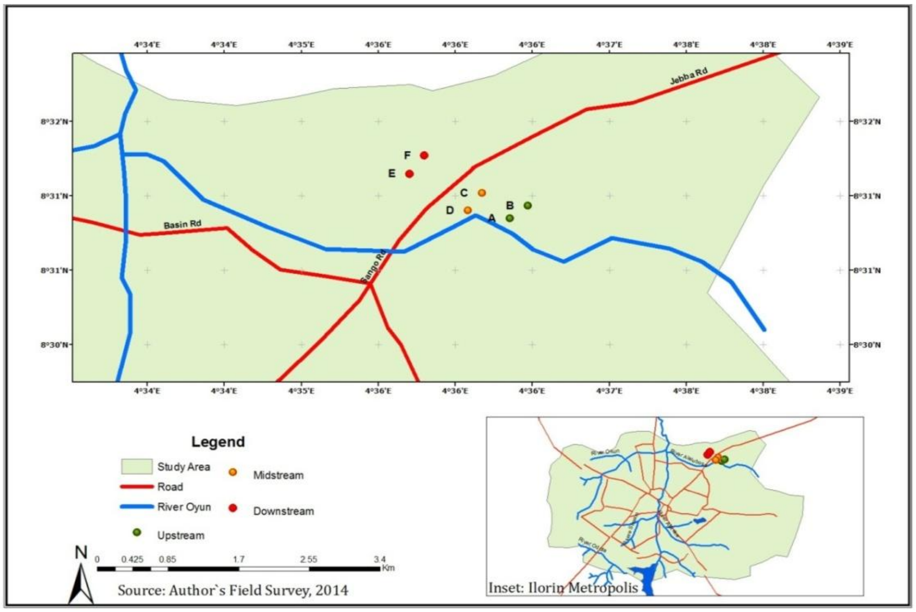
River Oyun is a stream in Sango, Ilorin, Kwara State, Nigeria. It is located at an elevation of 269 meters above sea level. Its coordinates are 8°34'60" N and 4°34'0" E in DMS (Degrees Minutes Seconds) or 8.58333 and 4.56667 (in decimal degrees). It is used for agricultural and other household activities. An incinerator and quarry industries are located around the river at its downstream and upstream respectively. The locations of sampling sites are given in Table 1. The map of the sampling points in Oyun River along Sango, Ilorin is shown in Figure 1.

Table 1. Location sites and description.

Location	Description	Coordinates	Temperature (^{o} C)	Depth (m)
A	Upstream	8^o 31' 17"N, 4^o 36' 18"E	28	9
B	Upstream	8^o 31' 31"N, 4^o 36' 6"E	27	12
C	Middle-stream	8^o 31' 24"N, 4^o 32' 3"E	27	12.5
D	Middle-stream	8^o 31' 24"N, 4^o 36' 5"E	30	15
E	Downstream	8^o 31' 43"N, 4^o 35' 46"E	33	23
F	Downstream	8^o 31' 43"N, 4^o 37' 21"E	29	15

Samples collection and preparation

Samples were collected in triplicate from six different sites within the Oyun River, Sango area by simple random sampling for the research. Samples of the river sediment were taken from the selected six sites. The distance between the selected sites for sample collection were carefully noted to be 100 m apart. The sediment samples were then stored in polyethylene bags which were transferred to cooler boxes already containing ice packs and then transported to the laboratory for analysis. The sediment samples collected were air dried at room temperature for a week on aluminum foil sheet. After drying, the sediment samples was ground in a mortar with the use of a pestle, sieved with a laboratory test sieve of size 500 µm, homogenized and finally stored in polyethylene bags that had already been pre-treated at 4 °C prior to sequential extraction.



Source: Author`s Field Survey, 2014

Figure 1. Map of River Oyun located at Sango, Ilorin, Kwara State, Nigeria.

Reagents and instrumentation

A deionized water was used for the preparation of solutions throughout the study. All reagents used were of analytical grade and were supplied by SUNAF ventures, Ilorin, Kwara. A Buck Scientific 210/211VGP Atomic Absorption Spectrometer: 220GF Graphite Furnace and 220AS Auto sampler was used for the priority metals determination. A centrifuge was used to obtain supernatant extracts at 4000 rpm for 20 min.

Determination of total heavy metal concentration in sediment samples

A gram of the sediment sample was weighed into a 250 mL digestion flask and was acid digested with 10 mL aqua regia on a hot plate until it was properly digested. The digest was then cooled and filtered with a Whatman No. 1 filter paper. The filtrate was then diluted with distilled water in a 100 mL volumetric flask. The resulting solution was then aspirated into the atomic absorption spectrophotometer.

Sequential extraction procedures

Speciation experiments were performed using the modified Tessier method [16]. The main modifications included the use of 1 M sodium acetate instead of $MgCl_2$, and centrifugation steps of 20 and 5 min to get a clear supernatant clear solution. The extraction was applied to the fine particles with the amount of 1 g, and the experiments were conducted according to modified Tessier's sequential extraction conditions [16]. The extraction procedure was carried out in a centrifuge (Table 2).

Table 2. Experimental conditions in a sequential extraction procedure.

S. No.	Chemical fractions	Extraction conditions
1	Exchangeable fraction	8 ml of 1 M Sodium acetate at pH 8.2 at room temperature
2	Metals bound to carbonate	8 ml of 1 M sodium acetate (pH 5 with glacial acetic acid)
3	Metals bound to Fe-Mn oxides	8 ml of 0.1 M $NH_2OH.HCl$ (in 25% v /v acetic acid)
4	Metals bound to organic matter	3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2.0
5	Residual fraction	Acid digestion using HCl: HNO_3 aqua regia (7.5 ml HCl: 2.5 ml HNO_3)

Extraction time

The extraction was first carried for 20 min and later 5 min to rinse the residual samples in the extraction tube.

Statistical analysis

This was carried out using Microsoft Excel 2007 edition and Statistical package for Social Sciences (SPSS) to determine the relationships between the variables and correlation coefficient with $p \leq 0.05$ was regarded as significant. Principal component analysis was also carried out on the data variables.

RESULTS AND DISCUSSION

Priority metals total concentration in sediment samples of Oyun River, Sango, Ilorin

Priority metals are natural constituents of sediments, some are essential for living organisms but are relatively toxic at higher concentrations. Sediments are thus sinks of priority metals. Total metal concentration in sediment samples of Oyun River, Sango are illustrated in Figure 2. The readings for Manganese showed the highest value of 3.483 mg/kg at location E and a mininum value of 1.087 mg/kg at location F. manganese metal concentration has an average of 2.047 ± 0.811 mg/kg. The average concentration value was found to be above the WHO limits of 1.00 mg/kg thus suggesting its toxicity and potential mobility in the sediment sample. Related research work carried out on this metal noted that the metal was generally very high above health standards of federal and world organizations [4, 17, 18]. The recorded values for lead metal ranged from a minimum of 0 mg/kg all locations except location A that has a maximum value of 0.413 mg/kg with an average concentrations of 0.069 ± 0.154 mg/kg.

The Pb ion concentration was found to be above the WHO limits. This could be due to the anthropogenic activities and natural factors which lead to the emission of Pb and other associated metals. Some authors had previously linked the presence of Pb in sediment samples as a result of industrial activities and chemicals used in agricultural activities [4, 19]. Most researchers found this metal to be toxic as it was generally found to be above health standard limits [4, 18]. Cu metal concentration was found to be highest in location E with a value of 0.12 mg/kg and least in locations C and F with an average of 0.077 ± 0.039 mg/kg. These values were very low but when compare with the WHO limits implying it was non-toxic. Some researchers found out that the level of Cu metal in samples was found to be low and within health limits whilst some found it to be relatively high [18, 20]. Cd metal concentration was found to be 0.033 mg/kg in location C with an average of 0.008 ± 0.013 mg/kg. These values were high in comparison with the WHO limits which implying that it was toxic. In comparison with other related works it was noted that the total concentration for this metal varied due to the activities carried out in each location [18, 20].

Metal speciation in sediment of Oyun River, Sango, Ilorin

Mean concentrations and standard deviation of some selected Priority metals in the different fractions of sediments from Oyun River, Sango, Ilorin after Tessier's sequential extraction are shown by the graphical representations illustrated in Figures 2 – 6 and Table 3–6.

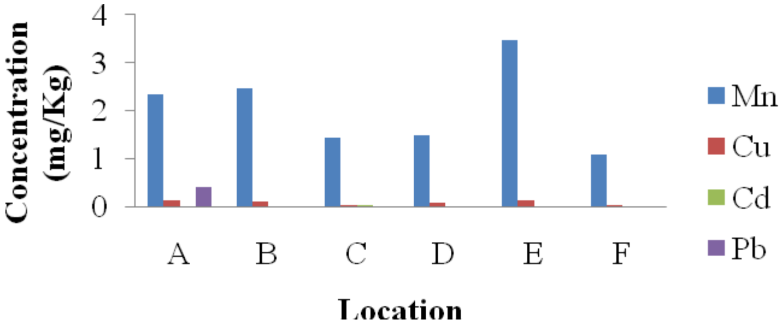


Figure 2. Distribution of all metals in all locations using Total metal digestion.

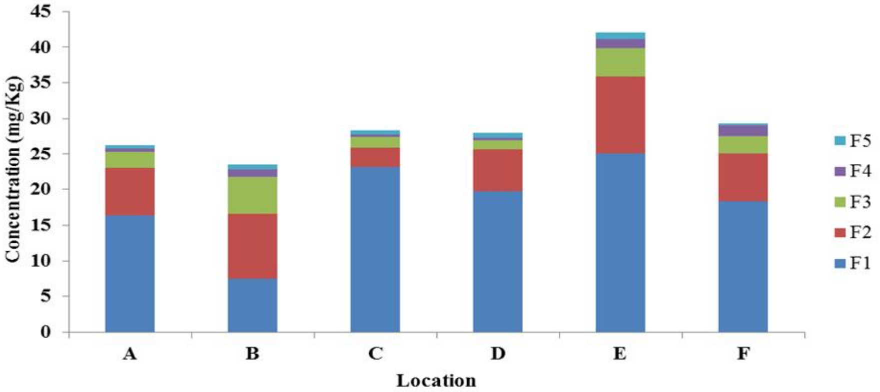


Figure 3. Distribution of Manganese in the five fractions.

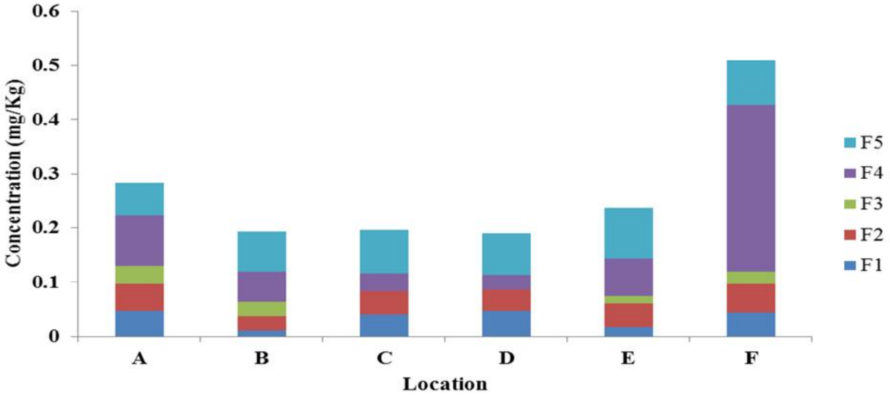


Figure 4. Distribution of Copper in the five fractions.

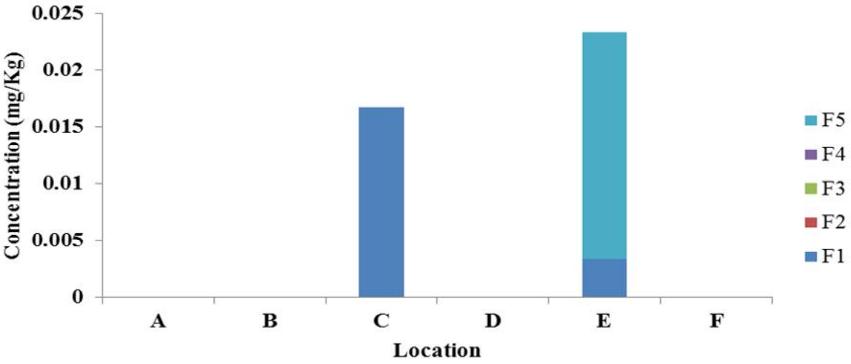


Figure 5. Distribution of cadmium in the five fractions.

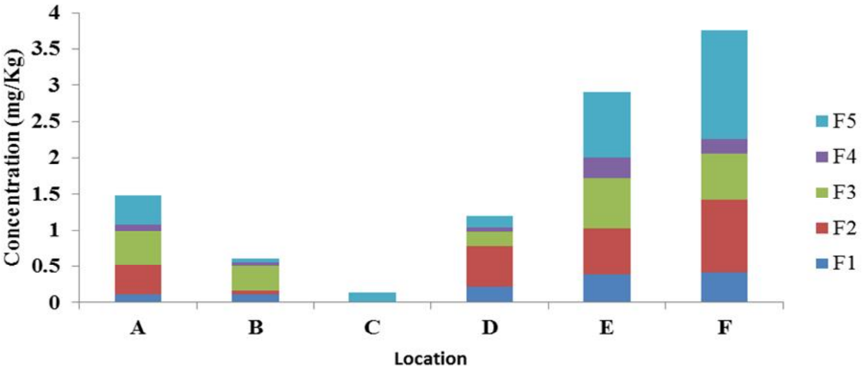


Figure 6. Distribution of lead in the five fractions.

Table 3. Mean concentrations and standard deviation of some selected Priority metals in the different fractions of sediments from Oyun River, Sango, Ilorin after Tessier's sequential extraction.

Fraction	Heavy metal concentration (mg/kg)			
	Mn	Cu	Cd	Pb
Exchangeable	18.37 ± 5.675	0.034 ± 0.015	0.003 ± 0.006	0.210 ± 0.152
Carbonates	7.003 ± 2.505	0.042 ± 0.007	ND±SD	0.442 ± 0.394
Fe – Mn oxides	2.767 ± 1.396	0.016 ± 0.013	ND±SD	0.3905 ± 0.242
Bound to Organic	0.797 ± 0.480	0.098 ± 0.097	ND±SD	0.115 ± 0.097
Residual	0.628 ± 0.156	0.075 ± 0.010	0.006 ± 0.009	0.5267 ± 0.522

***ND** = not detected. SD: standard deviation.

Table 4. Percentage level of bioavailable fractions.

SAMPLE	FRACTIONS	Mn	Cu	Cd	Pb
Location A	Bioavailable	96.55	45.88	0.00	66.82
Location B	Bioavailable	93.01	32.76	0.00	83.61
Location C	Bioavailable	96.65	42.37	100.00	0.00
Location D	Bioavailable	96.37	45.61	0.00	81.34
Location E	Bioavailable	94.98	30.99	14.28	58.94
Location F	Bioavailable	93.44	23.53	0.00	54.79

Table 5. Comparison of results for metal concentration from sediments of Oyun River, Sango, Ilorin and Other African Rivers.

LOCATION	Mn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
Oyun River, Kwara, Nigeria (recent work)	2.047	0.077	0.008	0.069
Dzindi River, South Africa [25]	-	2.600	3.300	12.300
Madanzhe River, South Africa [25]	-	2.500	4.800	20.100
Onyi River, Obajana, Kogi, Nigeria [20]	2.223	0.0620	-	0.037
Kubanni River, Zaria, Nigeria [18]	-	52.430	-	16.980

Table 6. Total variance explained using principal component analysis.

Component	Initial Eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1 (Mn)	1.306	32.65	32.65	1.306	32.65	32.65	1.278	31.94	31.94
2 (Cu)	1.159	28.97	61.62	1.159	28.97	61.62	1.187	29.67	61.62
3 (Pb)	0.923	23.08	84.69						
4 (Cd)	0.612	15.31	100.0						

Major amount of manganese was found to be present in the exchangeable fractions and carbonate fractions with the least being in the residual fraction. The amount present in the exchangeable fraction constituted about 62.13% and 23.69% for carbonate fraction of total mass while that of residual fraction constituted about 2.13% of the total mass. The high percent of Mn in the exchangeable and carbonate fraction may be due to the abundance of Mn in the earth crust including sediment. This is in agreement with the literature as several authors had previously reported high concentrations for manganese, especially in exchangeable and carbonates fractions [4, 19, 21]. The order is F1 > F2 > F3 > F4 > F5.

Substantial amount of Cu was found in the organic metal bound and Fe-Mn fractions with an average of 0.075 ± 0.0096 mg/kg constituting 28.27% and 0.098 ± 0.097 constituting 36.89% of total mass respectively. The higher concentration of Cu in fractions 3 and 4 may be due to the weathering of rocks. The high concentration in the latter two fractions and lesser concentrations in the former three fractions make Cu metal to be least strongly bioavailable in the sediment sample. Speciation works that involved Cu metals have not really been done [17, 22]. The order is F4 > F5 > F2 > F1 > F3.

Cadmium metal was observed to have a high percent value in the residual fraction (66.7%) closely followed up by the exchangeable fraction (33.3%) even though it was not detected in over 90% of the sediment samples making it to have no precise regular pattern. However, high percentage of Cd in the organic fraction and residual fractions was reported [21] and generally Cd showed greater affinity for organic fraction [22].

This metal was found to have high percent values in the carbonate, Fe-Mn and residual phases with an average percent value of 80.93%. This subsequently leads to the high bioavailability value of the metal leading to toxicity if not properly handled. Some literatures have however noted that there was no unique pattern except that fractions bound to carbonates and Fe-Mn are associated with the least of Pb or not detected while the exchangeable and residual fractions have the highest Pb in association with the geochemical fractions [22, 23]. The order is F5 > F2 > F3 > F4 > F1.

Bioavailability and mobility in relation to chemical speciation

Sequential extraction was used to determine the potential mobility and bioavailability of the priority metals. Metal bioavailability factor (MBF) is found to be ([F1+F2+F3]/[F1+F2+F3+F4+F5]) and the non-bioavailable fractions to be ([F4+F5]/[F1+F2+F3+F4+F5]) [22]. The bioavailable fractions for each metals were estimated to be within the range of: Mn (93.01–96.65), Cu (23.53–45.88), Cd (0–100) and Pb (0–83.61). These metals are classified as bioavailable groups on the basis of their relative mobility and toxicity to the sediment and eventually river water [19]. The bioavailability level of each site is shown in the Table 2.

For upstream (location A), the percentage of manganese shows a high bioavailability dominance of 96.55% closely followed up by lead with a percentage value of 66.82%, while that of copper was found to be 45.88%. This trend is the same at the in location B where a high percentage of Mn above 90% is seen and Pb is accrued a value of 83.61%. This goes to show that Mn and Pb metals are more mobile than the other two metals due to their high percentage bioavailability. High percentage of the Mn and Pb metals recorded in fractions 1 to 3 was due to the greater mobility as stated by some researchers [22, 19].

In mid-stream location C, Cd metal was found to have a very high bioavailability percent value of 100% closely followed up by Mn and Pb metal was found not to be bioavailable at all. For location D, Mn possessed a high bioavailable value of 96.37% closely followed up by Pb and Cu with a bioavailable percent value of 45.61%. Cd was noted not to be bioavailable at all. The trend observed for location D was also noted at downstream location E with the only difference being that Cd was found not to be bioavailable with a very low bioavailable value of 14.28%. The trend in location F was the same as that of location A. In general, Mn metal alongside Pb metal was found to be highly bioavailable. Cu metal was found to be least bioavailable in the sediment sample for all locations. The study thus relates the presence of heavy metals that were bioavailable, highly mobile and thus toxic as some earlier researchers earlier stated [17, 22, 24].

High percentage bioavailability is an indication of poor retention in the residual geochemical form partly due to old age of the river or saturation [22]. This subsequently poses potential danger to the water making it unsafe for drinking. The impact of a metal in an environment is determined by its ease of availability, the higher the level of bioavailability, the higher the impact on its target system (toxicity effect) [22]. The results obtained in this study were compared with other findings carried by researchers in other African countries (Table 3). The results obtained in this study the result obtained in this study is lower than the one obtained in other locations (Table 3).

Statistical analysis of priority metals concentration in sediments of Oyun River, Sango, Ilorin

The principal component analysis showed that manganese and copper metals to be of highest concentrations in Oyun River sediments closely followed up by Lead metal with a minimum value noted for the Cadmium metal. This was in accordance to the result of concentrations gotten for all metals in total metal determination. The principal component analysis (PCA) was used to show the distribution of metals across locations and how they correlate with each other. From Table 4, Mn and Cu has % variance (32.65 and 28.96, respectively) these show that they are both strongly correlated and have strong associations while Cd and Pb showed similar trends. The Eigen values decreased in the order Mn > Cu > Pb > Cd. The reasons for the two can be due the fact that they are from both natural and anthropogenic sources.

CONCLUSION

Sediment samples collected from Oyun River, Sango, Ilorin as at time of sampling was found to be contaminated which also affected the water quality making it unfit for human consumption and other purposes without proper treatment. This is so because with the exception of Cu concentration, all other sediment quality parameters were above the WHO acceptable limits. The sediment samples are generally basic. High concentration levels of Pb, Cd and Mn alongside their potentially bioavailable nature in the sediments pose potential toxicity to the aquatic life and human health and this could be due to heavy metal contamination from industrial and domestic sources and other non-point sources that comes from residential and industrial areas in and around the study area. It is thus recommended that Periodic and constant monitoring of Oyun river water and sediment samples is desirable to ensure that good quality standards are achieved. Maintenance and sanitation policies should be put in place for both inhabitants and visitors to avoid dumping of waste in River Oyun catchment

REFERENCES

1. lbe, K.M.; Sowa, A.H.O.; Osondu, O.C. *Nigeria J. Min. Geol*. **1992**, 28, 87.
2. UNESCO/WHO/UNEP *Water Quality Assessment*, Chapman & Hall: London; **1992**; p 585.
3. Fytianos, K.; Lourantou, A. *North Greece. Environ. Int*. **2004**, 30, 11.
4. Adekola, F.A.; Abdus-Salam, N.; Bale, R.B.; Oladeji, I.O. *Nigerian Chem. Spec. Bioavailab*. **2010**, 22, 43.
5. Loska, K.; Wiechula, D. *Water Air Pollut.* **2002**, 141, 73.
6. Ghrefat, H.; Yusuf, N. *Chemosphere* **2006**, 65, 2114.
7. Forstner, U.; Whitman, G.T.W. *Metal Pollution in the Aquatic Environment*, 2nd ed., Springer-Verlag: New York; **1981**; p 247.
8. Veena, B.; Radhakrishnan, C.K.; Chacko, J. *Ind. J. Mar. Sci*. **1997**, 26, 71.
9. Bunzl, K.; Trautmannsheimer, M.; Schramel, P. *J. Environ. Qual*. **1999**, 28, 1168.
10. Korfali, S.I.; Jurdi, M.S. *Environ. Monit. Assess*. **2010**, p.17.
11. Finney, B.P.; Huh, C.A. *Environ. Sci. Technol*. **1989**, 23, 427.
12. Santchi, P.H. *Limnol. Oceanogr*. **1984**, 29, 1100
13. Basta, N.T.; Ryan, J.A.; Chaney, R.L. *J. Environ. Quality* **2005**, 3, 49.
14. Wuana, R.A.; Okieimen, F.E. *ISRN Ecology* **2011**, 2011, 1-20, Article ID 402647, doi:10.5402/2011/402647.
15. Tessier, A.; Campbell, P.G.; Bisson, M. *Anal. Chem*. **1979**, 51, 844.
16. Horsfall, Jr. M.; Horsfall, M.N.; Ayebaemi, I.S. *Bull. Chem. Soc. Ethiop*. **1999**, 13, 1.

17. AbulKashem, M.D.; Singh, B.R.; Kawai, S. *Nutr.Cycl.Agroecosyst.* **2007**, 77, 187.
18. Uzairu, A.; Harrison, G.F.S.; Balarabe, M.L.; Nnaji, J.C. *Bull. Chem. Soc. Ethiop.* **2009**, 23, 9.
19. Okoro, H.K.; Fatoki, O.S.; Adekola, F.A.; Ximba, B.J.; Synman, R.G. *Chem. Speciat. Bioavail.* **2014**, 26, 126.
20. Inyinbor, A.A.; Adekola, F.A.; Abdul Raheem, A.M.O. *Ethiop. J. Environ. Stud. Manage.* **2012**, 5, 11.
21. Abdus-Salam, N.; Ibrahim, M.S.; Fatoyinbo, F.T. *Waste Manage. Bio-resour. Technol.* **2011**, 1, 21.
22. Fatoki, O.S.; Awofolu, R. *Water SA* **2005**, 31, 87.
23. Bhujr, J. Trace metals in soils irrigated with wastewater in a Periurban Area Downstream Hanoi City, Vietnam, Seminar Paper, Institutional for markvetenskap, Svergieslantbruksuniversitet (SLU), Uppsala, Sweden; **2007**.
24. Fytianos, K.; Lourantou, A. *Environ. Int.* **2004**, 30, 11.
25. Jonathan, O.O.; Mothiba, M. *J. Hydrology* **2005**, 308, 122.