GEOCHEMICAL DISTRIBUTION OF LEAD AND CHROMIUM IN RIVER GETSI- KANO

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ABSTRACT
Geochemical forms of lead (Pb) and Chromium (Cr) from the sediment of River Getsi Kano-Nigeria were determined using Atomic Absorption spectrometer for eighteen months. Apart from determination of the metals in water, geochemical forms of the metals were also evaluated into five fractions. Exchangeable, bound to carbonates, bound to concentrations of the metals in water alone will not be enough to tell on the toxicity of particular heavy metal, as such the need for the geochemical forms of the metal become necessary in order to quantify the form in which the toxic metals exist. The distribution of the metals at the sediment shows that the metals were distributed in all the fractions. This suggests different pollution sources. Hence the sediment may be said to be a reservoir for the heavy metals.
Keywords: Heavy metals, River Getsi, Environment, Pollution, Sediment, Geochemical forms

INTRODUCTION

Pollution is a phenomenon where natural ingredients are replaced or damaged by presence of dangerous unnatural ingredients which have potentiality to cause imbalance to the ecosystem and create a number of health hazards to animals and human beings(Ado, 2011).The determination of extractable trace metals in soilor sediment is often used to gain an insight into chemical speciation. The toxicity of metals depends especially ontheir chemical forms rather than on their total elementalcontents, and therefore, speciation studies increasinglygain importance.

River sediments are basic components of our environmentas they provide nutrients for living organisms andserve as sinks for deleterious chemical species. Unfortunately, industrial and household waste discharges—directly or indirectly,through leakages in thesewagesystems—into water sources cause excessive pollution of surface and underground water. Consequently, waterquality and irrigation value are lost. It is necessary toknow the mechanisms of the trace metals transportationand their complexes in rivers to understand theirchemical cycles in nature(Ure et al.,1993).

Industries contribute to the environmental pollution through the discharge of toxic obnoxious effluents ecosystem setting imbalance in the composition of the water and the aquatic lives thereby causing innumerable health problems to human and animal life. Since these industries pollute the water bodies through the discharge of effluents into the water bodies, the aquatic organisms require large amount of water to absorb oxygen, and by so doing they take the toxic substances into their body (Ayodele and Abubakar 2001).

Apart from heavy metals added as a result of the natural soil geochemical composition of an aquatic environment, both solubilized and non-solubilized heavy metals and other contaminants can be transferred into the aquatic system by runoffs from contaminated soil sites and agricultural farmlands, and through atmospheric deposition. The types of contaminants brought into the aquatic ecosystem are largely influenced by the kind of anthropogenic activities embarked upon within the surrounding farmlands. There are three possible mechanisms by which heavy metals reaching an aquatic system may be taken up by sediments and suspended matter: physicochemical adsorption from the water column; biological uptake by organic matter or organisms; and physical accumulation of metal-enriched particulate matter by sedimentation.

The various ways by which heavy metals associate with various soil/sediment components determine their mobility and availability (Tessier et al,1979;Bodoget al.1996; Ure and Littlejohn,1993 and Pardo et al, 1993). Determining the total content of heavy metals in the sediment may be useful for the characterization of pollution intensity, however, speciation of heavy metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in sediments and helps to assess the environmental impact of contaminated soil and sediment (Bourghriet,et al.1992).Monitoring of these toxicants in the sediments will indicate the extent and magnitude of pollution posed by these metals on the bottom of the shallow water ecosystem.

River Getsiaccording to Otitologbon (2008)is the primary receptor of domestic water. The river runs through from the south to the northern part of the Kano municipality. The river water is used for irrigation, recreation, industrial use and other domestic activities. Upstream the river, are some industries that discharge their effluents directly into the river with little or no treatment. The aim of this work was speciation of heavy metals on the level of the geochemical background, in bottom sediments of River Getsi as proposed by Tessier *et al.* (1979).

The study is justifiable because the geochemical distribution of the metals in the sediments of the river has not been reported in the literature. The bio-accumulative behavior of these metals in biota made necessary to determine the level of these metals in both land and aquatic environment. Although the determination of the metals alone will not be enough to tell on the toxicity of particular heavy metal, as such the need for the geochemical forms of the metal become necessary in order to quantify the form in which the toxic metal exist.

MATERIALS AND METHODS
Sampling
Sediment samples were collected monthly for a period of eighteen months. Samples were collected at 1KM apart from each sampling site. Twenty five samples were taken. The bio-accumulative behaviors of the metals were taken at random on each sampling site. Samples were scooped with a plastic shovel and then packed in air tight polythene bags.

EXPERIMENTAL PROCEDURE
Debris and other unwanted materials were removed from the samples. The samples were air-dried in the laboratory for few days. Each of the samples was pulverised using a mortar and pestle. The samples were then sieved through a 2mm mesh and homogenised to get a uniform grain size. Soil pH and organic carbon were determined according to Agbenin (1995) procedure. The geochemical forms of the metals were determined using Tessier et al (1979; Horsfall*et al* ; 1999).The procedure of Tessier*et al.* (1979), selected for thisstudy was designed to separate heavy metals into fiveoperationally defined fractions: water soluble,exchangeable, carbonate bound, Fe-Mn oxides bound,organic bound and residual fractions. A summary of theprocedure is as follows:

One gram of each soil was weighed into 30mlpolypropylene sample bottle and the following fractionsobtained..

(F1) Exchangeable. The residue from water solublefraction was extracted with 8ml of 1ml $MgCl_2$ (pH 7.0) for I hour.

(F2) Carbonate -Bound. The residue fromexchangeable fraction was extracted with 8ml of IMAmmonium acetate (adjusted to pH 5.0 with Aceticacid) for 5 hours.

(F3) Fe-Mn oxides-bound. The residue fromcarbonate fraction was extracted with 0.04M NH_4OH. 2HCl in 25% (v/v) Acetic acid at 96°C with occasionalagitation for 6 hours

(F4) Organic- Bound. The residue from Fe-Mn oxidesbound fraction was extracted with 3ml of 0.02M Nitricacid and 5ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) was added and the mixture heated to 85°C for 3 hours, with occasional agitation. A second 3ml2 the mixture heated again to 85°C for 3hours withintermittent agitation. After cooling, 5ml of 3.2mNH_4OAc in 20% (v/v) HNO_3 was added and the samples was made up to 20ml with deionized waterand agitated continuously for 30min.

(F5) Residual. The residue from organic fraction afterdrying was digested in a conical flask with 10ml of7M HNO_3 on a hot plate for 6 hours. After evaporation, 1ml of 2M HNO_3 was added and the residue after dissolution was diluted to 10ml. theresidue was washed with 10ml of deionized water.
The mobility factor of the metals in the sediment/ soil samples may be assessed on the basis of the absolute and relative contents of fractions weakly bound to soil/ sediment components. The relative index of metals was calculated as a mobility factor (MF) using the following equation (Aikpokpodion *et al.,* 2012).

$$MF = \frac{(F1 + F2 + F3)}{F1 + F2 + F3 + F4 + F5} \times 100$$

RESULTS AND DISCUSSIONS
pH - value of the sediment
The results for the pHvalues of the sediments were presented in table 7.Highest pH value was obtained at site $B_1$and B_2 (10.56) with least value at site B_5 (8.13). The pH of the sediment from the sampling sites was highly varied. The variability in the pH value of the sediment may probably be due to the level of discharged effluents at the sampling sites in addition to other anthropogenic activities. The pH of the soil solution maintained at neutral toslightly alkaline condition showed low mobility of all heavymetals. To increase the mobility of heavy metals, the pH ofthe soil solution should be lowered. The solubility of Pb insoil solution was pH dependent, increasing as the pH wasadjusted from 6 to 3. At near neutral pH, the activity ofPb^{2+} showed no clear relationship to pH and a small butsignificant increase resulting from changing organic mattercontent. In the near neutral pH range, higher Soil OrganicMatter (SOM) increases the Dissolved Organic Matter(DOM), thereby promoting the formation of organoPbcomplexes and increasing Pb solubility (Sebastien Sauve,1998).

In general, sorption increases with increasing pH. Thatis, the lower the pH value the more metal can be found in solution and thus more metal is mobilized. When pH falls to below 5 mobility is enhanced as a result of the increased proton concentration. At pH values above 7, some heavy metals tend to form hydroxy – complexes which will increase the solubility of the metal in question. Adsorption was greater at pH 6.5 than at pH 4.5. The adsorption of cromatedid not change as significantly as other metals with pH changes. This is due to its oxyanion character in oxidizing condition, and the adsorption mechanisms are very different compared to that of positively charged metals. These results confirm that adsorption for most metal cations increases as pH increases.(Sherene,2010).

Organic carbon (OC)
The results for the OC content of the sediment is shown in table 6.Maximum value of OC was obtained at site B_5(33.33%) while least value was obtained at site B_1(15.79%). The high variability of OC at site B_5 may be due to the fact that site B_5 was away from the effluent discharge point along the river as well as the

self-purification action of the river continuously flow, so also the effluents and other wastes are taken along the direction of the flow hence leading to a minimal deposition of these wastes on the sediments and hence the sediment becomes richer in organic carbon content.

Soil Organic Matter is a key for sorbingphase for metals. The dissolution of humic acid at higher pH is responsible for dissolution of Cu and Pb from soil.Organic matter is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability. However because of the complexation of metals by soluble OM, the addition of OM can result in release of metals from solids to the soil solution.The increase in the solubility of the Cu and Pb is related to the dissolution of the HA component of the organic matter. This indicates that solution phase speciation reactions with organic matter dominate the partition of these metals at higher pH. Because under high pH, the DOM increases as a result solubility of HA.(Sherene,2010*)*

Geochemical forms of Pb and Cr
The results for the geochemical distributions of Pb and Cr were presented in Tables (1-5).Experimental results showed that the metals were present in all the fractions in variable quantities. In site B_1, the geochemical distribution of Pb was highest (3.82mg/l), representing (28%)in both the exchangeable and carbonate fractions. If this value is compared with the average Pb content(1.14μgg^{-1}) of the water at site B_1, it could be said that there is an apparent Pb pollution for the river. The speciation data indicate that Pb is bound to exchangeable and and carbonate fractions. In site B_2highest Pb (16.3%)(Table2) was found in the exchangeable, oxides and organic matter respectively. While the lead content of the water at site B_2 was (1.14mg/l).The level of Pb at site B_3 was fairly distributed in all the fractions. The availability of Pb in almost all the fractions suggests different pollution sources at the sampling sites. Highest percentage (31.7%) was associated with the carbonates, followed by (24.4%) in the exchangeable fraction, with the least (12.0%) in the oxides fraction .Comparing this with the Pb content of the water at site B_3(1.59mg/l), it could be seen that the sediment accumulate higher amount of the metal than in the water. However, in site B_4 highest level of Pb(2.27μgg^{-1}) representing(29.4%) were obtained in both the exchangeable and residual fractions. These fractions were also important from environmental considerations. The level of ofPb at site B_5 was highest (29.3%) in the carbonate fraction, followed by (24%) in the oxide fraction. whereas the Pb content of the water at the same site was observed to be (1.36mg/l).A similar distribution of lead forms among the five fractions were reported by Tessier *et al.* (1979) and Zerbe et al.,(1991), in the fluvial deposits, and Pb was to be mainly in the residual fraction. Although its significant concentration was in the fraction bound to hydroxyl iron and manganese oxide or organic matter.

In site B_1 the distribution of Cr in the sediment was found to be highest (14.h19μgg^{-1}) representing (35.8%) in the exchangeable fraction,

with second highest value (10.98ugg-1) representing (27.6%) in the organic matter. Comparing the value with the Cr content of the water sample from the same site (1.29mg/l)It could be seen that the sediment accumulated higher proportion of the metal than in the water. In site B_2, Highest Chromium in the sediment (13.54μgg^{-1}) representing (33.1%) was found in the exchangeable fraction and(12.58μgg^{-1}) representing (30.7%) in the organic fraction. Where as in the water the value was observed to be(1.61ugg-1). Highest concentrations of Cr in the exchangeable fraction are of environmental concern.

Highest level of Cr at site B_3 (8.46ugg-1)representing (31%) was associated with the exchangeable fraction this was followed by (7.88μgg^{-1}), representing(28.9%) in the organic/oxidisable fraction, and the least (1.73μgg^{-1}), representing (6.3%) was associated with the residual fraction. Although the exchangeable fraction constitutes the highest percentage, it is of serious concern from the environmental point of view, as this may be leached in water due to the changes in pH or redox potential. The Cr content of the water at site B_3 was 1.13mg/l. Again the Cr content of the water is lower than that for the sediment.

In sit B_4, the level of Cr was highest (13.83μgg^{-1}) representing (28.3%) in the exchangeable fraction, with second highest value (13.23μgg^{-1}) representing (27%) associated with the oxidisable/ organic fraction. In site B_5,the level of Cr was highest (15.16μgg^{-1}) representing (37.3%) in the oxidisable/ organic fraction, followed by(10.32$\mu gg^{-1}\mu gg^{-1}$) representing (24.4%) in the reducible/ oxide fraction. The Cr contents of the water at sites B_4 and B_5 were found to be the same (1.13mg/l). These values were found to be lower compared with the value reported by Zerbe et al (1991), where 56% Cr was obtained with a lower value of 7.2% in the manganese oxide. The high concentrations of Pb and Cr in river Getsi may be associated to the anthroppgenic activities in and around the River. This is corroborated by Ure et al (1993), In natural media, trace metals undergo numerous changes during their transport due to dissolution, precipitation and sorption phenomena. Trace element concentrations of river basins depend on not only industrial and household waste inputs but also on the geochemical composition of the area. High concentrations of Zn, Mn and Cr are thought to have resulted from anthropogenic influences, practically from industry and pesticides used in agriculture, and are found to present a pollution risk. Fe concentrations in the river depend on the geochemical structure of the Menderes massif, which consists of Fe-rich metamorphic rocks. Pb enrichment in Gediz river sediments has an exchangeable character and represents pollution potential in this river.

The result for the mobility factor (MF) of heavy metals in the sediment is presented in Table 8. Mobility factor of Pb ranged from 50.06% to 69.96%, with the highest value at site B_1(69.96%), and the minimum value at site B_4. The result for mobility factor for Cr ranged between 57.93% at site B_5 to 67.77% at site B_4.

The range for both the Cr and Pb were higher than the values reported by Yusuf (2007) who reported the MF for copper to be 10% in the land. The indices of mobility were comparatively higher for both the PB and Cr with mean values of 61.97% (Pb) and 63.86% (Cr). High mobility factor values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soil/sediment(Yusuf,2007).
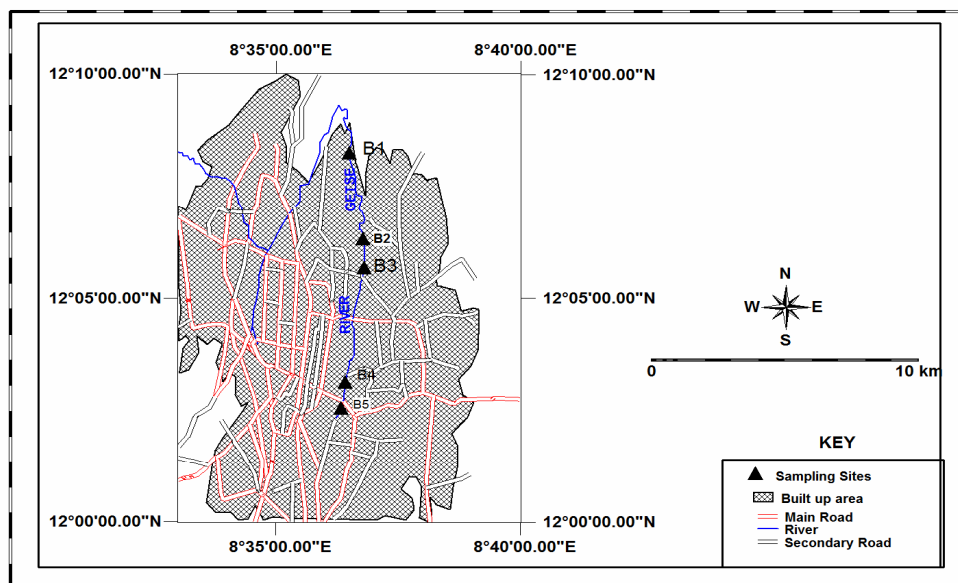

FIG. 3.2: RIVER GETSE SHOWING THE SAMPLING SITES
Source: Modified from google earth map, by GIS section Department of Geography, ABU, Zaria, 2011

Table 1: Distribution of the mean geochemical forms of Pb and Cr at site B_1

Fractions	Pb	Cr
F_1(Exchangeable)	3.182 (28%)	14.194 (35.8%)
F_2(Acid soluble/carbonates)	3.182 (28%)	4.194 (10.6%)
F_3(Reducible/0xides)	1.591 (14%)	7.419 (18.7%)
F_4(0xidisable/0rganic matter)	1.364 (12%)	10.968 (27.6%)
F_5(Residual)	2.046 (18%)	2.903 (7.3%)
Mt	11.364	39.677

Table 2: Distribution of the mean geochemical forms of Pb and Cr at site B_2

Fractions	Pb	Cr
F_1(Exchangeable)	1.818 (16.3%)	13.548 (33.1%)
F_2(Acid soluble/carbonates)	3.636 (10.7%)	5.161 12.6%)
F_3(Reducible/0xides)	1.818 (16.3%)	7.419 (18.1%)
F_4(0xidisable/0rganic matter)	1.818 (16.3%)	12.581 (30.7%)
F_5(Residual)	2.046 (18.4%)	2.258 (5.5%)
Mt	11.137	40.968

Table 3: Distribution of the mean geochemical forms of Pb and Cr at site B_3

Fractions	Pb	Cr
F_1(Exchangeable)	2,273 (24.4%)	8.462 (31%)
F_2(Acid soluble/carbonates)	2,955 (31.7%)	3.846 (14.1%)
F_3(Reducible/0xides)	1.136 (12.0%)	5.385 (19.7%)
F_4(0xidisable/0rganic matter)	1.136 (12.20%)	7.884 (28.9%)
F_5(Residual)	1.818 (19.5%)	1.731 (6.3%)
Mt	9.318	27.307

Table 4: Distribution of the mean geochemical forms of Pb and Cr at site B_4

Fractions	Pb	Cr
F_1(Exchangeable)	2.273 (29.4%)	13.871 (28.3%)
F_2(Acid soluble/carbonates)	1.136 (14.7%)	8.387 (17.1%)
F_3(Reducible/0xides)	0.455 (5.90%)	10.968 (22.4%)
F_4(0xidisable/0rganic matter)	1.591 (20.6%)	13.226 (27.0%)
F_5(Residual)	2.273 (29.4%)	2.581 (5.3%)
Mt	7.727	49.027

Table 5: Distribution of the mean geochemical forms of Pb and Cr at site B_5

Fractions	Pb	Cr
F_1(Exchangeable)	1.364 (14.6%)	5.161 (12.7%)
F_2(Acid soluble/carbonates)	2.727 (29.3%)	8.065 (19.8%)
F_3(Reducible/0xides)	1.136 (12.2%)	10.323 (25.4%)
F_4(0xidisable/0rganic matter)	1.818 (19.5%)	15.161 (37.3%)
F_5(Residual)	2.273 (24.4%)	1.936 (4.8%)
Mt	9.318	40.645

Table 6: Organic carbon (OC) content of the sediment at different sampling sites

Site	Max(mg/kg)	Min(mg/kg)	Mean(mg/kg)	std	CV(%)
B1	0.25	0.13	0.19	0.03	15.79
B2	0.23	0.10	0.15	0.04	26.67
B3	0.17	0.05	0.10	0.03	30.0
B4	0.27	0.10	0.16	0.05	31.25
B5	0.29	0.10	0.18	0.06	33.33

Table 7: Mean pH-value of the sediment at various sampling sites

Site	Min	Max	Range	Mean	std	CV(%)
B1	9.10	12.30	3.20	10.56	1.26	11.93
B2	9.10	12.30	3.20	10.56	1.26	11.93
B3	8.12	11.82	3.70	10.08	1.40	13.89
B4	7.09	9.69	2.60	8.89	0.72	9.10
B5	7.11	9.43	2.32	8.13	1.39	17.10

Table 8: Heavy metal mobility factor at the different sites

Sites	Pb(%)	Cr(%)
B1	69.96	65.02
B2	65.35	63.78
B3	68.35	64.81
B4	50.06	67.77
B5	56.12	57.93
Mean	**61.97**	**63.86**

CONCLUSION

Mean total amount of Pb (9.77mg/kg) and Cr (39.53mg/kg) were obtained in all the fractions. The concentration of the heavy metals may be due to the anthropogenic activities from the neighbouring industries as well as human activities has greatly contributed to the high level of these metals in both the water and the sediments. Toxicity of heavy metals does not depend on its total concentration but depends on different forms in which metals are present.The result from this study suggests that the bottom sediment of the river contained high amount of Pb and Cr. This may probably be as a result of industrial waste discharges from the nearby industries in addition to the other anthropogenic activities.

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