

EVALUATION OF SOME TRACE METALS CONCENTRATIONS IN BANK SEDIMENTS OF RIVER KADUNA, NIGERIA

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ABSTRACT

The soil along the River Kaduna bank sediments were sampled at ten different sites: Kawo, Malali, Federal Government College, Ungwa Rimi Ganji Gate Garden, Kabala Doki, Barnawa, Down Quarters, Nassarawa, and Kudende during the dry season. The soils were sequentially partitioned into five fractions comprising, exchangeable fraction, Carbonate fraction, bound to manganese and iron oxide fraction, bound to organic and residual fraction, bound to organic and residual fraction. The determination of six toxic metals of lead, Manganese, Nickel, Zinc, Cadmium and Cobalt were done using the Atomic Absorption spectroscopy and it reveals that they are present in appreciable quantities as you move from less polluted area to areas with high pollution index. The total metal determined in these soil samples ranged from Pb, 20.04 - 48.43; Mn, 7.42 – 57. 09; Ni, 0.29.91; Zn, 18.43 – 58.53; Co, 0 – 29.98, mg/kg respectively which indicates that most of the sites were polluted and require remediation. In the sequential extractions, most of the metals were extracted in the exchangeable and carbonate fraction of the soil sample which are readily available. The health implication of these metals in the soil which may find their way into the food chain and finally be consumed by man is examined in line with sustainable development.

Keywords: Trace metals, Sequential extraction, Speciation, Pollution index.

INTRODUCTION

Over the last century, global industrialization and natural processes have resulted in the release of large amounts of toxic compounds into the biosphere. These have led to the problem of environmental pollution and ecological concerns. Toxic substances that are introduced into the environment as a result of man's activities causes injury to the health of the environment including life forms present in it and appliances installed in it. Most of these pollutants enter the environment as emissions to the atmosphere or as discharges into water bodies or as dumps on the land.

Heavy metal such as cadmium, copper, lead, vanadium and mercury are important environmental pollutants. Their presence in the atmosphere, soil and water even in traces can causes serious problems to all organism especially humans Ejaz ul *et al* (1). This is because heavy metals are non-degradable and persistent in eco-system. Also physical, chemical and biological processes may combine under certain conditions to concentrate metals rather than dilute them.

According to Tariq *et al* (2), there is a global concern about the rapidly deteriorating state of rivers with respect to heavy metal pollution. Serious metal pollution could result from the discharge of unregulated effluents into natural fresh water bodies Spielgel and Farmer (3). River Kaduna is the

major source of water supply to the Kaduna city. The river basin is a booming crop farming area in both dry and raining seasons. Fertilizers, herbicides and insecticides are used on these crops – and are eventually washed into the river via surface run off. Most of the industries (Textile factories, NNPC Refinery, Peugeot Automobile Assembly Plants etc) located in the southern part of the city derive their water requirements from the river and discharge their wastes directly into the river. Trade wastes (from auto-mechanics, metal fabrication/finishing, abattoirs etc) are also directly or indirectly discharged into the river. Domestic sewage and refuse also found their way into the river from many settlements along the river via leaching, direct discharge and surface run off. Thus, there is every possibility of contamination of water, sediments and fish of River Kaduna by heavy metals since industrial effluents and municipal wastes are known to contain high amounts of heavy metals Abul Kashan and Singh (4). According to Oladimeji (5) there is presence of Copper, Chromium, Iron, Manganese, Nickel, Vanadium and Zinc in river Kaduna. Nwaedozie (6) found that effluent discharged into the river contained heavy metals above the minimum level allowed (FEPA) for discharge into water bodies. Ewalu (7) studied physicochemical parameters of the river and concluded that the river was polluted.

However, no published work has been done on the effects of Industrial, agricultural and domestic wastes discharged on the bank sediment of River Kaduna. This work investigates some trace metal geochemical distribution through extraction techniques of Lead, Cadmium, Cobalt, Zinc, Nickel and Manganese in bank sediments along River Kaduna Bank.

EXPERIMENTAL SAMPLING

Soil samples were collected from ten sites along River Kaduna bank in the following sites namely; Kawo, Malali, Federal government college, Ungwan Rimi, Gamji Gate Garden, Kabala Doki, Barnawa, Down quarters, Nassarawa and Kudende. 20 aggregate samples were collected per site using plastic spoons. They were harmonized, grounded, sieved with 250micro mesh size and stored in plastic containers. The samples were taken in the month of November, a dry season period. The samples were then analyzed as follows:

Trace Metal Determination and Specification

The sequential extraction described by Tessier *et al* (1979) (8) was used.

The exchangeable fraction: 1.0g of finely divided sediment sample was extracted with 40cm³ of 1mol per dm³ MgCl₂ solution at pH 7.0 using a Stuart flask shaker.

The carbonate fraction: The sediment residue from exchangeable fraction was leached with 40cm³ of 1.0mol per dm³ of sodium acetate (adjusted to pH 5 with acetic acid) for 5hr using shaking device.

The easily reducible fraction: The residue from carbonate fraction was extracted with 50cm³ of 0.04mol per dm³ NH₂OH.HCL in 25% (v/v) acetic acid for 6hr and the solution mixed occasionally.

Organic fraction: The residue from easily reducible fraction was mixed with 15cm³ of 0.02mol per dm³ HNO₃ and 25cm³ of 30% H₂O₂ and heated for 2hr at 85⁰C with intermittent agitation. After cooling, 25cm³ of 3.2 mol per dm³ CH₃COONH₄ in 20% (v/v) acetic acid to the mixture and agitated continuously at room temperature for 30 minutes.

After each successive extraction the sample was centrifuged at 4500rpm for 20minutes. The supernatant were removed with pipette and filtered with Whatman No 40. The residue was washed with distilled water, followed with 15 mins centrifugation before next extraction.

Elemental Analysis

The trace metal concentrations in each fraction were determined by using atomic absorption spectrophotometer. Possible matrix effect was taken care of by the standard addition method. All samples were analyzed in duplicate.

RESULTS AND DISCUSSION

The results of the total metal concentrations of Lead (Pb), Manganese (Mn), Cadmium (Cd), Zinc (Zn), Nickel (Ni) and Cobalt (Co) determined from ten sites along the river Kaduna bank stretching from Kawo in the north to Kudenda Industrial area in the south are reported in Appendix II. The geochemical partitioning of the metals in various sites is shown in Appendix I. The total metals determined along the ten sites ranged from Pb (20.94-48.43); Mn (7.42-57.09); Cd (0-58.59); Zn (18.43-58.53); Ni (24.58-575.60) and Co (0-29.98) mg/Kg, which indicates, that soil along the river bank are highly polluted and deserves remediation. The extent of these metal distributions could also vary with the season. However, these samples were collected during the dry season period of November, when the seasonal variation of the flow of the river and the speed is minimal. Therefore the above results will to great extent represent a true reflection of the soil characteristic within the period of the season.

The concentration of lead along the river course shows a fair constancy with a gradual increase in areas where great human or industrial activities take place. The low value of lead obtained at Malali and Barnawa may have been one of the reasons why the Kaduna State government sited in these places the water intake pumps for the supply of water to the municipality. The highest level of soil lead concentration was found in United Textile Limited/Down Quarters area where great industrial effluents from textile, automobile and brewery industries enter the river.

Lead contamination of living environment is well documented. According to Odukoya and Ajayi (1987) (9), it is very toxic and has very chronic health implications, even at low levels. Infection of it causes mental retardation in children and renal disease. Lead replaces calcium in the bone and its' effects is cumulative and long term exposure has been noted to cause serious health hazards Essien (1992) (10).

The variation of manganese shows a pattern different from lead. It is found in high levels in Malali, Gamji Gate, Baranawa and towards Kudenda Industrial area. It seems to show antagonist behavior to lead. The ratio of Pb: Mn in these areas is 0.408, 0.645 and 0.695 respectively. The ratio of 1.958 and 6.518 got at Down Quarters and UNTL areas indicates area with higher pollution index in Kaduna.

The concentration of Nickel was found to be very high along Down Quarters and UNTL area/Nassarawa axis with 575.60 and 220.44mg/Kg respectively. This is the highest concentration of metal found in this investigation. This is not unexpected as this area is associated with the highest industrial pollution activities with all the Textile Industries dumping their untreated waste water effluent into this River Kaduna

The distribution of Zinc and Cadmium along the water course shows a similar pattern as seen in Cobalt. This is not unexpected as this group of metals have similar characteristic. Their origin and source must have been from anthropogenic sources.

The high level of cadmium at Down Quarters may be associated with ;the discharged effluents from National Power Authority Transformer/Motor Yard and the old Railway Maintenance Yard/Market activities that drain into the area..

Nickel is the only metal found in large quantities in the entire Kaduna Water Course. Its trend is similar to other metals where there is an increased amount in areas with intense industrial activities.

The order of mobility of the metals in the various fractions at Kawo site is: - exchangeable fraction $Co > Pb > Ni > Vd > Mn$; bound to Carbonate is $Ni > Co > Pb > Mn > Zn > Cd$. Furthermore the Iron-manganese order is $Mn > Cd > Z > Ni > Pb > Co$ and the Organic fraction $Pb > Cd, Zn > Mn > Ni > Co$. Lead content is low in the residual fraction while Nickel is highest. This shows that only a negligible

amount of lead is of lithogeneous origin that is “inert phase” or lattice – bound metals, which cannot be mobilized.

The presence of high quantities of lead, cobalt and Nickel in the exchangeable and carbonate fraction is important from the environmental point of view as the corresponding quantities is leached by water and made available to plants grown in these areas.

In Malali site the variation of the various metals in the exchangeable and carbonate fractions are $Pb > Mn > Zn > Ni > Pb > Mn > Cd$ respectively. Cobalt was not detected in this site. The predominantly availability of Pb, Mn, Zn and Ni must have originated from the quarrying activities in these areas as only peasant agricultural farming takes place within the area with less pollution impact to the environment.

Manganese and Nickel are the highest extractable metals in the manganese Iron bound fraction at Malali site and the use of Hydroxylamine hydrochloride to extract the metal associated with easily reducible manganese was found to remove most of the metal of the metal in this group. The easily reducible fraction could be considered stable (slowly mobile, poorly available) but could be changed with variations in redox conditions becoming more soluble under reducing conditions and less so under oxidizing ones. Since the mobility of a metal is related to its' toxicity, an increase in reducing conditions in the soil will increase the toxicity.

At Federal Government location Nixckel and Zinc is well distributed in all the five fractions in appreciable quantities in this site. Their presence might be associated with the old Kaduna waste Dump site located near the site. The near absence of cobalt in this site is similar to what was obtained in Malali. This is not unexpected as these two locations are in the same geographical area. Their absence could mean that it does not exist in this form in the soil analyzed or this form was present in concentration below the detection limit of the instrument, the order of $Ni > Pb > Cd > Mn > Zn > Co$ while in Carbonate fraction it is $Ni > Pb > Zn > Cd > Mn > Co$ was obtained. The high amount of metals associated with non residual phase shows that they may be easily transferred into the food chain through water reservoirs, uptake of plants growing in the soil or any other mechanism.

The order of mobility in exchangeable fraction in Ungwan Rimi location is $Ni > Pb > Zn > Cd > Mn > Co$ while in Carbonate fraction the order is $Ni > Mn > Pb > Cd > Zn > Co$. The exchangeable carbonate fractions are mobile phases and the elements are in mobile forms. These elements may be easily transferred into food chain through uptake by plants growing in the soils. The high amount of Zn is in residual fraction. This indicates that Zn occurs in immobile forms in soils. It may be strongly bound to minerals and resistant components. *Cd, Pb, Mn Ni and Zn* and in the soil samples are partitioned into the reducible, iron-manganese oxide and zinc forms. A high mobile level of any metal may also be an indication that the soil is polluted.

The distribution of trace metals along River Kaduna bank of Gamji gate Garden location gave the order of mobility of the metals in the exchangeable fraction as $Zn > Ni > Mn > Pb > Co$. Zn Seams to be the most easily mobilized in this fraction while Pb and Mn are the minimum mobilizable elements. Co is absent in this fraction. It may be present below detectable limit of the instrument. The distribution of metals in the carbonate associated fraction was low. The carbonate fraction is relatively stable. Pb and Zn were the only metals in the organic associated fraction. The organic fraction is not very mobile or available, since it is thought to be associated with high molecular weight stable humic substance, which could release small amounts of metal in a very slow process. The only elements in Iron-manganese oxide fractions are Zn, Mn and Pb which has been attributed to their association within the matrix.

Cobalt was not indicated in any of the fractions at Kabala and this could mean that it does not exist in any detectable form in the soil. Nickel recorded the highest concentration in this fraction while Mn is least. The distribution of metals in carbonate fraction was moderate ranging from Cd to Mn followed by Pb and finally Zn. The element Ni, Zn, Cd, Pb and Mn are evenly portioned in the residual

fraction. A small quantity of Pb, Ni Mn Cd and Zn are distributed in the organic fraction. It could mean that the quantities of these elements are few in non mobile phase.

At Gamji Gate location the order of mobility metals in exchangeable fraction is $Ni > Z > Pb > Cd$ all the elements were evenly partitioned in all the fractions at this site. Within this zone lead and cadmium and manganese were in low quantities in the exchangeable fraction which hither to has shown increased values in other sites.

Down Quarters area is where the river starts to receive her Industrial effluents from industries an appreciable quantity of cobalt has been indicated in the exchangeable and the metal bound to carbonate fraction. Nickel is evenly disturbed in this zone and it is in appreciable quantities which could have been as a result of effluents from the Textile Industries and old railway Yard adjoining the area.

The heavy level of toxic metals in Nassarawa/UNTIL continues to manifest itself within these industrial areas. The order of magnitude of these metals is $Ni > Pb > Co$ in the exchangeable while it is $Ni > Pb > Co$ in the carbonate fraction. Their source could still be traceable to the discharge of dyes, chemicals and other pigments by the Textile industries and other metal manufacturing industries whose waste are dumped indiscriminately into the water course. The level of metal pollution in this area is high and this is not unexpected due to the unabated environmental pollution activities going on in this areas.

In Kudende location the presence of all the elements are well spread within the five fractions. The order of abundance of the metal in the exchangeable fraction is $Cd > Co > Ni > Pb > Zn > Mn$. The high level of the elements are not unexpected because this area that receives the highest quantity of effluents. In fact the Kaduna River is continually coloured within this zone. The fishing activity that used to flourish in this area is completely absent due to the high pollution in the area.

In general the accumulation of these heavy metals in the soil which are readily available for FADAMA irrigation for plants, roots and stems cultivation along the banks has been reported (Ojeka and Achi 2004) (11). Okoronkwo *et al* 2005 a 12, b reported the level of Pb, Ni, Cr, Cd and Ag present in soil and uptake of roots and leaves of cocoyam and cassava harvested from abandoned waste dumping sites in Umuahia South East of Nigeria.

Anikwe and Nwabodo (2002) (13) also reported high level of heavy metals (Pb, Fe, Cu and Zn) in their study on long term effect of municipal waste disposal on soil properties and productivity of sites used for urban agriculture in Abakaliki.

Chiroma *et al* (2003) (14) has studied heavy metal contamination of vegetables on soils irrigated with sewage water in Yola Nigeria and reported high concentration of the metals (Fe, Zn, Cu, Mg, Mn and Pb) suggesting heavy metal contamination which latter accumulated in plants cultivated in the soil. They also showed that the accumulation vary in different parts of the plant. It also revealed that Pb does not accumulate in the fruiting part of vegetable and fruit crops. Higher concentrations are more likely to be found in leafy vegetable (e.g. lettuce and cabbage and on the surface of root crops (Nwoko *et al*, 2002) (15).

The bank of River Kaduna is predominantly used for peasant vegetable crop farming of lettuce, cabbage and dry season fresh corns. The presence of these toxic metals bears a lot of health risk factors and acts as biological poisons even at parts per billion (ppb) levels. The toxic element accumulated in Organic matter in soils is taken up by growing plants. These metals are not toxic as free elements but are dangerous in the form of cautions and when bonded to short chains of carbon atoms.

Chanay (1980) and Smith *et al* (1996) (16) cautioned on the use of wastes in crop production since it may be possible for heavy metals from waste to accumulated in soil and thereby enter the food chain, contaminate surface and underground water thus causing health hazards.

In conclusion it has been observed that the level of heavy metals of lead, manganese, nickel, zinc, cobalt and cadmium investigated were higher than normal soil. It should be noted from this examination of the River Kaduna bank sites that, all the heavy metals fall within the critical concentration levels for agricultural activities and the soil. It should be noted from this examination of the River Kaduna bank sites that, all the heavy metals fall within the critical concentration levels for agricultural activities, and the soil needs remediation. Some of the metals could not be traced to immediate pollution activity in Kaduna and must have arisen from other anthropogenic factors like mining activities in Jos Plateau.

It is therefore recommended that there should be caution in the use of river Kaduna and its banks in the cultivation of the Fadama crops of lettuce, Cabbage, carrot and other crops, as the soil is highly polluted. The most effective way to reduce the impact of these metals on the environment is to develop and implement an effective waste management plan. Detailed plans to identify the materials and wastes at a particular site and to adopt the Best management Practices (BMP) to sort treat and dispose these wastes should be put in place by both the government and in community. The use of water from these areas with high concentration of trace metals for domestic and agricultural activities should be avoided. An integrated wastes treatment technology should be adopted by the industries within the river vicinity to reduce the environment impact of waste dump.

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APPENDIX I: RESULTS OF SPECIATION FOR EACH SAMPLING LOCATION**(X10mg/kg)**

KAWO LOCATION	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.04	0.107	0.156	0.209	2.44	0.803
Carbonate	0.632	0.623	0.080	0.461	0.417	0.417
Reducible (Fe/Mn)	0.259	1.472	0.853	0.638	0.503	Nd
Oxidisable (Org)	0.464	0.443	0.453	0.453	0.150	0.15
Total	2.395	2.645	1.542	1.761	3.510	1.37

MALALI LOCATION	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.438	1.224	0.050	0.423	0.203	Nd
Carbonate	0.643	1.214	0.220	0.797	1.724	Nd
Reducible (Fe/Mn)	Nd	0.725	0.393	1.016	0.59	Nd
Oxidisable (Org)	0.264	0.265	1.073	0.537	0.161	Nd
Total	2.336	3.428	1.736	2.773	2.678	nd

FED GOVT COLLEGE	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.494	0.306	0.316	0.255	6.06	nd
Carbonate	1.265	0.045	0.045	0.470	3.388	0.0002
Reducible (Fe/Mn)	ND	0.305	0.305	0.075	3.782	nd
Oxidisable (Org)	0.495	0.610	0.610	0.542	2.383	nd
Total	3.254	1.266	1.266	1.337	15.613	0.0002

UNGWAN/RIMI	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	0.881	0.461	1.303	0.601	1.514	nd
Carbonate	0.652	0.983	0.530	0.390	2.359	0.148
Reducible (Fe/Mn)	0.625	0.470	0.173	0.959	0.206	nd
Oxidisable (Org)	0.383	0.304	1.023	0.520	ND	nd
Total	2.541	2.218	3.029	2.470	4.079	0.148

GAMJI GATE GARDEN	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.585	1.776	nd	3.096	1.935	nd
Carbonate	0.314	0.643	nd	0.416	0.273	nd
Reducible (Fe/Mn)	ND	0.4815	nd	0.638	nd	nd
Oxidisable (Org)	0.343	ND	nd	0.881	nd	nd
Total	2.242	2.901	nd	5.031	2.208	nd

KABALA DOKI	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.462	0.223	0.079	0.382	2.684	nd
Carbonate	0.540	0.635	0.736	0.502	1.819	nd
Reducible (Fe/Mn)	0.231	0.299	0.323	0.599	0.568	nd
Oxidisable (Org)	0.208	0.415	Nd	0.871	0.241	nd
Total	3.441	1.199	1.138	2.354	5.312	nd

BARNAWA LOCATION	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	0.799	0.902	0.652	1.456	3.267	1.295
Carbonate	0.500	1.380	1.248	0.610	1.506	1.295
Reducible (Fe/Mn)	0.357	0.184	1.010	1.646	0.542	0.086
Oxidisable (Org)	0.163	0.660	0.093	0.834	0.499	0.197
Total	1.819	3.126	3.003	4.546	5.814	2.873

DOWN QUARTERS	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.637	0.362	0.833	0.419	5.891	1.665
Carbonate	0.320	0.629	0.403	0.402	6.224	1.286
Reducible (Fe/Mn)	0.095	0.260	1.803	0.530	12.4	nd
Oxidisable (Org)	0.233	0.051	0.991	0.662	11.02	nd
Total	2.285	1.302	4.030	2.013	35.535	2.951

UNTL/NASS	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.637	0.362	0.833	0.419	2.891	1.665
Carbonate	0.319	0.629	0.403	0.402	6.224	1.286
Reducible (Fe/Mn)	0.095	0.260	1.803	0.529	12.395	nd
Oxidisable (Org)	0.233	0.991	0.051	0.662	11.025	nd
Total	2.284	1.302	4.03	2.012	32.535	2.951

KUDENDA LOCATION	Pb	Mn	Cd	Zn	Ni	Co
Exchangeable	1.381	0.541	0.605	0.405	1.626	1.343
Carbonate	0.471	0.670	0.89	0.469	1.434	1.212
Reducible (Fe/Mn)	0.160	0.549	0.149	1.576	0.446	0.301
Oxidisable (Org)	0.513	0.715	0.160	0.719	ND	0.023
Total	2.525	2.475	1.003	3.169	3.506	2.879

LOCATION	Pb	Mn	Cd	Zn	Ni	Co
KAWO	2.395	2.645	1.542	1.761	1.37	1.37
MALALI	2.336	3.428	1.736	2.773	2.678	nd
FED GOVT COLL	3.524	1.266	1.681	1.337	15.613	0.0002
UNGWAN RIMI	2.541	2.218	3.029	2.470	4.079	0.148
GAMJI GATE	2.242	2.901	nd	5.031	2.208	nd
KABALA	2.441	1.199	1.138	2.352	5.312	nd
BARNAWA	1.819	3.126	3.003	4.546	5.814	2.873
DOWN QUARTER	2.285	1.302	4.030	2.013	35.535	2.951
UNTL/NASS	2.284	1.302	4.03	2.012	32.535	2.951
KUDENDE	2.525	2.475	1.003	3.169	3.506	2.879