Trace Metals Speciation in Floodplain Soil in Enugu Metropolis, Nigeria.

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Abstract: *Soil samples were collected from floodplain sediment in Enugu Urban, Nigeria to investigate the speciation and bioavailability of some trace metals, namely; iron, manganese, copper, zinc, lead, nickel and cadmium. Extracts from the soil were obtained by sequential extraction as described by Horowitz et al. The metals occurred with the following percentage bioavailability: Fe(67.00%), Mn(65.10%), Cu(44.70%), Zn(52.90%), Pb(53.80%), Ni(53.90%) and Cd(8.30%). Exchangeable metals and metals bound to carbonates accounted for over 50% of the total fractions. Metals bound to Fe-Mn oxides and humic materials accumulated 4.50% and 7.96% respectively, while residual metals bounded 34.93% of the sediment fraction. Lead had the highest distribution in exchangeable, carbonate and residual fractions while zinc was partitioned mostly in reducible and oxidizable forms. The high concentration of lead in both the carbonate and exchangeable forms depict its greater mobility tendency in the soil and consequently, bioavailable to biota. The results of the finding indicated that these trace metals with exception of cadmium were readily bioavailable in this urban soil, therefore, phytoremediation is advocated.*
Keywords: *Speciation; Trace metals; Floodplain sediments; Bioavailability; Pollution.*

I.   Introduction

During the past three decades, the state of the nation's metal pollution has become a matter of growing national 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.

Physicochemical characteristics of urban soil were significantly changed as a result of increasing pollution hazards resulting from intensive urbanization and industrialization.

Urban soil is thus characterized by large fluctuations of physicochemical properties in short distance [2]. Plants on their own usually demonstrate a high tolerance towards increased contents of metals; however, excessive concentrations of metals in the soil are harmful to the plants due to the ease of their accumulation, which is likely to result in diminished volume and deteriorated quality of yields [3].

The increased availability of heavy metals for plant uptake may lead to phytotoxicity, which may accumulate in higher amounts in plants. This enhances their transfer into the food-chain, thus posing serious environmental hazards to the population [4].

Toxic metals as well as many other organic substances, tend to accumulate in certain reservoirs (soil, sediments, etc.) from which they may be released by various processes of remobilization. They may also change form or speciation and become available to the biological food chain, thereby affecting life, including human life, by causing chronic and acute disorders [5].

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 [7].

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 whereas limited information exists concerning the partition and bioavailability of trace metals in the floodplain soil sediment in Enugu, Nigeria. Hence, there is a need to establish the chemical forms of these trace metals in the soil 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 [8].

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 Enugu urban, as all flood water end at this point. 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.

II.   Experimental

2.1 Sampling site
Enugu is the capital of Enugu State in Nigeria. It is known as coal city because of the large deposit of coal in the city. It is situated between 6°27′9.60″N 7°30′37.20″E coordinates. It covers an area of 113 km^2. It has a population of 722,664 in 2006. The mean temperature in Enugu State in the hottest month of February is about 36.2^{0}C, while the lowest temperatures occur in the month of November, reaching 20.3^{0}C. The lowest rainfall of about 0.16cm^3 is normal in February, while the highest is about 35.7cm^3 in July. The Ekulu, Asata, Ogbete, Aria, Idaw and Nyaba rivers are the six largest rivers located in the city. The Ekulu River is the largest body of water in Enugu urban and its reservoir contributes to part of the city's domestic water supply [9].

2.2 Sample Collection and Preparation
Floodplain soil sediment was collected at Miroocha, Ekulu road, Enugu in Enugu 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^{0}C prior to leaching.

2.3 Sequential Extraction Procedure
The method as modified by Horowitz et al (1991) [10] was used for the sequential extraction of the trace metals.
  I.   Exchangeable fraction: 1.0g 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.

2.4 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
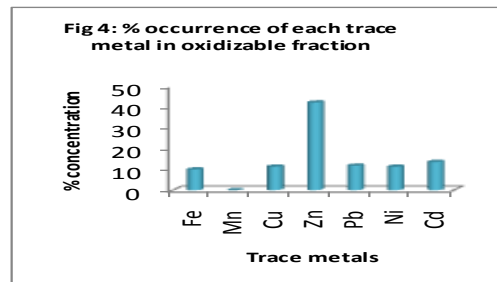
The results of this analysis are presented in the table below.
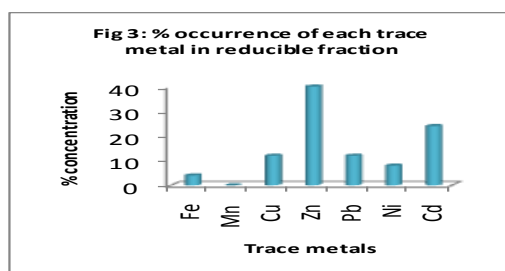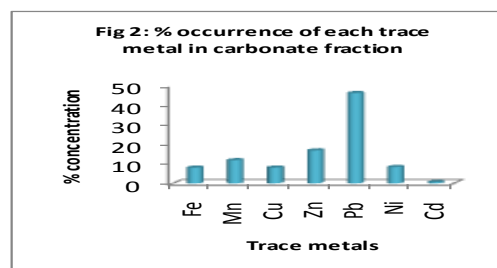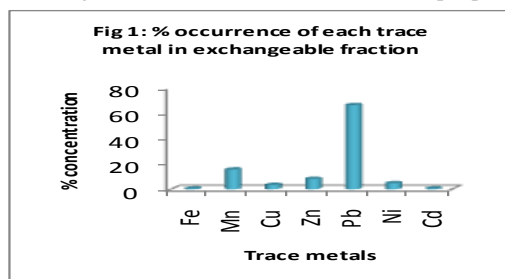
Result of sequential extraction of some selected trace metals from floodplain soil sediment in Enugu, Nigeria.

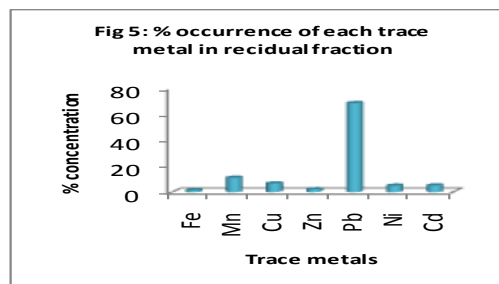| Sample	Fe	Mn	Cu	Zn	Pb	Ni	Cd	Total	Mean	% Fraction
Exchangeable	0.50	11.20	2.50	5.90	47.70	3.50	0.50	71.80	10.26	25.86
Carbonate	6.00	8.80	6.00	12.50	34.30	6.20	0.50	74.30	10.61	26.76
Reducible	0.50	0.00	1.50	5.00	1.50	1.00	3.00	12.50	1.79	4.50
Oxidizable	2.20	0.00	2.50	9.30	2.60	2.50	3.00	22.10	3.16	7.96
Residual	1.50	10.70	6.50	2.10	66.40	4.80	5.00	97.00	13.86	34.93
Total Fraction	9.70	30.70	19.00	34.80	152.50	18.00	12.00	**277.70**	39.68	
Mean Fraction	1.94	6.14	3.80	6.96	30.50	3.60	2.40			
Bioavailability	6.50	20.00	8.50	18.40	82.00	9.70	1.00			
% Bioavailability	67.00	65.10	44.70	52.90	53.80	53.90	8.30	345.70	49.40	

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

$$\% \text{ Bioavailability } = \left(\frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \quad X \quad \frac{100}{1} \right) \%$$

Where F_1 =   Exchangeable fraction
        F_2 =   Carbonate fraction
        F_3 =   Reducible fraction
        F_4 =   Oxidizable fraction
        F_5 =   Residual fraction [11].

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

Fig 2: % occurrence of each trace metal in carbonate fraction

Fig 3: % occurrence of each trace metal in reducible fraction

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

Fig 5: % occurrence of each trace metal in recidual fraction

IV. Discussion

The table above shows the results of partitioning of trace metals in the soil sample. Figures 1-5 also represent the percentage composition of each trace metal accumulated in the five fractions. In carbonate fraction, the metals partitioned in the sediment in the order: $Pb > Zn > Mn > Ni > Fe /Cu > Cd$.

Lead had the highest concentration value of the total fractions which was put at 152.5mg/kg with a mean value of 30.50mg/kg. It was widely followed by Zn(34.80mg/kg) with a mean value of 6.96mg/kg, while the least value was associated with Fe(9.7mg/kg) which put the mean at 1.94mg/kg. Both exchangeable Cd(0.5mg/kg) and Cd bound to carbonate (0.5mg/kg) are closely related to the values obtained for the same metal by Tessier et al (0.8µg/g; 0.8µg/g) and Horowitz (1.3µg/g; 0.8µg/g) in the Ružin sediment leachates [12]. Exchangeable Fe(0.50mg/kg), Cu(2.50mg/kg), Ni(3.50mg/kg), Zn(5.90mg/kg) and Cd(0.50mg/kg) were generally found to represent a minor portion of the total metal concentration. This was evidenced with the results conducted by Tessier et al [13] on Yamaska and Saint-Francois rivers, which put the metals concentrations at Fe(0.4µg/g; 0.4µg/g), Cu(0.15µg/g; 0.2µg/g), Ni(0.2µg/g; 0.2µg/g), Zn(0.1µg/g; 0.1µg/g) and Cd(0.1µg/g; 0.1µg/g). Exchangeable and carbonate fractions of cadmium had the same concentration values of 0.5mg/kg, likewise the reducible and oxidizable fractions had the same values of 3.0mg/kg. Manganese was not detected in reducible and oxidizable fractions. The concentration of lead in residual fraction was 66.40mg/kg. The high value may not pose any threat to human and his environment considering the fact that metals in this form are not readily released into solution but incorporated in the crystal lattices of clay minerals and silicate [12]. Conversely, the distribution of lead in exchangeable (47.70mg/kg) and carbonate (12.50mg/kg) forms, which are known as the major contributors to the mobility and bioavaiability of the metals in the soil [11] were very high. Lead had the highest bioavailability of 82.0mg/kg widely followed by manganese (20.0mg/kg) and least value of 1.0mg/kg was associated with cadmium. % bioavailability fraction ranged from 8.3% (cadmium) to 67.0% (iron) with mean value of 49.4%. The values were moderate but most parts of the trace metals were adsorbed or found in the exchangeable and carbonate fractions. This small amount entering biota may not pose an immediate environmental hazard.

It was also found that the % bioavailability of trace metals studied followed the order: Fe(67.00%) > Mn(65.00%) > Ni(53.90%) > Pb(53.80%) > Zn(52.90%) > Cu(44.70%) > Cu(44.70%) > Cd(8.30%). The % bioavailability of nickel was found to be 53.90%. The result of this investigation was on high side when compared with the finding of distribution pattern of nickel in the topsoil within Awkuzu area of Anambra State, Nigeria as reported by Omuku et al (2009) [11].

The concentrations of trace metals evaluated in reducible form were relatively low which accounted for only 4.50% of the total fractions. The low concentrations of these metals in this fraction compared favourably with those obtained by Skvaria (1998) [13]. Zinc had the highest concentration of 5.00mg/kg. Nickel had a concentration of 1.00mg/kg, this value is low and tolerable but should be monitored considering the fact that inorganic form of nickel is known to be perilous at high concentration [14].
In the metals bound to organic matter (oxidizable), zinc also had the highest concentration (9.30mg/kg) followed by Cd(3.00mg/kg.

For the selected trace metals evaluated, they occurred in the fraction in the order: Residual > Carbonate > Exchangeable > Oxidizable > Reducible.
In exchangeable fraction (fig.1), the occurrence of Fe and Cd are the least (0.69%) while Pb occurred as the highest (66.43%).

Fig.2 depicts the % occurrence of the trace metals studied in carbonate fraction. Cadmium had the lowest percentage (0.67%) while the highest value was associated with lead (46.16%) widely followed by zinc with a percentage of 16.82%. It a known fact that zinc is scanvaged by non-dentrital carbonate minerals, organic matter and oxide minerals and it is less mobile [15], therefore the possibility of its release into biota is reduced.
Manganese had 0% occurrence in the fraction bound to Fe-Mn oxides and minor parts of other trace metals were concentrated in this fraction which ranged from 0-40% (fig.3). A major part of Cd accumulated in the reducible (24.00%) and oxidizable (13.57%) fractions; while Zn dominated the same fractions with the values of 40.00% and 42.08% respectively (fig.3&4).

Also, in the metals bound to humic materials, Zn had the highest occurrence (42.08%) widely followed by Cd with percentage of 13.57% while manganese had 0.0% occurrence. Copper and nickel had the same percentage occurrence of 11.31% (fig. 4).

In residual fraction, 34.93%, which was the highest of the % fraction of the metals investigated, are unable to be released into solution and therefore pose no danger to biota [13]. Also in this fraction, Lead had the highest occurrence of 68.45% widely followed by manganese. Iron was the least with a value of 1.55%. Occurrence followed the order: Pb >> Mn > Cu > Cd > Ni > Zn > Fe (fig.5).

V.   Conclusion

The results obtained and presented in this paper revealed that the concentration of lead in this urban soil sediment is worrisome, despite the sharp increase of unleaded fuel utilization followed by a rapid decline of lead levels in the atmosphere. The high concentration could be as a result of the use of recycled battery cases in the area as well as geological composition of the soil. The mean concentration of zinc, though essential to maintain the metabolism of organisms, has to be monitored, because at high concentration, it can lead to poisoning and may cause anaemia and copper deficiency [14] as a result of bioaccumulation [16].

The total concentration of cadmium in the fractions though minimal must also be monitored considering the fact that it is relatively mobile in solution and has no nutritional benefit to both plants and animals [17]. Exchangeable and carbonate fractions accounted for 52.62% (25.86 + 26.76)% which accumulated parts of trace metals that are mobile, soluble in anoxic environment and readily available to biota. Reducible metals which are the most important scavengers represented only a minor fraction of the sediment (4.5%). Bound to organic matter (humic substances) fraction also bounded small portion of the trace metals (7.96%) instigated. Residual metals, i.e. those that bound to crystal lattices and silicates, were found to be 34.93%. This portion is not easily released into ecosystem over a time frame; therefore the easy of bioavailability is negligible. The continuous injection of these metals into ecosystem increases their concentration levels, consequently their toxicity. These toxic metals may be made insoluble possibly by the use of chelating agents; this should be encouraged in this urban centre. Floatation (a form of separation technique) could also be adopted in cleaning the sediments.

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