Appraisal of Heavy Metals Pollution in the Stream Sediments from Okemesi-Ijero Area, Southwestern Nigeria: Insight from Geochemical Fractionations and Multivariate Analysis Techniques

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ABSTRACT

The distribution and accumulation of heavy metals in the stream sediments of Okemesi – Ijero area, southwestern Nigeria was examined. Stream sediment samples from ten sites were characterized for metals content such as cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), iron (Fe), manganese (Mn) and zinc (Zn). The extractable heavy and macro metals such as, Cd, Pb, Cu, Zn, Ni, Fe and Mn in the stream sediment samples were analysed using atomic absorption spectrometry (AAS). Apart from total concentration, the general distribution of these metals into five physico-chemical phases such as aqueous, exchangeable, bound to inorganic, bound to organic matter, and residual was explored using modified sequential chemical extraction scheme. The results showed higher vulnerability and bioavailability of Ni with non-lithogenous source. This was due to its higher percentage in the most mobile fraction. A significant amount of Cd, Cu, Mn and Fe in lithogenous fraction could be attributed to formation of stable complexes with Fe and Mn oxides. Considerable amount of Ni, Pb and Fe existed in the organic fraction due to their preference to the organic matters which often can form complex with humic substances. Principal component analysis (PCA) result reveals high concentration of Cd and Pb in study sites such as Odo-Owa-2, Ijero/Ipoti, Odo-Owa-5, Erigbe, Oke-Asa-1 and Arapate which could be contributed by anthropogenic sources. This result pattern is consistent with clustering groups, which could provide more information about contributing sources. Therefore, suggests heavy metal contamination could be linked to the socio-economic activities around the stream's catchment.

Key words: Assessment, Heavy metals, Stream sediment, Geochemical fractionations and Multivariate analysis.

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INTRODUCTION

Rapid population growth and urbanization in southwestern Nigeria is envisaged to have led to the pollution of aquatic environment, due to largely uncontrolled contaminants discharge into the river's ecosystem. In a river ecosystem, sediment is a main concern as related to issues such as 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 sink of the

pollutants to the water body and inhabitants of the ecosystem (that is, aquatic organism). Therefore, its transport and stockpile heavy metals and consequently reveals the quality of the water system (Chapman and Wang, 1999). The concentration of heavy metals in sediments depends not only on anthropogenic/non-lithogenic and lithogenic sources. Nonetheless, it also depends on the grain size, organic matter, mineralogy and depositional environment of the sediments (Kayastha, 2015 and reference therein). Heavy metals pollution is a major environmental challenge throughout the world. This is due to its destructive and harmful effects on living organisms when their concentrations exceed a permissible limits (MacFarlane and Burchette, 2000; Pekey, 2006). Heavy metals previously fixed on sediments could be released to the water body due to changes in environmental conditions. For instance, pH, redox potential and chelation in the aquatic ecosystem (Sutherland et al., 2007).

The mobility and bio-accessibility of heavy metals depends on their chemical forms or type of the binding. This practice is very appropriate for site assessment and risk analysis (Howard and Shu, 1996). Thus, the physico-chemical forms of the metals in the sediment are of great importance in evaluating their mobility potential (Lopez-Gonzales et al., 2006). Bioavailability and mobility of heavy metals in aquatic environment is not appropriately described by total metal concentration (Singh, 2003; Zakir et al., 2008). The determination of the total concentration of the metals gives no indications on their various forms (Tokalioglu et al., 1999; Marengo et al., 2006). Therefore, sequential chemical extraction approach have been considered, developed and applied to the aquatic sediments. Sequential chemical extractions, although rigorous, furnishes comprehensive information about the source, mode of occurrence, biological and physico-chemical availability, mobility and transport of trace metals. Chemical extraction is very useful for evaluating the degree of association of the metals and also determine the extent of remobilization in the environment (Kayastha, 2015 and reference therein). Furthermore, it could be used for distinguishing between those metals from lithogenic and non-lithogenous (that is, anthropogenic sources). The study purposively examined the study of heavy metals in different physico-chemical phases in the sediments of the rivers around Okemesi – Ijero areas, southwestern Nigeria. Sediment samples were obtained from ten locations and analysed for metal content which includes Cd, Pb, Cu, Zn, Ni, Fe and Mn.

ACCESSIBILITY AND DRAINAGE SYSTEM

The study area lies within Latitudes 7^0 45'N and 8^0 00'N and Longitudes 4^0 52'E and 5^0 08'E. The study areas is 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 areas cover parts of Ekiti and Osun States, southwestern

Nigeria with a total surface area of 821.4km². Accessibility is 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 includes River Osun which is 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 rivers are actively flowing but some are stagnant and others have dried out channels attributed to direct evaporation during dry season. The nature of rivers is controlled by the gradient (slope), the prevailing climatic conditions, the structural features (such as joints, fractures, veins and foliations), geomorphology and physiology and the lithology (Akanni, 1992).

MATERIALS AND METHODS

The sampling density of one sample per 4sqkm² for the collection of stream sediments samples (Figure 1). Samples were obtained at a depth of 20 to 25 cm; 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 samples were pulverized and milled into homogenous and fine materials.

Total Acid Digestion

Pulverised samples (0.1 g) are dissolved using 4ml of an oxidizing mixture (HNO_3: HCl =3:1) and 6 ml HF was added. The solution in a Teflon recipient was put in a microwave oven (800w, 4 min; 20 min. of ventilation). The samples were treated with 5.6 g HBO_3 to avoid silica evaporation and diluted to 100 ml by distilled/de-ionized water. The solutions were analyzed for selected metals using Atomic Absorption Spectrometer (AAS, Perkin Elmer Model 306).

Modified Single Sequential Extraction Technique

A five-step modified chemical extraction procedure was applied to evaluate heavy metal fractions (chemical phases) in the river sediments. The method is designed/ formulated to separate the heavy metals into the following five fractions.
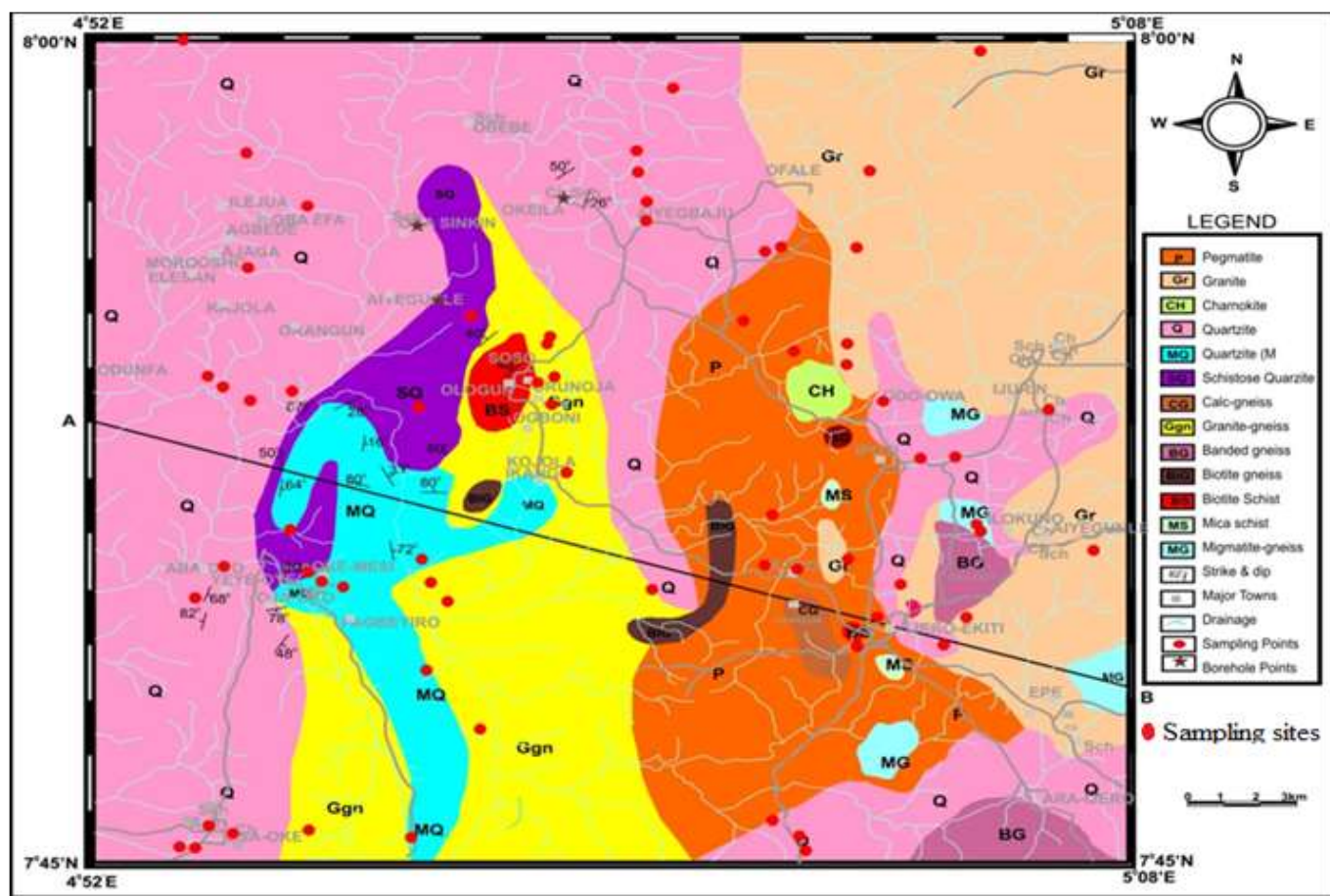
Figure 1. Stream sediment sampling points.

Aqueous Phase (Step I)

45 ml of 1 M ammonium acetate adjusted to pH5 with acetic acid was added to 2.5 g of samples. The mixture was stirred for 24 h at a room temperature. The suspension was then centrifuged at 300 rpm for 20 min, filtered and diluted to 100 ml with distilled/deionised water. The solution was analyzed for considered metals using Atomic Absorption Spectroscopy (AAS).

Exchangeable Phase (Step II)

22.5 ml of hydroxyl ammonium acetate was added to residue from previous step and followed by acetic acid (25%). After 24 h stirring at a room temperature, the solution was centrifuged and filtered through micro pore membrane. The solution was diluted to 100 ml by deionised water and analyzed for heavy metals using AAS.

Inorganic Phase (Step III)

12.5 ml of HCl (0.1 M) was added to residue from exchangeable phase and stirred for 24 h at room temperature. The solution was centrifuged, filtered through micro pore membrane. The solution was diluted to 100 ml with deionised water and analysed for heavy metals using AAS.

Organic Phase (Step IV)

12.5 ml of NaOH (0.5 M) was added to residue from previous step and stirred for 24 h at a room temperature. For sediment samples with large organic content, this procedure was repeated until a clear solution was obtained. All the solutions separated from the solid were then dried using IR lamp at 60ºC and dissolved using 4 ml of HNO_3 (65%) and 2 ml HF (40%) in a microwave oven (250 w, 1min; ow, 2 min; 250w, 5 min; 400w, 5 min; 600w, 5 min). The solution was diluted to 25 ml and analyzed for heavy metals using AAS.

Residual (Step V)

12.5 ml of HNO_3 (8 M) was added to residue from previous step and digested for 3 h at 80ºC. The solution was diluted to 25 ml and analyzed for heavy metals using AAS. The

residual solid from the step V was finally digested as described in section 3.6.2. The analysis was done at Atomic Absorption Spectrophotometry (AAS) Laboratory, Centre for Research and Development, Obafemi Awolowo University (O.A.U.) Ile-Ife, Nigeria.

Multivariate Statistical Analysis

Principal component analysis (PCA) is as an unverified pattern recognition method using Varimax rotation and Kaiser normalization. This is used for data reduction and extraction of small number of principal components. This is used for investigating the probable similar distribution behaviour of metals and analyzing relationships among the numerous variables (Loska and Wiechuła, 2003). PCA is used to evaluate interactions among the variables and identify heavy metals pollution sources. In this study, it is carried out using the SPSS V17.0 for Windows. Cluster analysis combines all variables together and could be used to trace similarities and differences between the observed data sets. This could also give more clues to further corroborate the results of the PCA analysis. Dendogram clusters of the elements using Euclidian distance and Ward procedure (Laursen et al., 2014). This is illustrated as horizontal dendogram (Figure 3).

RESULTS AND DISCUSSION

Total Metal Content

Metal contents in the stream sediments from Okemesi – Ijero areas 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 – 2.8 mkg⁻¹; Cu, 3.0 -4.8 mgkg⁻¹, Pb, 1.6 – 3.0 mgkg⁻¹, Zn, 2.1 – 3.8 mgkg⁻¹, Ni, 12.3 – 18.9 mgkg⁻¹ and Fe, 29.7 – 55.1 mgkg⁻¹. The average content of Mn, Ni and Pb are lower than those documented in a study done by Akintola et al. (2014). Conversely, the mean Zn concentration obtained is higher than those reported from stream sediments contaminated by mining activities in Ibodi, southwestern, Nigeria (Akintola et al., 2014). The average contents of all considered metals decreased in the order of Fe > Ni > Mn > Cu > Zn > Cd >Pb. In order to appraise the likely environmental concerns of the selected metals, results shown in Table 1 were compared to US NOAA's sediment quality guidelines (Ramirez et al., 2005; Turki, 2007) (Table 2). In this study, the effects range-low (ERL) and effects range- median (ERM) contents was used. The ERL signifies chemical contents below which adverse biological effects were rarely seen but ERM characterizes contents above which effects were more usually observed. Mostly, the adverse effects take place in < 10% of studies in which concentrations were below the respective ERL values. On the other hand, it was observed in > 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. All the investigated metals have lower concentration when compared with ERM values. Likewise, all metals with the exception of Cd showed lower concentration when compared with ERL. In the case of Cd, all the studied sites showed higher concentration than the ERL values. Turki (2007) indicated that the toxicity is a function also of the degree to which data exceed ERM values. Therefore, some environmental or toxicological effects of Cd studied sites cannot be expected.

Chemical Fractionation Results

Figure 2 depicts the distribution of the studied metals in the five extractable fractions in percent bar graphs. The partitioning reveals 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. This indicated that these metals were predominantly derived from anthropogenic inputs somewhat than the geochemical sources. 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 possibly available for exchange and/or release into the coastal environment. The selected metals in the non-lithogenous fractions increased in the order of Cu > Pb > Cd > Zn > Mn > Ni >Fe (Table 3).

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 significant 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 (Figure 2 and Table 4). The insignificant amount of Cd at the exchangeable phase indicates lesser amount of bioavailable cadmium. From the above mentioned fact, it can be indicated that the Cd is bound to the inorganic phase (that is, carbonate phases). This suggestion is in accordance with the available literature data (Todorović et al., 2014).

Copper

Cu dominates the lithogenous fraction of the sediments, accounting for 50.9% of the total Cu concentration. This indicates that a considerable amount of Cu is expectedly bound to aluminosilicate minerals. This bounded Cu is somewhat unaffected towards the change of environment conditions (Nemati et al., 2011). This is followed by

Table 1. Contents of macro and trace elements in the studied samples.

Locations	Cd	Cu	Pb	Zn	Ni	Mn	Fe
Odo Owa 2	2.0	4.8	2.8	2.1	18.3	6.1	33.8
Odo Owa 5	2.0	3.7	1.6	3.8	15.4	8.7	29.7
Oke-Asa 1	1.8	2.8	1.8	3.0	18.9	4.8	40.6
Ijero/Ipoti	2.0	4.2	1.9	3.3	14.3	5.1	44.9
Ipoti 3	2.3	4.1	3.0	3.0	14.6	5.5	52.4
Soso	1.9	4.5	2.2	2.8	16.4	5.2	48.0
Lawrence 1	2.3	3.8	2.1	2.6	13.5	4.0	55.1
Lawrence 2	2.2	3.2	2.1	2.8	14.7	4.5	29.9
Erigbe	2.8	3.0	2.0	2.2	13.0	5.2	60.0
Arapate	2.4	3.2	2.0	2.3	12.3	5.0	46.1
Mean	2.2	3.7	2.2	2.8	15.1	5.4	44.1
Stdev.	0.29	0.67	0.43	0.52	2.17	1.28	10.49

Table 2. United State National Oceanic Atmospheric Administration's effect range low (ERL) and effects range median (ERM) concentrations for the studied metals (values are in mg/kg dry weight) (after Ramirez et al., 2005; Turki, 2007).

Metals	ERL (mg/kg)	ERM (mg/kg)
Cd	1.2	9.6
Cu	34	270
Pb	46.7	218.0
Zn	150	410
Mn	***	***
Ni	20.9	51.6
Fe	***	***

N.B: *** = Values not given.
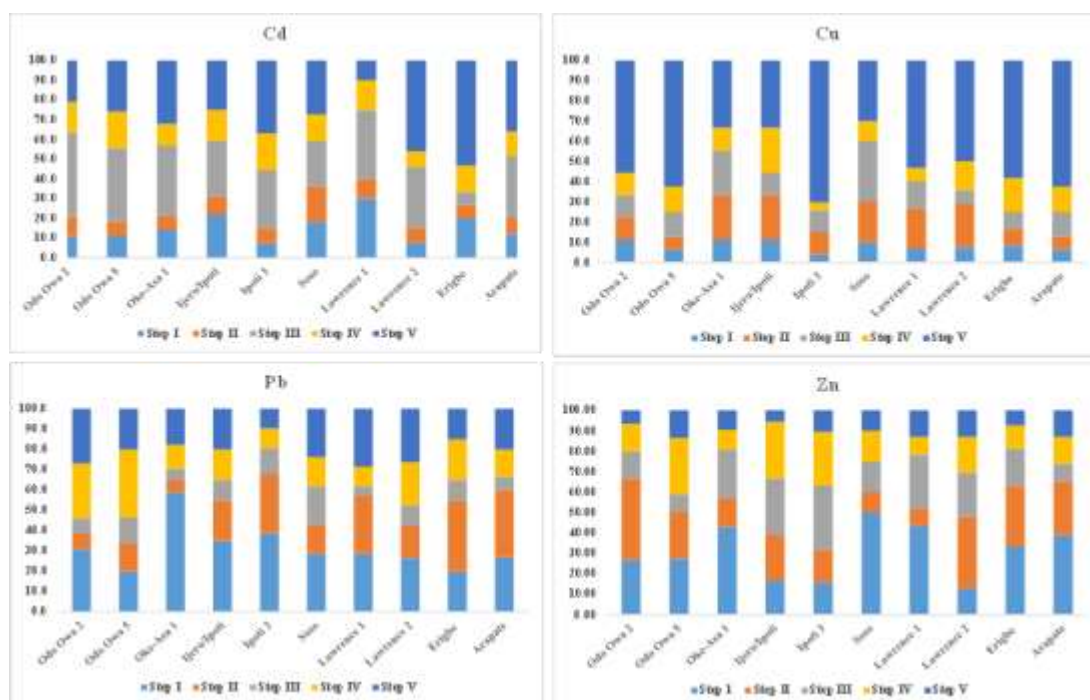
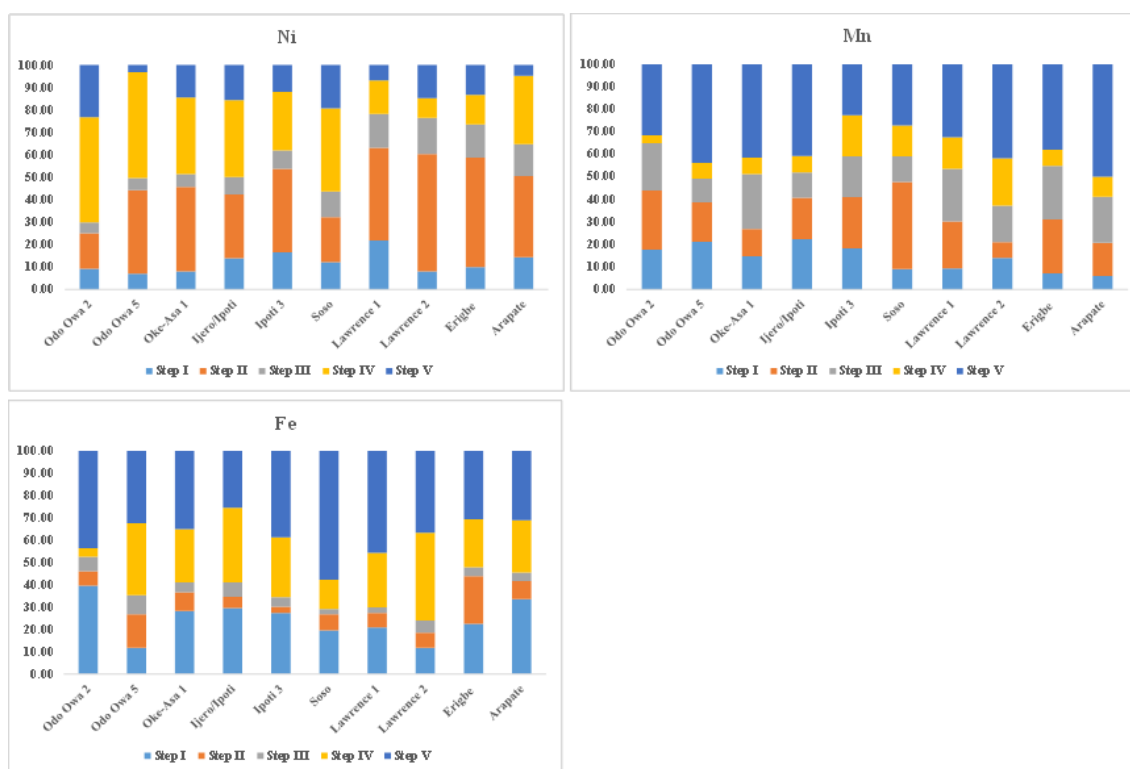**Figure 2.** Percentage distribution of Cd, Cu, Pb and Zn in the five geochemical phases in stream sediments.

Figure 2: Contd.

Table 3. Averages and medians of metal contents in five geochemical fractions (mg Kg^{-1}).

		Step 1	Step II	Step III	Step IV	Step V
		0.36	0.22	0.74	0.34	0.75
Cd	Stdev.	0.17	0.08	0.27	0.12	0.29
	Median	0.30	0.20	0.80	0.30	0.80
	Mean	0.1	0.19	0.18	0.15	0.75
Cu	Stdev.	1.4E-17	0.08	0.07	0.05	0.46
	Median	0.1	0.2	0.2	0.15	0.7
	Mean	0.65	0.42	0.21	0.35	0.42
Pb	Stdev.	0.28	0.25	0.11	0.16	0.15
	Median	0.6	0.35	0.2	0.3	0.35
	Mean	0.66	0.47	0.41	0.35	0.22
Zn	Stdev.	0.31	0.23	0.17	0.14	0.08
	Median	0.75	0.45	0.50	0.30	0.20
	Mean	1.60	4.73	1.36	4.04	1.78
Ni	Stdev.	0.58	1.56	0.53	2.15	1.05
	Median	1.50	4.90	1.30	3.75	1.70
	Mean	0.67	0.94	0.81	0.48	1.69
Mn	Stdev.	0.37	0.44	0.23	0.23	0.44
	Median	0.60	1.00	0.75	0.40	1.70
	Mean	8.11	2.87	1.43	7.69	12.26
Fe	Stdev.	3.33	2.56	0.39	3.42	4.72
	Median	9.00	2.15	1.45	9.10	11.15

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%) (Figure 2 and Table 4). The least percentage of Cu is found in the bound to aqueous phase (that is, 8.2%) of the sediments. In spite of high stability constants of the organic Cu compounds (Han et al., 1996;

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

Locations	Cd		Cu		Pb		Zn	
	Non-lithogenous fraction[a]	Lithogenous fraction[b]	Non-lithogenous fraction[a]	Lithogenous fraction[b]	Non-lithogenous fraction[a]	Lithogenous fraction[b]	Non-lithogenous fraction[a]	Lithogenous fraction[b]
Odo Owa 2	78.95	21.05	44.44	55.56	73.08	26.92	93.33	6.67
Odo Owa 5	74.07	25.93	37.50	62.50	80.00	20.00	86.36	13.64
Oke-Asa 1	67.86	32.14	66.67	33.33	82.35	17.65	90.48	9.52
Ijero/Ipoti	75.00	25.00	66.67	33.33	80.00	20.00	94.44	5.56
Ipoti 3	62.96	37.04	29.63	70.37	90.32	9.68	89.47	10.53
Soso	72.73	27.27	70.00	30.00	76.19	23.81	90.00	10.00
Lawrence 1	90.00	10.00	46.67	53.33	71.43	28.57	86.96	13.04
Lawrence 2	53.85	46.15	50.00	50.00	73.68	26.32	86.96	13.04
Erigbe	46.67	53.33	41.67	58.33	85.00	15.00	92.59	7.41
Arapate	64.00	36.00	37.50	62.50	80.00	20.00	86.96	13.04
Mean	68.61	31.39	49.07	50.93	79.21	20.79	89.76	10.24
Stdev.	12.5	12.5	14.1	14.1	5.8	5.8	3.0	3.0

Lithogenous fraction[a]= Residual. Non-lithogenous = aqueous phase + exchangeable phase + inorganic phase + organic phase.

Table 4: (Contd.).

Locations	Ni		Mn		Fe	
	Non-lithogenous fraction[a]	Lithogenous fraction[b]	Non-lithogenous fraction[a]	Lithogenous fraction[b]	Non-lithogenous fraction[a]	Lithogenous fraction[b]
Odo Owa 2	76.83	23.17	68.42	31.58	56.49	43.51
Odo Owa 5	96.90	3.10	56.14	43.86	67.72	32.28
Oke-Asa 1	85.55	14.45	58.54	41.46	64.95	35.05
Ijero/Ipoti	84.48	15.52	59.26	40.74	74.60	25.40
Ipoti 3	88.06	11.94	77.27	22.73	61.32	38.68
Soso	80.71	19.29	72.73	27.27	42.26	57.74
Lawrence 1	93.23	6.77	67.44	32.56	54.46	45.54
Lawrence 2	85.29	14.71	58.14	41.86	63.44	36.56
Erigbe	86.78	13.22	61.90	38.10	69.36	30.64
Arapate	95.24	4.76	50.00	50.00	68.99	31.01
Mean	87.31	12.69	62.98	37.02	62.36	37.64
Stdev.	6.3	6.3	8.3	8.31	9.3	9.3

Lithogenous fraction[a]= Residual. Non-lithogenous = aqueous phase + exchangeable phase + inorganic phase + organic phase.

concentration. This is consistent with available data in literature (Ma et al., 2016). Substantial amount of Ni in the exchangeable fraction could be due to anthropogenic inputs (that is, combustion of fossil fuels). Nickel contents could be added by bedrocks as well as anthropogenic sources (Adamo et al., 1996; Ma et al., 2016).

This is in accordance with the previous study (Todorović et al., 2014). Metals bound to exchangeable fraction can be released to body of water in the suspended or dissolved form. Thus, presents an eventual danger

Todorović et al., 2014), the organic matters bound Cu seemed to be less pronounced which could be attributed to low content of the organic matters. Therefore, low organic matters content in sediment suggest that the residual fraction could significantly binds copper.

Lead

Substantial contents of Pb were present in the aqueous phase (that is, 31.3%) of non-lithogenous fractions. This is followed by the lithogenous fraction, which accounts for about 20.8% of the total Pb content. The percentage of Pb associated with other non-lithogenous fractions in all samples was in the order: exchangeable (20.2%) > organics (17.5%) >inorganic (10.1%) (Figure 2 and Table 4). Pb is tightly bound by sulfide mineral under reducing conditions through precipitation and complexion with insoluble organic matter. On the other hand, it is immobilised by precipitated iron oxide under well-oxidized conditions (Gambrell et al., 1991). Inorganic Pb forms compounds such as sulfide, carbonate, and sulfate minerals. These are universally abundant in sediment nevertheless have low solubilities in natural water. Relative abundance of Pb in the easily mobilised (that is, exchangeable) fraction agreed with the available data in the literature (Todorović et al., 2014).

Zinc

Substantial percentage of Zn was extracted from aqueous phase (that is, 30.82%) of the sediments. The amounts of Zn associated with other non-lithogenous fractions in all samples was in the order: exchangeable (22.42%) > inorganic (19.65%) > organic (16.95%) (Figure 2 and 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 $CaCO_3$ which is strong absorbent and form complexes with Zn as double salts (that is, $CaCO_3 \cdot ZnCO_3$). Zinc co-precipitate with the carbonates which could become an important chemical form; especially when the hydrous iron oxide and the organic matter are less abundant. Zinc is relatively more mobile when compared with Pb and is freely adsorbed by clay minerals, and carbonates or hydrous oxides (Rodríguez et al., 2009).

Nickel

In this study, large amounts of Ni were concentrated in the exchangeable phase (35.49%) of the samples. The amount of Ni in other non-lithogenous fraction in all samples was in the order: organic phase (29.36%) > aqueous phase (12.07%) > inorganic phase (10.39%) (Figure 2 and Table 4). The lithogenous fraction in the sediments accounts for over 12.96% of total Ni

for an aquatic ecosystem (Zakir and Shikazono, 2011).

Manganese and Iron

Manganese is mostly concentrated in the lithogenous fraction of the sediments, which accounts for over 50% of total Mn concentration. The amounts of Mn in the non-lithogenous fraction of all samples was in the order: inorganic phase (20.59%) > exchangeable phase (14.71%) > organic phase (8.82%) > aqueous phase (5.88%) (Figure 2 and Table 4). The sediments have more Mn in the not easily mobilized fraction. Fe however, is concentrated in the lithogenous fraction. This accounts for over 37.64% of total Mn concentration. The average contents of Fe in the non-lithogenous fraction of all samples 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).

Multivariate Analysis Results

The obtained geochemical extraction data for the ten analysed samples (Table 3) were submitted for multivariate analysis using SPSS 17 version. The factor analysis would outline the importance of Fe and Mn as indicators for forecasting the necessary behaviour of the selected metals. The factor showed exchangeable metals together with the corresponding variance values. This represents the proportion of the samples which could be divided only on the basis of selected metals. The results of the factor analysis after varimax rotation were proved to be more appropriate for application. In this study, the loadings which are higher than 0.4 are used for describing a factor.

Metals Bound To Aqueous Phase

Macro and micro metals extracted in the aqueous phase (Figure 3) are divided into two clusters. First cluster is Ni, which is distant from other cluster, and very near to the point of Fe which suggests that Ni could be bound to amorphous iron oxyhydroxide. The second cluster is Zn, Mn, Cu, Pb and Cd which are connected in the dendogram. This indicates their close connection and similar nature. The principal component analysis of aqueous fractions could not be computed because of zero variance (Table 5).

Metals Bound To Exchangeable Phase

Factor loading values for the exchangeable metals in components I, II and III are shown in Table 5. Component I (Table 5) represents 32.94% of the total data variations and have high positive loadings for Ni and Cu.

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

| Step II | | | | | Step III | | | |
Variables	Comp. I	Comp. II	Comp. III	Communalities	Comp. I	Comp. II	Comp. III	Communalities
Ni	0.92			0.78		0.85		0.91
Pb		0.95		0.88	0.94			0.94
Mn	-0.92			0.91	-0.58			0.65
Zn		0.79		0.81		0.62		0.48
Cu	0.45	-0.77		0.90	0.70		-0.53	0.77
Cd	-0.56	-0.65		0.86		-0.80		0.47
Fe		0.76	0.45	0.75			0.95	0.91
EV	2.31	2.23	1.36		1.79	1.79	1.55	
VAR (%)	32.94	31.84	19.42		25.56	25.55	22.11	
CVAR (%)	32.94	64.78	84.20		25.56	51.11	73.22	

| Step IV | | | | | Step V | | |
Variables	Comp. I	Comp. II	Comp. III	Communalities	Comp. I	Comp. II	Communalities
Fe	0.88			0.90	0.94		0.93
Pb	-0.81			0.99	-0.94		0.65
Mn	0.71			0.85		-0.79	0.62
Cd		0.92		0.68		0.74	0.71
Zn		0.89	0.43	0.98		0.72	0.30
Cu			0.99	0.61		0.54	0.91
EV	1.92	1.76	1.33		2.08	2.04	
VAR (%)	32.05	29.30	22.08		34.73	34.04	
CVAR (%)	32.05	61.35	83.43		34.73	68.77	

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

Nevertheless, they show different bonding reaction within the same groups of cluster suggesting different sources. Component II (Table 5) contributes 31.84% to the total data variation and have high positive loadings for Zn and Fe. Iron is near to zinc which suggests a similar behaviour and form of metallic reaction (Figure 3). Component III (Table 5) accounts for 19.42% of the total data variation and have strong loadings for Pb and Fe but showed similar metallic reactivity within the same groups of cluster (Figure 3). Metals bound to exchangeable are separated into two clusters. First cluster shows Ni which is very far from other cluster and very close to Fe. This indicates a similar nature for metals in most mobile fraction. Second cluster comprises of Zn, Mn, Cu, Pb and Cd indicating their close correlation and comparable nature (Figure 3). This fraction contains elements that are mobile and consequently pose more vulnerability to the environment (Quispe et al., 2011).

Metals Bound To Inorganic Phase

Metals bound to inorganic phase are shown in Table 5. Component I (Table 5) accounts for 25.56% of the total data variation and strong loadings for Cu and Pb. Their similar bonding ris eaction is indicated inside the same groups of cluster (Figure 3). Component II (Table 5) represents 25.55% of the total data variation and described by strong loadings for Ni and Zn. Their different reactivity depicted in the same groups of cluster (Figure 3).

Metals Bound To Organic Phase

The obtained factor loadings value of metals bound to organic phase are shown in Table 5. Component I (Table 5) accounts for 32.05% of the total data variation and described by positive loadings of Fe and Mn. Their similar pattern of bonding reactivity in the same groups of cluster is shown in Figure 3. Component II (Table 5) contributes 29.30% to the total variance and has positive loadings of Zn and Cd, both have similar behaviour inside the same groups of cluster (Figure 3). Component III (Table 5) represents 22.08% of the total data variation and has positive loadings for Zn and Cu. They both have similar reactivity pattern in the same groups of cluster (Figure 3). Metals extracted from organic phase are separated into two clusters. One is Fe, which is far from other cluster, and very close to Mn. Second cluster includes Pb, Cu, Cd and Zn which could be in nature with insoluble organic matter (Figure 3).
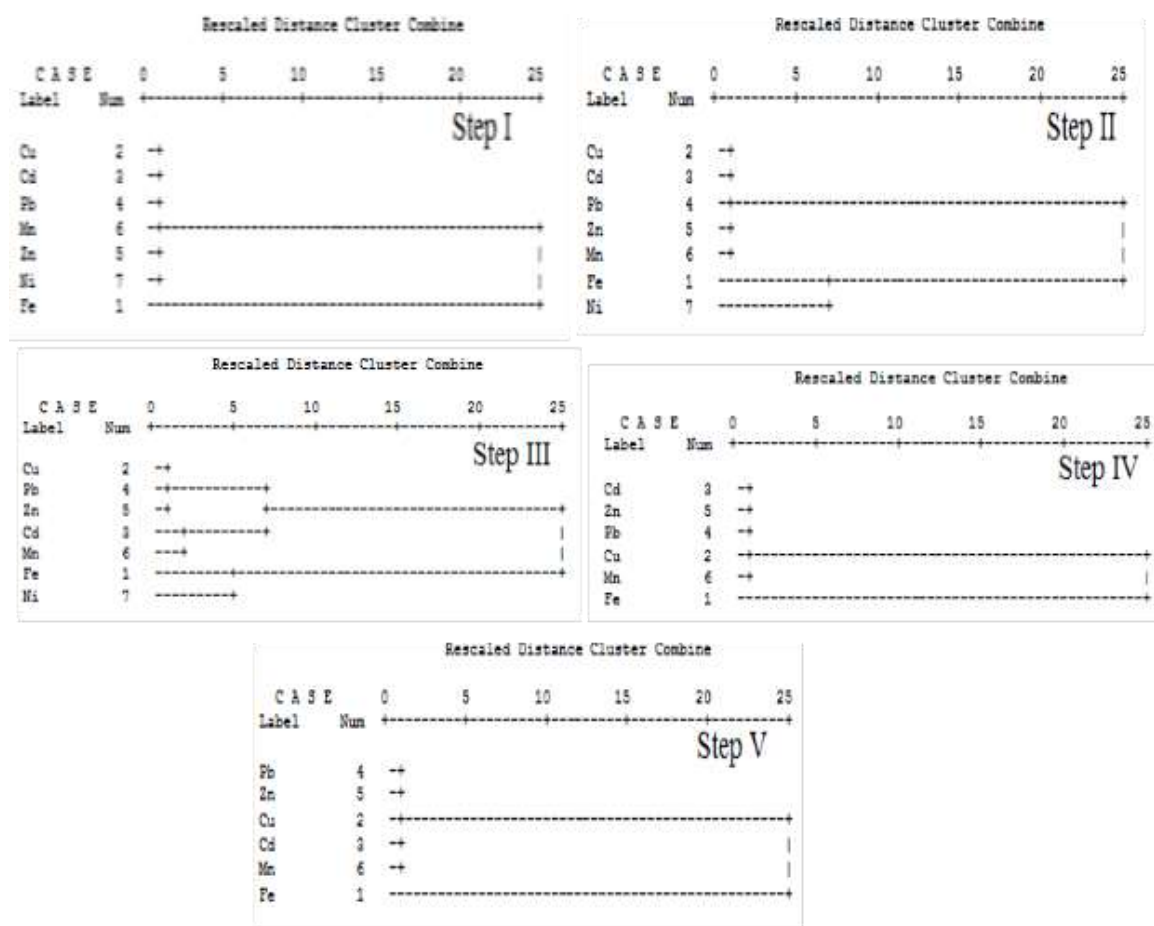
Figure 3. Dendrogram cluster analysis of five geochemical fractions from stream sediments.

Metals bound to inorganic phase

Metals bound to inorganic phase are shown in Table 5. Component I (Table 5) accounts for 25.56% of the total data variation and strong loadings for Cu and Pb. Their similar bonding ris eaction is indicated inside the same groups of cluster (Figure 3). Component II (Table 5) represents 25.55% of the total data variation and described bystrong loadings for Ni and Zn. Their different reactivity depicted in the same groups of cluster (Figure 3). Component III (Table 5) contributes 22.11 to the total variance and has strong loadings only for Fe suggesting a different nature. The same conclusion can be obviously seen from the dendogram (Figure 3). Selected metals obtained in the inorganic fractions (Table 5 and Figure 3) are separated into two clusters. First cluster is Ni, is far away from other cluster, and very adjacent to the point of Fe. This indicated that Ni could be bound to amorphous iron oxy hydroxide. The second cluster consists of Pb, Cd, Cu and Zn which is adjacent to manganese which can be

carbonate co-precipitated with Mn-oxyhydroxides (Figure 3).

Metals Bound To Residual Phase

In the residual phase, the dissolution of crystalline Fe-oxide is relatively complemented by alumino-silicates destruction (Polić and Pfendt, 1996). Table 1 indicates iron as the main constituent (Table 1). The obtained loading values for metals bound to residual phase are shown in Table 5. Component I (Table 5) contributes 34.73% to the total variance of the data. It has strong association only for Fe which suggests a different nature of Fe. This conclusion is supported by the behaviour of Fe within the same exhibitive reaction (Figure 3). Component II (Table 5) represents 34.04% of the total data variation and consists of strong loadings of Cu, Cd and Zn. Cadmium is adjacent to Cu which suggest comparable source. Zinc has similar behaviour inside the same groups of cluster (Figure 3). Based on the dendogram for the metals associated to the

residual phase (that is, detritus silicates, crystalline Fe oxide) as indicated in Figure 3. It is possible to conclude that all selected metals are associated with crystalline Fe-oxide and silicates.

Conclusions

Macro and micro metal geochemical phases and principal component analysis have been employed for evaluation of river sediments from Okemesi –Ijero area, southwestern, Nigeria. The results indicates highcontents of Zn, Cd, Pb, and Ni. This could be ascribed to the anthropogenic inputs from indiscriminate discharge of contaminants and traffic pollution. The above average contents of the selected metals 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 contents of the Cu in considered samples are in the order: Ipoti 3 > Arapate > Odo Owa 5 > Odo Owa 2 > Lawrence 1. Heavy metal pollution is of great concerns because of its toxicity poses serious threats to human health and the aquatic ecosystem. The investigators are principally recommending that, these rivers should be put under surveillance to prevent indiscriminate discharge of domestic sewage.

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