Partitioning Of Some Trace Metals in Floodplain Soil in Onitsha, Anambra State, Nigeria.

[1]Onwukeme, V.I, [1]Anarado, J.C. and [2]Ajala, L.O.

[1]*Department of Pure and Industrial Chemistry Nnamdi Azikiwe University, Akwa, Nigeria.*
[2]*Department of Science Laboratory Technology Akanu Ibiam Federal Polytechnic, Unwana, Nigeria.*

Abstract: *A research was conducted to verify the degree of partitioning of some selected trace metals in the soil sediment collected from floodplain soil in Onitsha, Anambra State, Nigeria. The investigation was carried out using standard method in accordance with the modified Horowitz et al procedure of trace metals speciation. Lead had the highest total fraction of 86.50mg/kg widely followed by zinc with a value of 33.30mg/kg and the least value was associated with cadmium (6.50mg/kg). Manganese was not detected in reducible, oxidizable and residual fractions while organically bound cadmium was found to be below the detection limit. The % bioavailability of the trace metals investigated ranged from 9.01%(zinc) to 100%(Manganese) with a mean value of 67.41%. The trend in the % bioavailability followed the order: Mn > Pb >> Cd > Ni >> Cu >> Fe > Zn. Of the fractions employed, exchangeable was found to accumulate the highest percent of the metals (51.02%) widely followed by metals bound to carbonates (16.39%) while reducible form partitioned the least metals (9.91%). The high value of % bioavailability of the most metals investigated called for immediate removal of the sources of these metal pollutants and appropriate cleaning method(s) should be applied to the area in order to minimize the amount entering into the food chain.*
Keywords: Trace metals, Pollution, Floodplain, Bioavailability, Environment, Speciation

I.   Introduction

During the past three decades, the state of the metal pollution has become a matter of growing international concern. The increasing population densities of people, human activities and environmental impact of site locations have affected the soil composition [1]. Raised levels of several trace metals, released into the soil by natural and anthropogenic sources have been noticed in different parts of the country [1,2]. Intense pollution of the soil has inevitably increased the levels of heavy metals in the soil. The nature of biological responses to metal exposure is defined through close-effect relationship [3].

The concentration levels of heavy metals in environment are continually changing due to man's activities. These have generated a lot of interest in pollution studies. Major natural sources of these metals are rock-weathering, releases from terrestrial and sub-marine sediments while anthropogenic sources include Industrial emissions, vehicular emissions, municipal wastes, agricultural wastes, etc [4]. Heavy toxic metals also entered into the environment through waste water from metal plating industries and industries of lead, Cd-Ni batteries, phosphate fertilizers, mining, pigments, electroplating, corrosion and other industrial wastes [5]. Heavy metals are produced in large amounts and discharged into the environment where they become toxic to plants and aquatic organisms and bio-concentrate within the organisms, sometimes to levels greater than that in the environment [6].

A large number of potentially harmful metals are known as pollutants but some have been implicated to several man's diseases. [3]. Taking for instance, lead causes cancer, damage the brain and kidneys and ultimately death [7]. Cadmium causes kidney disease, lung damage, and fragile bones [8].

During transportation, trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena [6] which affect their behaviour and bioavailability. Trace metals are easily influenced by environmental factors such as surface runoff, groundwater, dissolution from sediment, deposition from the atmosphere and anthropogenic pollutants. Hence trace metals may be sensitive indicators for monitoring changes in the environment [9].

During soil erosion, materials are settled at floodplain which collects the load of sediments carried by the runoff around a particular area and afterward distribute the deposited materials into water bodies nearby. Most studies of trace metals in the soil focused on the total metal concentrations. The fact that total concentrations of metals should be used as a yardstick to determine the potential health risk of these metal pollutants in the environment implies that the bulk metal concentration is available to the biota. This assertion has been refuted by many authors [10,11,12,13]. It is evidence that the speciation of trace metal pollutants with the various sediment phases determines their specific impact on the environment. Also, the type of the phase specific bonding of the trace metals in contaminated natural sediments specifies suitable methods of their potential cleaning and utilization [14].

The solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents and each metal quantified separately. The use of sequential extraction furnishes detailed information about the origin, mode of occurrence, biological and phytochemical availability, mobilization and transport of trace metals [11]. Apart from Horowitz et al used in this study, other notable speciation techniques have been documented [2,11,15].

This preliminary study is to examine the speciation of these trace metals in the anoxic environment with a view to evaluating possibilities of their physical and physicochemical treatment. The choice of this sediment site lies on the fact that, it remains the collection point of all flood water in Onitsha, as all flood water end at this point before entering the Niger River. There is therefore, need to assess the impact of heavy metals in the area to assess mobility and health consequences as well as cleaning and utilization. This research is pertinent since there has not been any information documented concerning the partitioning and bioavailability of trace metals in floodplain soil near Niger River despite the economic importance of this river to the people of this geo-political zone. Hence, there is a need to establish the geochemical forms in which these trace metals exist in the sediment via sequential extraction since the chemical forms of inorganic components in soils and sediments determine their mobility and availability to plants and their geochemical interactions [16].

II.   Experimental

Sampling site
Onitsha lies between $6^0 10'$N $6^0 47'$E of Southeastern part of Nigeria. It has a land mass of 36.12 km^2. It has a Population of about 511,000 in 2002. Onitsha lies at a major east-west crossing point of the Niger River, and occupies the northernmost point of the river regularly navigable by large vessels. These factors have historically made Onitsha a major center for trade between the coastal regions and the north, as well as between eastern and western Nigeria [17].

Sample Collection and Preparation
Floodplain soil sediment was collected at Onitsha International Market, near Niger Bridge, Onitsha in Anambra State, Nigeria. The sample was collected with plastic spoon. Composite sampling technique was adopted in taking representative sample. The sample was air-dried and homogenized by using 90 mesh size sieve and stored in polythene bag at 4^0C prior to leaching.

Sequential Extraction Procedure
The method as modified by Horowitz et al (1991) [13] was used for the sequential extraction of the trace metals under investigation. The procedure is as follows:

 I. **Exchangeable fraction:** 1g of the dried sediment sample was weighed into a beaker. 50cm^3 of MgCl$_2$ solution was measured and added. The extraction was done at room temperature for 1hr with continuous agitation on an electric shaker. The supernatant was allowed to settle and filtration was done into a 100cm^3 standard volumetric flask. Excess deionized water was used to wash the residue on the filter paper. This was later made up to the mark and stored in a sample bottle, labeled and kept until needed for the analysis.

 II. **Bound to carbonate fraction:** The residue from above was transferred into a clean and dry beaker. It was leached at room temperature with 50cm^3 solution of 1MCH$_3$COONa prepared and adjusted to pH 5.0 with ethanoic acid. Continuous agitation was maintained for 1hr on an electric shaker and the resulting solution was filtered through whatman No1 filter paper into 100cm^3 standard volumetric flask. The residue on the filter paper was further washed to remove the remaining reagent that might retain in the residue. The filtrate was made up to the mark with deionized water. The extract was stored in a sample bottle labeled and kept ready for analysis.

 III. **Bound to Fe-Mn oxides:** The residue from (ii) above was transferred into a beaker. It was extracted with 50cm^3 mixture of ammonium oxalate and oxalic acid for 1hr with continuous agitation over an electric shaker. The resulting solution was filtered into a 100cm^3 standard volumetric flask. The residue on the filter paper was further washed with deionized water. The leachate was made up to the mark. The extract was stored in a sample bottle and finally labeled ready for AAS analysis.

 IV. **Bound to organic matter:** The residue from the previous leachate was transferred into a clean and dry beaker. It was extracted with 50cm^3 solution of 0.1MNaOH with continuous agitation over an electric shaker for 1hr. this was then filtered through whatman No1 filter paper into a 100cm^3 standard volumetric flask. The residue on the filter paper was further washed with deionized water. The content was later made up to the mark, stored in a sample bottle and labeled properly prior to analysis.

 V. **Residual:** The residue from (iv) above was digested with a mixture of hydrochloric and hydrofluoric acids for 5hrs. This was later washed and filtered with deionized water into a 100cm^3 standard volumetric flask and made up to the mark. The filtrate was allowed to cool and stored in a sample bottle and labeled accordingly ready for AAS analysis.

Chemical Analysis: All the supernatant solutions from stages (I) to (IV) and the residual digest (v) were analyzed for the following trace elements: iron, manganese, copper, zinc, lead, nickel and cadmium, using Perkin Elmer Atomic Absorption Spectrophotometer (model 403).

III.   Results

Result of sequential extraction of some selected trace metals from floodplain soil sediment in Onitsha, Anambra State, Nigeria is presented in the table below:

Fraction	Fe	Mn	Cu	Zn	Pb	Ni	Cd	Mean	% Fraction
Exchangeable	0.50	13.70	2.00	0.10	61.50	3.20	4.00	12.14	51.02
Carbonate	0.50	1.40	1.50	2.90	18.50	2.00	0.50	3.90	16.39
Reducible	0.50	0.00	1.50	8.70	4.30	0.50	1.00	2.36	9.91
Oxidizable	4.50	0.00	1.00	11.60	0.70	1.00	0.00	2.69	11.28
Residual	4.50	0.00	1.00	10.00	1.50	1.00	1.00	2.71	11.40
Total Fraction	10.50	15.10	7.00	33.30	86.50	7.70	6.50	**23.80**	
Mean Fraction	2.10	3.02	1.40	6.66	17.30	1.54	1.30		
Bioavailability	1.00	15.10	3.50	3.00	80.00	5.20	4.50		
% Bioavailability	9.52	100.00	50.00	9.01	92.49	67.53	69.23		67.41

NB: Concentrations of the metals are in mg/kg.

$$\% \text{ Bioavailability } = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times \frac{100}{1} \%$$

Where F_1 =   Exchangeable fraction
        F_2 =   Carbonate fraction
        F_3 =   Reducible fraction
        F_4 =   Oxidizable fraction
        F_5 =   Residual fraction [18]

Fig 1: % occurrence of each trace metal in exchangeable fraction

Fig 2: % occurrence of each metal in carbonate fraction

Fig 3: % concentration of each metal in reducible fraction

Fig 4: % occurence of each trace metal in oxidizable fraction

Fig 5: % concentration of each metal in residual fraction
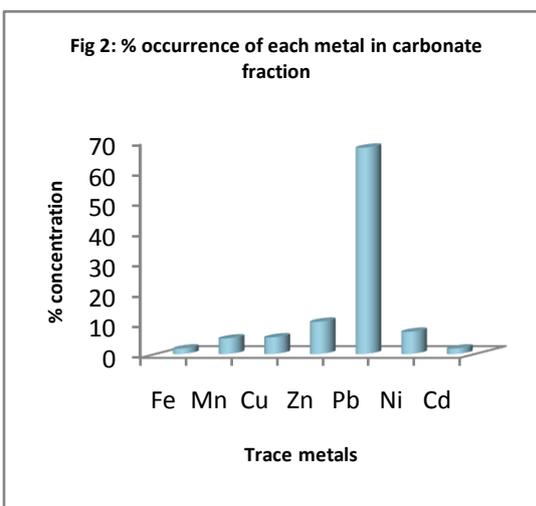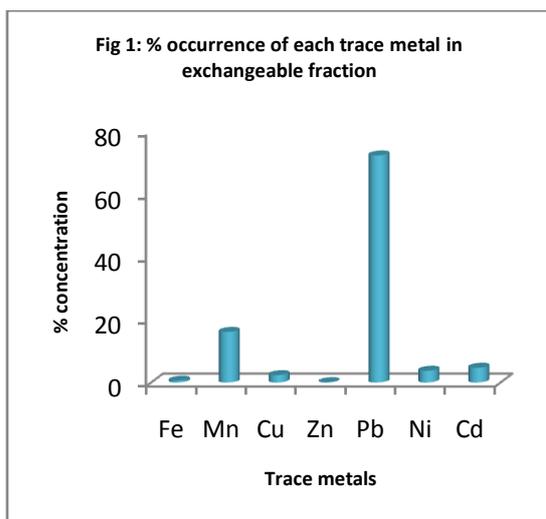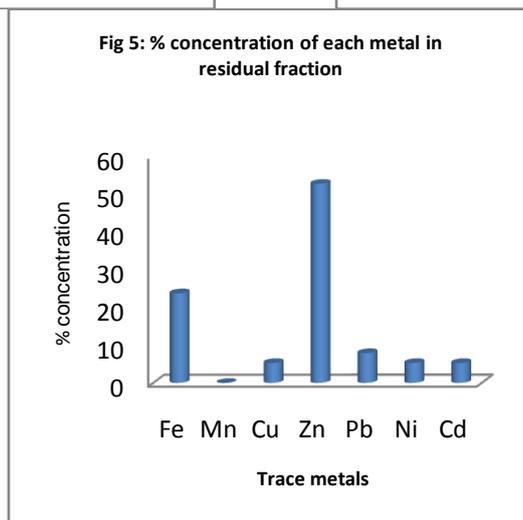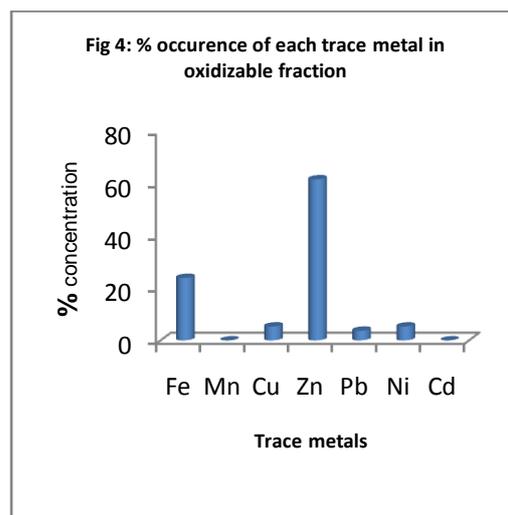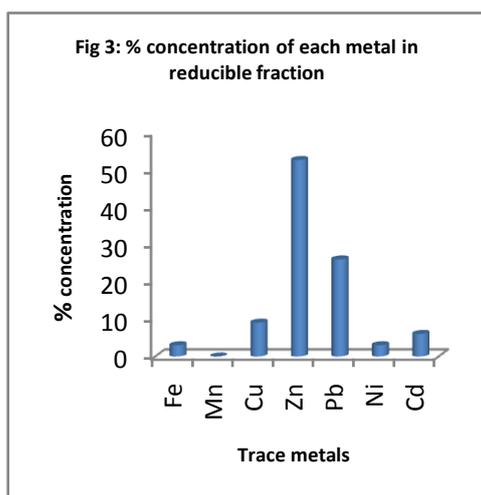
IV. Discussion

The table above shows the result of sequential extraction of trace metals investigated in floodplain soil sediment in Onitsha, Nigeria. The occurrence of lead in exchangeable form was found to be 61.50mg/kg which is widely followed by 18.50mg/kg associated with metals bound to carbonates. The concentration of iron in exchangeable, carbonate and reducible fractions was the same with value of 0.5mg/kg. It also had the same concentration in both oxidizable and residual fractions (4.50mg/kg).

Manganese was not detected in the reducible, oxidizable and residual fractions. The highest concentration of it was found in exchangeable form with a value of 13.70mg/kg.

Copper had its highest concentration partitioned also in exchangeable form (2.00mg/kg). 1.50mg/kg of copper was detected in carbonate and reducible fractions. Organically and residual forms of copper concentration has a unit concentration. 11.60mg/kg of zinc was partitioned in oxidizable portion closely followed by residual (10.00mg/kg) and the least value was associated in exchangeable fraction (0.10mg/kg).

Nickel had a mean fraction of 1.54mg/kg with the highest concentration adsorbed to exchangeable fraction while small portion of it partitioned in reducible fraction. Cadmium was not detected in organically form of the metal. It had a mean fraction of 1.30mg/kg with the highest concentration bound to exchangeable fraction.

Lead had the highest concentration in all the fractions with a sum of 86.50mg/kg widely followed by zinc (33.30mg/kg) and the least value of 6.50mg/kg was linked with cadmium. The occurrence of these metals followed this trend: Pb >> Zn >> Mn > Fe > Ni > Cu > Cd of the total fractions. All the metals investigated had their highest concentrations in exchangeable fraction with exception of iron and zinc. Exchangeable fraction alone had 51.02% among the five fractions.

Metals bound to carbonates constituted the second largest fraction that partitioned trace metals from this area investigated with a percentage occurrence of 16.39%. Likewise, lead had the highest concentration of 18.50mg/kg widely followed by zinc (2.90mg/kg) while iron and cadmium had the least value of 0.50mg/kg

each. In metals bound to Fe-Mn oxides, only 9.91mg/kg of the metal concentration partitioned in this fraction. Iron and Nickel had the same value of 0.50mg/kg while zinc partitioned mostly (8.70mg/kg).

Zn also accumulated mostly in organically bound metals with a value of 11.60mg/kg followed by iron (4.50mg/kg). Both copper and nickel had a unit concentration in this fraction.

In the same manner with reducible and oxidizable fractions, zinc partitioned mostly in residual fraction (10.00mg/kg) followed by iron (4.50mg/kg). Interestingly, a unit concentration was associated with copper, nickel and cadmium in this fraction. Low level of cadmium in this fraction has been reported earlier [11,13,19]. The % bioavailability of these metals followed the trend: Mn > Pb >> Cd Ni >> Cu >> Fe > Zn.

The % bioavailability of nickel was determined to be 67.53. This value is in variance with average value (35.88%) obtained by Omuku et al [18] from three sites within Awkuzu area of Anambra State, Nigeria. The mean % bioavailability of the metals studied was 67.41%. This was in consonant with the value obtained by the same authors [19] on previous research, where the mean value was put to be 66.70%. The percentage bioavailability of copper and lead are 50% and 92.49% respectively. The values are of high side when compare to those values obtained by Tessier et al [11] where the values were documented to be between 15.58 to 18.58% and 18.90 to 25.50% respectively.

The % bioavailabilities of copper and manganese were 50% and 100% respectively. It is a known fact that metals such as copper, manganese, iron, zinc are essential to maintain the metabolism of the human body [81]. However, they can become toxic when they exceed the threshold limit [1]. The % bioavailabilities of lead and cadmium were put at 92.49% and 69.23% respectively. This signifies that they are highly available to plants and aquatic organisms. This is call for immediate attention as a result of possible health risk to humans through the plants/aquatic organisms' uptake-dietary route [12] and do not have explicit exposure threshold for the introduction of adverse effects [20]. Cadmium has an exact toxic effect even at low concentration [21].

Cadmium, like mercury exhibits a profound capacity of combining with thiol group (-SH) to form a stable complex. Cadmium and mercury however compete with and displace zinc with a number of zinc containing metaloezymes by irreversibly binding to the active site, thereby destroying normal metabolism [21]. Also, lead has high affinity for thiol group (-SH) and phosphate ligands, thus inhibiting the biosynthesis of hormone by displacing Fe^{3+} from the heamoglobin, which adversely affect membrane permeability of kidney, liver and brain cells [21]

Figure 1 shows the % occurrence of each trace metal in exchangeable fraction. Lead accumulated mostly (72.35%) widely followed by manganese (16.12%) and the least 0.12% was associated with zinc. The exchangeable manganese was found to be 16.12%. This was consistent with the values obtained by Osakwe [22] with the values ranged from 13.15 to 18.07%. Evidence from many types of sediments [11] showed that exchangeable copper, nickel, zinc and iron are generally found to represent a minor fraction of the total metal concentration of the solid. The relatively high concentration of exchangeable manganese suggests that it exists in a reduced form; it is recognized that in most natural environment, Mn^{2+} oxidation is a much slower process than Fe^{2+} oxidation [10]. It is believed that metals in this form are highly soluble, mobile and easily release into solution, hence bioavailability to biota is expected. Metals here are likely affected by sorption-desorption processes [10,11].

The % occurrence of trace metals bound to carbonates was shown in figure 2. Lead also partitioned mostly (67.77%) widely followed by zinc (10.62%) while cadmium and iron had least values of 1.83% each. The most significant occurrence of Nickel was in carbonate fraction (7.33%). This result compared favourably with similar study [23] where nickel had an average value of 10.47%. The % occurrence of zinc in this fraction fell within the values obtained in a similar study (7.90-10.02%) by Adaikpoh [21], while manganese in this fraction was detected to be 5.13% which is lower than the value obtained by the same author. Metals in this form are susceptible to pH changes and are also soluble and easily release into the environment [10,11,15].

Figure 3 depicted the % occurrence of metals bound to Fe-Mn oxides. Metals in this fraction exist as cement between soil particles. They are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions [10,11,15]. In this study, zinc had the highest occurrence (52.73%) while manganese did not occur (0%). Low level of nickel (3.03%) was in agreement with other findings [23,24,25]. It has been suggested that the levels of nickel in this fraction depends on how much manganese oxide is absorbed in soil because Ni^{2+} can substitute for surface manganese in mixed valence manganese oxides [23]. The % occurrence of iron was 3.03. This corroborated the findings of Osakwe [23] where iron had an average value of 3.06%. Cadmium was found to be 6.06% of this fraction. This result was in line with some other similar studies [23,26]. The fraction could be considered relatively stable but could change within variations in redox condition [26]. The trend in occurrence of these metals investigated in this fraction followed the order: Zn >> Pb >> Cu > Cd > Fe/Ni > Mn.

Trace metals may also bound to various forms of organic matter. The % occurrence of organically bound trace metals was shown in figure 4. Zinc was also fractionated mostly (61.70%) followed by iron (23.94%). Metals partitioned here are not stable. Under oxidizing condition, organic matter can be degraded, leading to a release of soluble of soluble trace metals [10,11]. Organically complexed cadmium was not detected. Low level of

cadmium in this fraction has been reported [23]. The high distribution of iron and zinc in bound to organic matter is expected due to the strong complexes these metals tend to form with humic material [15].

The appreciable % values of iron in oxidizable (23.94) and residual (23.68) fractions were in line with the values obtained for the same metal in the same fractions which were put at 28.27-44.39% and 26.01-42.64% respectively in accordance with the findings of Adaikpoh [21]. The % occurrences of metals bound to residual were revealed in figure 5. In like manner, zinc concentrated mostly (23.68%). Manganese had 0% occurrence. It is evidenced that residual solid holds trace metals within their crystal matrix and are in all likelihood, associated within silicate mineral [10,23]. Therefore, metals in this fraction are not expected to be released into solution over a reasonable time span under the condition normally encountered in nature. [10,11,21,23]. Therefore, they are not available to biota. Residual forms of zinc and iron are predominant. This is in line with numerous studies [2,10,23].

V.   Conclusion

As urbanization and industrialization increase, heavy metal pollution of the environment becomes a serious threat to mankind. The increasing load of heavy metals in several components of environment is of great interest to scientists all over the world. There have been a number of catastrophic incidences in both developed and developing countries involving the release of toxic chemicals and improper disposal of toxic wastes which are sources of heavy metals [27]. Despite the sharp increase of unleaded fuel utilization, followed by a rapid decline of lead levels in the atmosphere, it content in this area is still remains high with a consequence associated risk via the soil-hand-mouth pathway [2].

The observed contamination of the area investigated is probably as a result of agricultural, industrial, exhaust from vehicles, leachate from automobile mechanic waste dumps or municipal wastes which increase the concentration of specific heavy metals and such excessive levels could be hazardous to man, plants and aquatic organisms.

Efforts should be made to reduce the sources of emission of these trace metal pollutants into the environment. It is recommended that all activities that are contributing to the high load of heavy metals in this environment should be controlled.

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