**Geochemical fractionation of metals in the stream sediments from Okemesi-Ijero area, southwestern Nigeria.**

\*Ayodele, O. S., \*\*Oshin, O. O., \*Akinyemi, S. A., \*\*\*Awokunmi, E. E.

\*Department of Geology & Applied Geophysics, Ekiti State University, P.M.B. 5363, Ado Ekiti.

\*\*Department of Chemistry, Ekiti State University, P.M.B 5363, Ado Ekiti

\*\*\*Department of Earth Sciences, Ajayi Crowther University, Oyo.

Email: [samuelayodeleolusiji@yahoo.com](mailto:samuelayodeleolusiji@yahoo.com); [riksam2002@yahoo.com](mailto:riksam2002@yahoo.com)

**Abstract**

The distribution and accumulation of heavy metals in the stream sediments of Okemesi – Ijero area, southwestern Nigeria were investigated. Stream sediment samples from ten locations were collected and characterized for metals content (cadmium, lead, copper, nickel, iron, manganese and zinc). The determination of extractable heavy and macro metals such as, Cd, Pb, Cu, Zn, Ni, Fe and Mn in the stream sediment samples was carried out by atomic absorption spectrometry (AAS). Apart from total concentration, the distribution of the above metals into five fractions: aqueous, exchangeable, bound to inorganic, bound to organic matter, and residual, was studied by means of an analytical procedure involving modified sequential chemical extraction. The results showed that higher susceptibility and bioavailability of Ni with non-lithogenous source were due to their higher percentage in the exchangeable fraction. A significant of Cd, Cu, Mn and Fe in lithogenous fraction may be due to the fact that they can form stable complexes with Fe and Mn oxides. Considerable amount of Ni, Pb and Fe was observed in the organic fraction due to their strong affinity to the organic matters so that they can complex with humic substances in sediments. Principal component analysis (PCA) revealed that high toxic Cd and Pb in polluted sites (i.e. Odo- Owa-2, Ijero/Ipoti, Odo-Owa-5, Erigbe, Oke-Asa-1 and Arapate) may be contributed by anthropogenic sources. This observation is consistent with dendogram hierarchical clustering analysis (DHCA), which could provide more details about contributing sources. This study therefore suggests metal pollution may be related to the socio-economic development in the study sites.

**1. Introduction**

Rapid population growth and urbanization in southwestern Nigeria is envisage to have led to the pollution of aquatic environment, due to largely uncontrolled contaminants discharge into the rivers ecosystem. In a river ecosystem, sediment is a primary concern as related to several important issues including water quality, aquatic habitat and reservoir water-storage capacity (Juracek and Ziegler, 2009). Sediment is an important source of heavy metal pollutants as they have a long residence time (Forstner and Wittmann, 1983). The pollution of sediments is closely linked to contamination of water by domestic sewage, untreated municipal wastewaters, industrial effluents and heavy traffic (Kayastha, 2015). Sediment serves as a sink where contaminants can be stored and also act as a source of the pollutants to the overlying water and to the inhabitants of the ecosystem (aquatic organism). Therefore, it serves as the carrier and reservoir of the heavy metals and reflects the quality of the system (Chapman and Wang, 1999). The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon the grain size, organic matter contents, mineralogical composition and depositional environment of the sediments (Kayastha, 2015 and reference therein). Pollution of heavy metals is a worldwide problem because the metals are in destructive and most of them have toxic effects on living organisms when metals exceed a certain concentration (MacFarlane and Burchette, 2000; Pekey, 2006).

Heavy metals are not permanently fixed on sediments and can be released back to the water column by changes in environmental conditions, such as pH, redox potential, and chelation in the aquatic environment (Sutherland et al., 2007). The mobility and bio-availability of heavy metal in the environment depends on their chemical forms or type of the binding of the element; this approach is very useful for site assessment and risk analysis (Howard and Shu, 1996). Thus, the chemical form of the metals in the sediment is of great significance in determining their remobilization potential (Lopez-Gonzales et al., 2006). Bioavailability and mobilization of heavy metals in aquatic environment does not describe by total metal concentration (Singh, 2003; Zakir et al., 2008). The determination of the total concentration of the metals gives no information on their various forms (Tokalioglu, et al., 1999; Marengo et al., 2006). Therefore, sequential extraction techniques have been developed and applied to the aquatic sediment samples. The use of sequential extractions, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals. Speciation is not only very useful for determining the degree of association of the metals in the sediments and to what extent they may be remobilized into the environment (Kayastha, 2015 and reference therein), but also for distinguishing those metals with a lithogenic origin from those with an anthropogenic origin.

The main objective of this study was to evaluate distribution and accumulation of heavy metals in the sediments of the rivers around Okemesi – Ijero areas, southwestern Nigeria. Sediment samples from ten location were collected and analysed for metal content (i.e. Cd, Pb, Cu, Zn, Ni, Fe and Mn).

**2. Accessibility and drainage system**

The study area lies within latitudes 70 45’N and 80 00’N and longitudes 40 52’E and 50 08’E. It covers part of the topographic map sheet No. 243 (Ilesha N.E. 1:50,000) and sheet No. 244 (Ado N.W. 1:50,000).The study areas cover parts of Ekiti and Osun States, southwestern Nigeria with a total surface area of 821.4km2. The study area is generally accessible through network of all seasonal roads and motorable tracks which links it with other part of the country. Similarly, villages and towns have major and minor roads and also footpaths which are inter-linked to one another. The streams spread out from a central point forming dendritic drainage pattern as a result of its branching, they develop where the cover channels follow the slope of the terrain. Dendritic system forms in V-shaped valleys as a result of the rock types whether porous on non-porous, while the drainage pattern where the topography is dominated by series of ridges is the trellis type which suggests that the drainage is structurally controlled. Major rivers in the study area include river Osun found along Okemesi road, river Oyi which flows in a southerly direction. A waterfall was encountered around Oke-Ila called Ayikunnugba waterfalls and river Isa etc. Most of the streams in the study area are actively flowing while some are stagnant and others have dried channels owing to dry season. The disposition of rivers and stream within the study area is controlled by the following factors namely; the gradient(slope) of the highland, the prevailing climatic conditions, the structural features such as joints, fractures, veins and foliations, geomorphology and physiology of the area and the lithology of the area (Akanni,1992).

**3. Materials and methods**

The sampling density of one sample per 4sqkm2 for the collection of stream sediments samples (Fig. 1). Sediment samples were taken at a depth of 20-25cm; they were bagged and labeled to avoid mix up before transportation to the laboratory. The geographical locations of each sample collected and characteristic features of the stream sediments were noted. The laboratory operations involve pulverization and homogenizing the stream sediment samples using a pulverizer to allow to crush the coarse particles in the sediments after which the milling machine was used for further pulverization until the samples became very fine.

**3.1 Total acid digestion**

Homogenous and grounded bulk sediment samples (0.1 g) are treated with 4ml of an oxidizing mixture (HNO3: HCl =3:1) and 6ml HF in a Teflon recipient put in a microwave oven (800w, 4 min; 20 min. of ventilation). Recovered sample were then treated with 5.6g HBO3 to avoid silica evaporation and diluted to 100ml by distilled/de-ionized water. Metal concentrations in solution were determined by Atomic Absorption Spectrometer (AAS, Perkin Elmer Model 306).

**3.3. Modified single sequential extraction technique**

A five-step sequential extraction procedure was used to determine heavy metal fractions (chemical phases) in the stream sediment. The method is modified and designed to separate the heavy metal into five fractions:

**Aqueous phase (Step I):** 2.5 g of sediment sample was treated with 45ml of ammonium acetate 1M at pH5 with acetic acid under stirring for 24hours at room temperature; suspension was then centrifuged at 300rpm for 20min, diluted to 100ml with distilled/deionised water and analyzed by Atomic Absorption Spectroscopy (AAS).

**Exchangeable phase (Step II):** The residual solid of the previous step was treated with 22.5ml of hydroxyl ammonium acetate followed by acetic acid (25%). After 24h stirring at room temperature solid –liquid separation is performed by centrifugation as before and the metal bearing solution is diluted (to 100ml) and analyzed by AAS.

**Inorganic phase (Step III):** The residual solid of the previous step was treated with 12.5ml of HCl (0.1 M) and stirred for 24 h at room temperature. As in previous steps, solid – liquid separation was performed and the solution diluted to 25 ml was analyzed for metal concentration**.**

**Organic phase (Step IV):** The residual solid of the previous step was treated with 12.5 ml of NaOH (0.5 M) under stirring for 24 h at room temperature for sediment samples with large organic content; this treatment was repeated until a clear solution was obtained. All the solutions separated from the solid were then dried by an IR lamp at 60oC and then digested by using 4ml of HNO3 65% and 2ml HF (40%) in a microwave oven (250w, 1min; ow, 2min; 250w,5min; 400w, 5min; 600w, 5min). The acid solution was then diluted to 25ml and analyzed for metals by AAS.

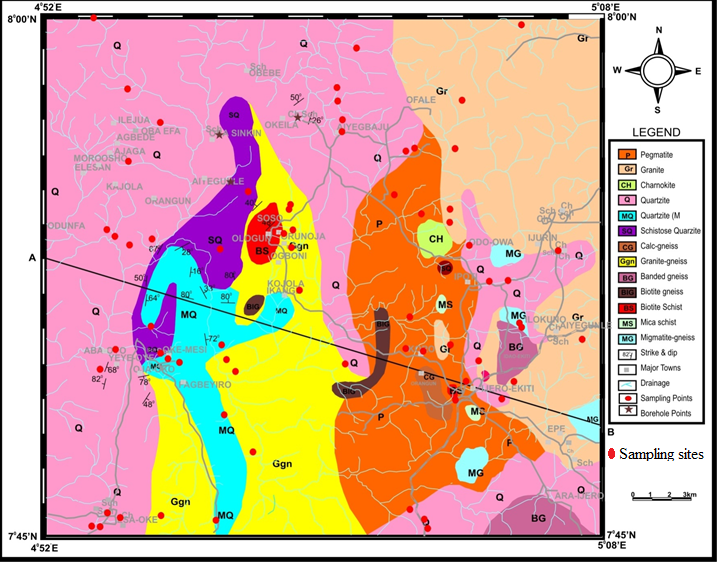


Fig. 1: Stream sediment sampling points.

**Residual (Step V):** The residual solid of the previous step was treated with 12.5ml of HNO3 (8M) and digested for 3h at 80ºC. The solution was then diluted to 25ml and analyzed by AAS for metal concentrations. The residual solid of the fifth step was finally digested as described in section 3.6.2 to determine the metals in the mineralogical matrix. The analysis was done at Atomic Absorption Spectrophotometry (AAS) Laboratory, Centre for Research and Development, Obafemi Awolowo University (O.A.U.) Ile-Ife, Nigeria.

**3.4 Multivariate statistical analysis**

Principal component analysis (PCA) is as an unsupervised pattern recognition method with Varimax rotation and Kaiser normalization, which is widely used to reduce data and extract a small number of latent factors (principal components, PCs) for exploring the possible similar distribution behaviour of metals and analyzing relationships among the observed various variables (Loska and Wiechuła, 2003). PCA is thus applied to analyze relationships among the observed variables and identify heavy metals pollution sources for this study, and it is performed by using the SPSS V17.0 for Windows. DHCA incorporates all variables (heavy metals concentrations) at the same time and could be used to trace similarities and differences of them, which could give more details to further verify the results of the PCA analysis. Dendogram clusters the elements as clustering variable using Euclidian distance and Ward procedure (Laursen et al., 2014). This is depicted as horizontal dendogram (Fig. 3) Then a cut-off and percentage of each dendogram is selected. They define clusters of the objects and of variables.

**4. Results and discussion**

**4.1. Total metal content**

Metal concentrations in the stream sediments from Okemesi – Ijero area are shown in Table 1. It is evidently shown from the data that the concentrations of the seven metals varied as follows: Cd, 1.8 – 2.8mkg-1; Cu, 3.0 - 4.8mgkg-1, Pb, 1.6 – 3.0mgkg-1, Zn, 2.1 – 3.8mgkg-1, Ni, 12.3 – 18.9mgkg-1 and Fe, 29.7 – 55.1mgkg-1.

Table 1: Concentrations of macro and trace elements in the stream studied sediments



Table 2: US NOAA's ERL and ERM concentrations for the studied metals (values are in mg/kg dry weight) (after Ramirez et al., 2005; Turki, 2007).



*N.B: \*\*\* = Values not given*

The mean concentration of Mn, Ni and Pb are lower than those reported in a previous study by Akintola et al. (2014). Conversely, the mean Zn concentration in the study is higher than those obtained from stream sediments contaminated by mining activities in Ibodi, southwestern, Nigeria (Akintola et al., 2014). The mean concentration of all metals decrease in order of Fe > Ni > Mn > Cu > Zn > Cd >Pb. In order to appraise the possible environmental consequences of the investigated metals, results shown in Table 1 were also compared to US NOAA's sediment quality guidelines (Ramirez et al., 2005; Turki, 2007; and reference therein)(Table 2). In this study the effects range-low (ERL) and effects range- median (ERM) concentrations are considered. The ERL represents chemical concentrations below which adverse biological effects were rarely observed, while ERM represents concentrations above which effects were more frequently observed. Generally, adverse effects occurred in less than 10% of studies in which concentrations were below the respective ERL values, and were observed in more than 75% of studies in which concentrations exceeded EMR values (Long et al., 1997). ELR and EMR values for the metals are shown in Table 2. Comparing results of the present study with ERL and ERM values, all metals showed lower concentration than ERM. Likewise, all metals with the exception of Cd showed lower concentration than ERL. In the case of Cd, all the studied sites showed higher concentration than the ERL values. Considering that toxicity is a function also of the degree to which data exceed ERM values (Turki, 2007), therefore some environmental or toxicological effects of Cd studied sites, cannot be expected.

**4.1. Chemical fractionation results**

Figure 2 shows the distribution of the studied metals in the five extractable fractions in percent bar graphs. The partitioning shows that the percentages of metals associated with the non-lithogenous fractions (aqueous + exchangeable+ adsorbed on inorganics+ associated organics) (Table 4) were notably greater for Cd, Pb, Ni, Mn and Fe in all studied sites than those of the lithogenous fraction suggesting that these metals are predominantly derived from anthropogenic inputs rather than the geochemical background. On the other hand, Cu is considerably greater in lithogenous fraction that non-lithogenous fraction indicating geochemical sources. Therefore, the results show that such metals are potentially more available for exchange and/or release into the coastal environment. The studied macro and trace metals in the non-lithogenous fractions increased in the order of Cu > Pb > Cd > Zn > Mn > Ni >Fe (Table 3).

4.1.1 Cadmium

The sediments lithogenous fraction is dominated by Cd, which accounts for over 31.9% of the total Cd concentration. Among the non-lithogenous fractions, the adsorbed on inorganic phases was much more important than other fractions, which account for about 30% of the total Cd. The second in the order is aqueous phase which accounted for 15.3% of the total Cd concentration. The absorption at the organics phase is higher than the exchangeable phase (Fig. 2 & Table 4). The insignificant amount of Cd at the exchangeable phase, indicates there is a lesser degree of bioavailability for high toxic Cd. This fact allows the conclusion that the Cd fraction was bound to the inorganic phase (i.e. carbonate phases). This hypothesis is in accordance with the literature data (Todorović et al., 2014).



Fig. 2. Results of the percentage distribution of Cd, Cu, Pb and Zn in the five extracted phases in stream sediments.



Fig. 2 (contd.). Results of the percentage distribution of Ni, Mn and Fe in the five extracted phases in stream sediments.

4.1.2 Copper

Cu dominates the lithogenous fraction of the sediments, accounting for 50.9% of the total Cu concentration. This is indicating that an appreciable amount of Cu is likely to be incorporated in aluminosilicate minerals and it is relatively insensitive to the change of surrounding conditions (Nemati et al., 2011). This is followed by exchangeable phase among the non-lithogenous fraction, with average percentage of 14.9% of the total Cu concentration. Absorption at the bound to inorganic phases accounted for 13.9%, this is followed by bound to organic phases (12.1%) (Fig. 2 & Table 4). The least percentage of Cu is found in the bound to aqueous phase (i.e. 8.2%) of the sediments. Despite high stability constants of the organic Cu compounds (Han et al., 1996; Todorović et al., 2014) the association of Cu with the organic matters appeared to be less pronounced due to low content of the organic matters in these sediments. Therefore, when the content of the organic matter is low, the residual fraction might become more significant for binding Cu.

4.1.3 Lead

Significant amounts of Pb were extracted from the aqueous phase (i.e. 31.3%), among the non-lithogenous fractions of the sediments. This is followed by the lithogenous fraction, which accounts for about 20.8% of the total Pb concentration. The percentage of Pb associated with other non-lithogenous fractions in the sediments from all sites was in the order: exchangeable (20.2%) > organics (17.5%) > inorganic (10.1%) (Fig. 2 & Table 4). Pb is tightly bound under strongly reducing conditions by sulfide mineral precipitation and complexion with insoluble organic matter, and is very effectively immobilized by precipitated iron oxide minerals under well-oxidized conditions (Gambrell et al., 1991).Inorganic lead compounds are sulfide, carbonate, and sulfate minerals) are commonly abundant in sediment but have low solubilities in natural water. Relative abundance of Pb in the exchangeable fraction is in agreement with the available data in the literature (Todorović et al., 2014).

Table 3: Means and medians of metal concentrations in five operationally defined geochemical fractions (mg Kg-1).



4.1.3 Zinc

Substantial percentage of Zn were extracted from aqueous phase (i.e. 30.82%), among the non-lithogenous fractions of the sediments. The amounts of Zn associated with other non-lithogenous fractions in the sediments from all the sites was in the order: exchangeable (22.42%) > inorganic (19.65%) > organic (16.95%) (Fig. 2 & Table 4). Although, the percentage of Zn associated with lithogenous fraction accounts for 10.24% of Zn concentration. The inorganic phase are metals associated with sulfide, sulfate and carbonates; the calcium carbonate was a strong absorbent to form complexes with Zn as double salts (CaCO3•ZnCO3) in the sediments. The Zn co-precipitation with the carbonates may become an important chemical form, especially when the hydrous iron oxide and the organic matter are less abundant in the sediment. Zn is readily adsorbed by clay minerals, carbonates or hydrous oxides and it is more mobile than Pb due to its relatively high mobility (Rodríguez et al., 2009).

4.1.4 Nickel

In this study, large amounts of Ni was concentrated in the exchangeable phase (35.49%), among the non-lithogenous fractions of the sediments. The percentage of Ni in other non-lithogenous fraction in the sediments from all sites was in the order: organic phase (29.36%) > aqueous phase (12.07%) > inorganic phase (10.39%) (Fig. 2 & Table 4). The lithogenous fraction in the sediments accounts for over 12.96% of total Ni concentration. This is consistent with available data in literature (Ma et al., 2016). The large portion of Ni in exchangeable fraction may be is the result of anthropogenic inputs from combustion of fossil fuels. Ni can be contributed by natural rocks as well as anthropogenic sources (Adamo et al., 1996; Ma et al., 2016). This is in accordance with available data in the literature (Todorović et al., 2014). Metals accumulated in exchangeable fraction can return to waters in the suspended or dissolved form and represent a potential risk for an aquatic ecology as well as the environment (Zakir and Shikazono, 2011).

4.1.5 Manganese and Iron

Manganese is mostly concentrated in the lithogenous fraction of the sediments, accounting for over 50 % of total Mn concentration. The amounts of Mn in non-lithogenous fraction of the sediments from all the sites was in the order: inorganic phase (20.59%) > exchangeable phase (14.71%) > organic phase (8.82%) > aqueous phase (5.88%) (Fig. 2 & Table 4). The sediments have more Mn in the not easily mobilized fraction. In the case of Fe, is typically concentrated in the lithogenous fraction. This accounts for over 37.64% of total Mn concentration. The average percentage of Fe in the non-lithogenous fraction of the sediments from all the sites was in the order: aqueous phase (24.54%) > organic phase (24.22%) > exchangeable phase (8.77%) > inorganic phase (4.83%). The recoverable amount of Fe in the exchangeable fraction is very low but Mn is relatively high in the exchangeable fraction. This is in accordance with available data in the literature (Zakir and Shikazono, 2011).

**4.2. Multivariate analysis results**

The obtained geochemical extraction data for the ten investigated sediment samples (Table 3) were submitted to the multivariate analysis using SPSS 17 version. The factor analysis was expected to define the significance of macroelements (Fe and Mn) as markers for predicting the binding behavior of the investigated microelements (Ni, Pb, Cd, Cu and Zn). The factor observed the second step extraction (exchangeable metals), together with the corresponding variance values representing the percentage of the samples which may be characterized, only on the basis of parameters involved in the factor under consideration. Based on the up-to-date statistical investigations, the results of the factor analysis after varimax rotation were shown to be more suitable for application. According to the principles of the factor analysis only parameters, the loadings of which are higher than (0.4), are valuable for defining a factor.

4.2.1.1 Metals bound to aqueous phase

Macro and micro metals extracted in the aqueous fractions (Figure 3) are separated into two clusters. One is Ni, which is far from other cluster, and very close to the point of Fe indicating that Ni could be abundantly incorporated into amorphous iron oxyhydroxide. The second are Zn, Mn, Cu, Pb and Cd are connected in the dendogram which suggests their close correlation and similar nature. The principal component analysis of aqueous fractions could not be computed because of zero variance (Table 5).

4.2.1.2 Metals bound to exchangeable phase

Factor loading values of the exchangeable metals in components I, II and III are shown in Table 5. Component I (Table 5) represents 32.94% of the total variance and have high positive loadings for Ni and Cu but show different behaviour within the same groups of cluster in dendogram suggesting different origin. Component II (Table 5) contributes 31.84% to the total variance and characterized by high positive loadings for Zn and Fe. Iron is very close to zinc, which suggest that iron is also of a similar origin as zinc. Their similar behaviour is shown within the same groups of cluster in dendogram (Figure 3). Component III (Table 5) accounts for 19.42% of the total variance and have high positive loadings for Pb and Fe but showed similar behaviour within the same groups of cluster in dendogram (Figure 3). Metals bound to exchangeable are separated into two clusters. One is Ni, which is very far from other cluster, and very close to Fe suggesting a close nature for metals in exchangeable fraction.

Table 4. The mean percentage proportion of metals (%) in the non-lithogenous and lithogenous fractions of the stream sediments



*Lithogenous fractiona= Residual*

*Non-lithogenous = aqueous phase + exchangeable phase + inorganic phase + organic phase.*

The second are Zn, Mn, Cu, Pb and Cd are connected in the dendogram which suggests their close correlation and similar nature (Figure 3). It should be noted that for exchangeable metals the small changes in redox potential or pH of surrounding water can lead to their mobility.

4.2.1.3 Metals bound to inorganic phase

Factor loading values of the metals bound to inorganic phase in components I, II and III are shown in Table 5. Component I (Table 5) accounts for 25.56% of the total variance of data and have positive loadings for Cu and Pb. Their similar behaviour is shown within the same groups of cluster in dendogram (Figure 3). Component II (Table 5) represents 25.55% of the total variance and characterized by positive loadings of Ni and Zn. Their different behaviour is shown within the same groups of cluster in dendogram (Figure 3). Component III (Table 5) contributes 22.11 to the total variance and has high positive loadings only for Fe which suggests a different nature of Fe. The same conclusion can be obviously seen from the dendogram in Figure 3. Metals extracted in the inorganic fractions (Table 5 and Figure 3) are separated into two clusters. One is Ni, which is far from other cluster, and very close to the point of Fe indicating that Ni could be abundantly incorporated into amorphous iron oxyhydroxide. The second are Pb, Cd, Cu and Zn which are very close to manganese which can be carbonate co-precipitated with Mn-oxyhydroxides (Figure 3).

4.2.1.4 Metals bound to organic phase

Factor loading values of the metals bound to organic phase in components I, II and III are shown in Table 5. Component I (Table 5) accounts for 32.05% of the total variance and characterized by positive loadings of Fe and Mn. Their similar behaviour within the same groups of cluster in dendogram is shown in Figure 3. Component II (Table 5) contributes 29.30% to the total variance and have positive loadings of Zn and Cd, both have similar behaviour within the same groups of cluster in dendogram (Figure 3). Component III (Table 5) represents 22.08% of the total variance and have positive loadings for Zn and Cu. They both have similar behaviour within the same groups of cluster in dendogram (Figure 3).

Table 5: Varimax rotated factor loadings matrix and communalities obtained from principal component analysis for five extractable fractions from stream sediments



*N. B. EV=Eigen value, VAR= explained variance, CVAR=cumulative variance explained.*

Metals extracted from organic phase are separated into two clusters. One is Fe, which is far from other cluster, and very close to Mn. The second are Pb, Cu, Cd and Zn could be in nature with insoluble organic matter (Figure 3).

4.2.1.5 Metals bound to residual phase

In the residual phase extraction step, dissolution of crystalline Fe-oxide is partly accompanied by silicates destruction (Polić and Pfendt, 1996). As it is to be expected, iron is the main constituent (Table 1). Factor loading values of the metals bound to residual phase in components I and II are shown in Table 5. Component I (Table 5) contributes 34.73% to the total variance of the data. It has positive loadings only for Fe which suggest a different nature of Fe. This conclusion is supported by the behaviour of Fe within the same of clusters in dendogram (Figure 3).



Fig. 3. Dendrogram cluster analysis of five extractable fractions from stream sediments.

Component II (Table 5) represents 34.04% of the total variance. It is characterize by positive loadings of Cu, Cd and Zn. Cadmium is very close to copper which suggest similar origin. Zinc has similar behaviour within the same groups of cluster in dendogram (Figure 3). Based on the dendogram diagram for the metals fraction bound to the residual phase (detritus silicates, crystalline Fe oxide) (Figure 3) it can be concluded that all extracted metals are bound to crystalline Fe-oxide and silicates as expected for the fifth extraction fraction.

**Conclusions**

Macro and micro metal geochemical fractions and multivariate analysis techniques have been employed for evaluation of stream sediments from Okemesi – Ijero area, southwestern, Nigeria. The results indicates elevated concentrations of Zn, Cd, Pb, and Ni in the studied sites which is ascribed to the anthropogenic inputs from indiscriminate discharge of contaminants and traffic pollution. The above average concentrations of these metals in the studied sites are in the order: Ni: Odo Owa 5 > Arapate > Lawrence; Cd: Lawrence 1 > Odo Owa 2 > Ijero/Ipoti > Odo Owa 5; Pb: Erigbe > Oke Asa 1 > Arapate > Odo Owa 5; Zn: Ijero/Ipoti > Odo Owa 2 > Erigbe > Ipoti 3. The distribution of Cu in the studied sites is controlled by geochemical background. The above average concentrations of the Cu in the studied sites are in the order: Ipoti 3 > Arapate > Odo Owa 5 > Odo Owa 2 > Lawrence 1. Heavy metal pollution is of great concern because of their toxicity threatens to human health and the aquatic ecosystem. It is thus recommended that, these rivers should be put under surveillance since it is one of the major sources of fresh water in the study areas.

**Acknowledgements**

We gratefully acknowledge the technical assistance of final year students who participated in the field work (2014/2015 session). The authors would also like to thank the staff of Atomic Absorption Spectrophotometry (AAS) Laboratory, Centre for Research and Development, Obafemi Awolowo University (O.A.U.) Ile-Ife, Nigeria for metal analysis.

**References**

Adamo, P., Dudka, S., Wilson, M.J., McHardy, W.J., 1996. Chemical and mineralogical forms of Cu and Ni in contaminated soils from the sudbury mining and smelting region, Canada. Environ. Pollut. 91, 11–19.

Akanni, C.O. 1992. Aspect of Climate in Ogun State in maps edited by onakomuye, S.O., Oyesiku, and Jegede, F.J. Ife Journal of Science. Volume 4 (2): 5-6.

Akintola, A. I., Ikhane, P. R., Bankole, S. I., Mosebolatan, O. A. 2014. Preliminary Investigation of Stream Sediments Contaminations Caused by Mining Activities in Ibodi and Its Environs, S/W Nigeria Using Geological and Geochemical Assessment Approach. Environment and Natural Resources Research; Vol. 4, (No. 4), 16 – 27.

Forstner, U., Wittman, G.T.W., 1983, Metal Pollution in Aquatic Environment, Springer-Verlag Berlin, Heidelberg, New York.

Gambrell, R.P., Wiesepape, J.B., Patrick, W.H., Jr., and Duff, M.C., 1991, The effects of pH, redox, and salinity on metal release from a contaminated sediment: Water, Air, and Soil Pollution, v. 57-58, p. 359-367.

Han, B. C., Jeing, W. L., Hung, T. S., Wen, M. Y. 1996. Relationship between copper speciation in sediments and bioaccumulation by matine bivalves of Taiwan. Environmental Pollution, 91 (1996) 33-35.

Howard, J. L., Shu, J., 1996. Sequential extraction analysis of heavy metals using a chelating agent (NTA) to counteract resorption. Environ. Pollut. 91, 89–96.

Juracek, K.E., Ziegler, A.C., 2009. Estimation of sediment sources using selected chemical tracers in the Perry lake basin, Kansas, USA. Intern. J. sediment Research 24, 108-125.

Kayastha, S. P. 2015. Heavy metals Fractionation in Bagmati River Sediments, Nepal. Journal of Hydrology and Meteorology, Vol. 9, No. 1, 119 – 128.

Laursen, J., Milman, N., Pind, N., Pedersen, H., Mulvad, G., 2014. The association between content of the elements S, Cl, K, Fe, Cu, Zn and Br in normal and cirrhotic liver tissue from Danes and Greenlandic Inuit examined by dual hierarchical clustering analysis. J. Trace Elem. Med. Biol. 28, 50–55.

Long, E. R., Field, L. J. and McDoland, D. D. (1997) Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ, Toxicol. Chem., 17 (4): 714-727.

Lopez-Gonzalez, N., Borrego, J., Morales, J. A., Carro, O., Lozano-Soria, O., 2006 Metal fractionation in oxic sediments of an estuary affected by acid mine drainage (south western Spain), Estuar. Coast. Shelf Sci., 68: 297-304.

Loska, K., Wiechuła, D., 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere 51, 723–733.

Ma, Xi., Zuoa, H., Tiana, M., Zhanga, L., Menga, J., Zhoua, Xu., Mina, N., Changa, Xi., Liu, Y. 2016. Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere 144, 264–272.

MacFarlane, G.R., Burchette, M.D., 2000. Cellular distribution of Cu, Pb and Zn in the Grey Mangroove Avicennia marina (Forsk). Vierh Aqua. Bot., 68, 45- 59.

Marengo, E., Gennaro, M.C., Robotti, E., Rossanigo, P., Rinaudo, C., Roz- Gastaldi, M., 2006. Investigation of anthropic effects connected with metal ions concentration, organic matter and grain size in Bormida river sediments. Anal.Chim. Acta. 560,172–183.

Pekey, H., 2006. The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Marine Pollution Bulletin, 52: 1197- 1208.

Polić, P., Pfendt, P. 1996. Alluvial aquifer contamination: Carbonates and easily reducible oxyhydroxides as heavy metal substrates. Journal of the Serbian Chemical Society, 61 (11), 1001-1013.

Ramirez, M., Serena, M., Frache, R. and Correa, J. (2005) Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile, Mar. Pollut. Bull., 50: 62- 72.

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. J. Environ. Manage. 90, 1106–1116.

Singh, M., Muller, G., and Singh, I.B., 2003, Geogenic distribution and baseline concentration of heavy metals in sediments of the Ganges river, India, J. Geochem. Explor. 80: 1–17.

Sutherland, R.A., Tack, F.M.G., 2007. Sequential extraction of lead from grain size fractionated river sediments using the optimized BCR Procedure. Water Air Soil Pollut. 84,269–284. Tessier, P.G.C. Campbell, M. Bisson, 1979

Todorović, Z. B., Ranđelović, L. M., Marjanović, J. Z., Todorović, V. M., Cakić, M. D., Cvetkovic, O. G. 2014. The assessment and distribution of heavy metals in surface sediments from the reservoir “Barje” (Serbia) Advanced Technology 3(2), 85-95.

Tokalioglu,S., Kartal,S., Elçi, L., 2000. Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. Anal. Chimica Acta, 413, 33– 40.

Turki, A. J. 2007. Metal Speciation (Cd, Cu, Pb and Zn) in Sediments from Al Shabab Lagoon, Jeddah, Saudi Arabia. JKAU: Mar. Sci., Vol. 18, pp: 191-210.

Zakir, H. M., and Shikazono, N. 2011. Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river. Journal of Environmental Chemistry and Ecotoxicology Vol. 3(5), pp. 116-126.

Zakir, H.M, Shikazono, N., Otomo, K., 2008. Geochemical distribution of trace metals and assessment of anthropogenic pollution in sediments of Old Nakagawa River, Tokyo, Japan. Am. J. Environ. Sci., 4(6): 661-672.