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Research article

FRACTIONATION OF SOME TRACE METALS IN FLOODPLAIN SOIL IN AWKA, ANAMBRA STATE, NIGERIA.

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ABSTRACT: This paper presents the results of the levels of some selected trace metals namely; iron, manganese, copper, zinc, lead, nickel and cadmium speciation from soil sediment collected from floodplain soil in Awka, Anambra State, Nigeria. Metals were extracted by means of the procedure described by Horowitz et al for the sequential extraction of soil samples. Lead had the highest total fraction concentration of 160.2mg/kg among the trace metals examined widely followed by Manganese (36.4mg/kg) while the least value was associated with Nickel (5.3mg/kg). The bulk of the metal concentrations were found in exchangeable fraction (36.45%). Inorganic form of the trace metals in the sample was 8.22% and the organic form was 45.54%. All the trace metals studied had their % bioavailability above average and ranged from 56.4% (Zn) to 76.0% (Ni) while the mean % bioavailability in the sample was found to be (66.6%). The considerable presence of these metals in carbonate and exchangeable bound fractions suggest that they have high potential bioavailability and mobility through the soil.

Keywords: Floodplain soil; Sequential extraction; Trace metals; Bioavailability; Mobility.

INTRODUCTION

Man' quest for food, social and economic advancement has led to the destruction of natural environment. Many have benefited from the resulting economic growth and technological progress, but the society has continued to suffer from increasing pollution hazards resulting from intensive urbanization and industrialization.

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.

Urban habitats under the influence of people lost characteristics of primary type of soil. The human influence is manifested in the creation of embankments and landfills, disposal of construction materials and land abuse. Therefore, physicochemical characteristics of urban soil were significantly changed. Urban soil is thus characterized by large fluctuations of physicochemical properties in short distance [1].

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 macro and micro-elements contents depend mainly on the type of plant, environment (the level of industrial development of the region, air and soil pollution and climate conditions), in which the plant is grown [4,5].

The main sources of macro and micro-elements to the plants are their growth media (soil, air and nutrient solutions) from which minerals are taken up by the root or the foliage [4]. Plants growing in polluted environments can accumulate macro and micro-elements at high concentration, causing a serious risk to human health when plant based food stuffs are consumed [6,7,8].

Soils are the reservoir for many harmful constituents: elemental and biological, including heavy and trace metals [9]. The total metal content of soils is useful for many geo-chemical applications but often the speciation (bioavailability) of these metals is more of interest in terms of what is biologically extractable [10]. Impact of heavy metals on the environment depends on the phase specific bond type which in turn specify cleaning and utilization potentials.

In terms of bioavailability, various species of metals are more biologically available than others [11]. If bioavailability and the mobility of metals are related, then the higher the concentration of mobile toxic metals in the soil, the increase the potential for the plant uptake and animal/human consumption [12,13]. Research has also shown that bioavailability of heavy metals in anoxic environment is more and decrease with exposure time.

The use of total metal concentration as criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption has been criticized by many authors [14].

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 Awka, 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.

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 Awka metropolis 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.

EXPERIMENTAL

Sampling Site

Awka lies between $6^0 12'25''$N $7^0 04'04''$E coordinate of southeastern part of Nigeria. It is situated below 300 metres above sea in a valley on the plains of the Mamu River. Awka is in the tropical zone of Nigeria and experiences two distinct seasons, seven months of heavy tropical rains (May - October) are followed by five months of dryness (November - March). The temperature is generally hot and humid in the range $27\text{-}28^0$C during July through December but rising to 35^0C between February and April.

Sample Collection and Preparation

Floodplain soil sediment was collected beside Parktonia Hotel, along Onitsha road, Awka 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) [15] was used for the sequential extraction of the trace metals

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 $1MCH_3COONa$ 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).

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 Awka, Nigeria.

Sample	Fe	Mn	Cu	Zn	Pb	Ni	Cd	Total	Mean	% Fraction
Exchangeable	0.50	16.40	2.80	4.40	64.30	2.40	5.00	95.80	13.69	36.45
Carbonate	8.00	10.70	4.20	9.20	42.70	1.40	3.30	79.50	11.36	30.25
Reducible	3.50	0.00	2.30	5.40	8.40	0.50	1.50	21.60	3.09	8.22
Oxidizable	0.50	9.10	1.00	0.20	33.40	0.50	1.50	46.20	6.60	17.58
Residual	1.50	0.20	1.00	4.90	11.40	0.50	0.50	20.00	2.86	7.61
Total Fraction	14.00	36.40	11.30	24.10	160.20	5.30	11.80	263.10	37.60	
Mean Fraction	2.80	7.28	2.26	4.82	32.04	1.00	2.36			
Bioavailability	8.50	27.10	7.00	13.60	107.00	3.80	8.30			
% Bioavailability	60.70	74.50	61.90	56.40	66.80	76.00	70.00	466.40	66.6%	

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

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

Where F_1 = Exchangeable fraction

F_2 = Carbonate fraction

F_3 = Reducible fraction

F_4 = Oxidizable fraction

F_5 = Residual fraction

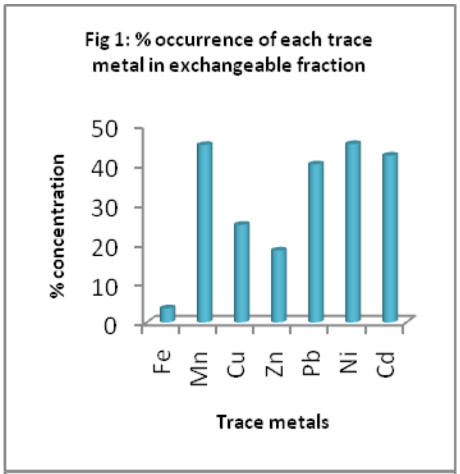
Fig 1: % occurrence of each trace metal in exchangeable fraction

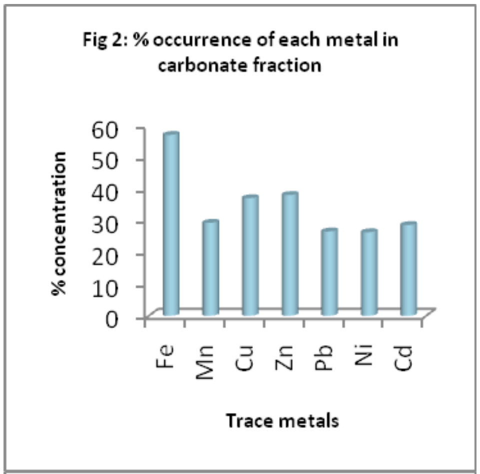
Fig 2: % occurrence of each metal in carbonate fraction

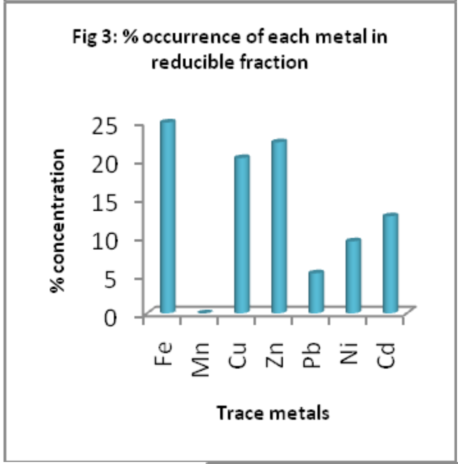
Fig 3: % occurrence of each metal in reducible fraction

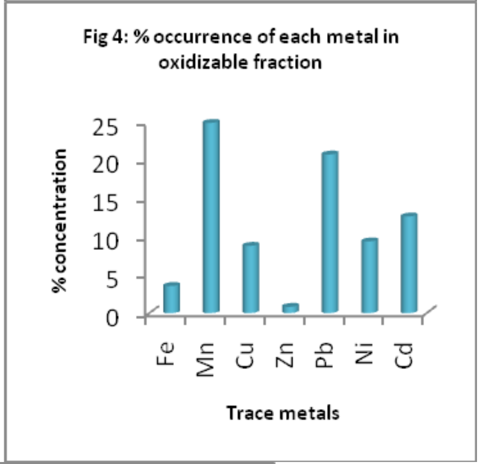
Fig 4: % occurrence of each metal in oxidizable fraction

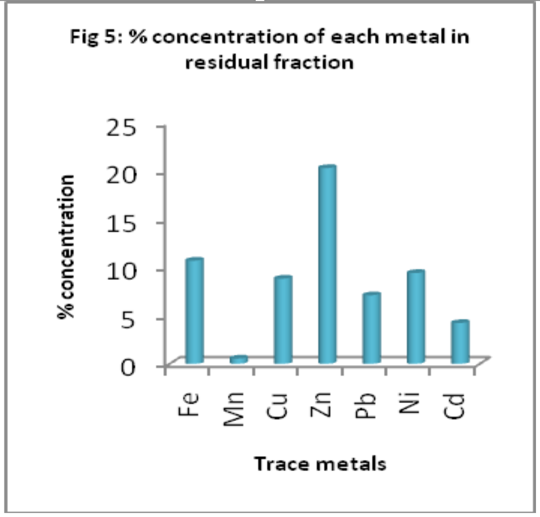
Fig 5: % concentration of each metal in residual fraction

DISCUSSION

The table above shows results of sequential extraction for the selected metals analyzed from Awka floodplain soil sediment. Lead had the highest total fraction of 160.20mg/kg while 5.00mg/kg was associated with nickel as the least concentrated trace metals. Also, the mean fraction of nickel was determined to be 1.00mg/kg which was very far lower than the values obtained by Omuku et al [16]. The highest concentration of iron was found in bound with carbonate fraction (8.00mg/kg) while that of manganese was in exchangeable form with the value of 16.4mg/kg.

The % bioavailability of these trace elements ranged from 56.4–76.0% with mean value of 66.6%. Nickel had the highest percentage of 76.0% followed by manganese (74.5%) and the least value was associated with zinc (56.4%). The % bioavailability of these trace metals were high in this location, meaning that most of these metals were found in exchangeable and carbonate fractions which are the major contributors to the mobility and availability of trace metals [17]. Metals in these fractions are mobile, hence dangerous and therefore can easily enter and accumulate in biota.

Concentrations of iron, copper, zinc and nickel found in exchangeable fraction are observed to be low compared to high concentrations of manganese, cadmium and lead. This fraction accounts for 40-45% occurrence for manganese, cadmium and lead of the total extract concentrations (fig. 1). Evidence from many types of sediments [14] 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 [18]. Iron had the highest % occurrence of the trace metals investigated widely followed by zinc while the least value was associated with nickel (fig. 2). This shows that iron accumulates mainly in bound to carbonate. The observed appreciable concentrations of almost all of these trace metals in this form (Fe - 57.14%; Cu – 37.17%; Zn – 38.17% and Mn – 29.40%) are similar to those reported by Tessier et al [16]. The observed trend is in order Ni < Pb < Cd < Mn < Cu < Zn < Fe. The concentrations of trace metals in reducible form are relatively low which accounts for only 8.22% of the total fraction. The low concentrations of these trace metals in this fraction compared favourably with those obtained by Skvaria (1998) [19] Lead had the highest concentration (8.40mg/kg) closely followed by Zn (5.4mg/kg). Nickel had a concentration of 0.50mg/kg, this value is very low and tolerable considering the fact that inorganic form of nickel is known to be perilous at high concentration [20]. Manganese was not detected in metals bound to Fe-Mn oxides and minor parts of other trace metals were concentrated in this fraction and ranged from 5.24 – 25% (fig. 3).

In the metals bound to organic matter, lead had the highest concentration (33.4mg/kg) and it is a known fact that the organic form of lead is more hazardous and therefore poses danger to human health [21]. Manganese had the highest percentage fraction (25.0%) and zinc was the least with a value of 0.83% (fig. 4).

The concentrations of residual metals in the last fraction are moderate with exception of zinc (20.33%) (fig. 5). Both nickel and cadmium had the same concentrations of 0.50mg/kg. Metals in this form are not release into solution and therefore not dangerous to biota [14].

CONCLUSION

From the result of the sequential extraction, it could be concluded that the amounts of selected trace metals entering the biota in the sampling location were high since bioavailability and mobility factors are on the high side. Repeated injection of these metals into the said environment will result into health risk. This, in turn, will increase their availability for plant uptake, dissolve in runoff entering the nearby water bodies as well as promote their downward leaching to the groundwater table.

Despite the sharp increase in the utilization of unleaded fuel by the automobiles, its content was high. This could probably be as a result of the use of recycled battery cases in the area as well as geologic composition of the soil. Proper remediation action such as phyto-remediation, improve recycling methods and use of unleaded fuel is advocated.

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