CHEMICAL FRACTIONATION OF HEAVY METALS IN SOILS NEAR METAL DUMPSITES IN ZARIA, NIGERIA

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Abstract: This research was carried out to determine the chemical form of metals and to evaluate their mobility and bioavailability in soils near metal dumpsites in Zaria, Nigeria. Sequential extraction was used to fractionate Cd, Cu, Ni, Zn, Co and Pb from soil collected from three selected metal dumpsites into six operationally defined groups: water soluble, exchangeable, carbonate, Fe -Mn oxide, organic, and residual. The results indicated that the concentrations of the studied metals in the soils from experimental sites were higher than the corresponding values from the control site, and higher than the recommended limits given by FAO/WHO. The bioavailability of the metals at the three different study areas was in the order: Dambo:- 40% Cd, 39% Co, 91% Cu, 66% Ni, 42% Pb and 73% Zn.; Agoro:- 39% Cd, 48% Co, 74% Cu, 59% Ni, 41% Pb and 60% Zn and Yankarfe:- Cu > Ni > Zn > Pb > Cd >Co. The result of this study indicated that the bioavailabilities of the studied metals at the test sites were higher than those at the control site except that of Co. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic or lithogenic ones.

Keywords: Bioavailability, dumpsites, heavy metals, mobility, sequential extraction, soil

Introduction

Due to the ever-increasing population and Industrialization, most environments are to some extent unnaturally polluted. Contamination of soils by heavy metals is the most serious environmental problem and has significant implication for human health process (Yen *et al*., 2012; Chen *et al*., 2012). Sources such as atmospheric deposition, waste disposal, fertilizer application and waste water in agricultural land constitute the major anthropogenic input (Salawu *et al*., 2014). Heavy metals are usually characterized by their toxicity and complexity of chemical behavior (Alloway, 1995). Thus, knowledge about the chemical speciation of heavy metals provides information on their bioavailability, mobility, and toxicity. Total metal content estimate is a poor indicator to assess the environmental behavior of contaminated soil.

Toxicity of a metal in soil depends not only on its mobility, transformation and potential bioavailability to plants but also its specific forms or binding state. Determining the total content of heavy metals in the sediments 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 soil and sediment and helps to assess the environmental impact of contaminated soil and sediment (Ogunfowokan, *et al*., 2013; Salomons *et al*., 1995). It provides information on potential mobility as well as bioavailability and plant uptake of heavy metals (Nagajyoti *et al*., 2010; Shuman, 1991; Singh, 1997). However, the bioavailable fraction can differ from one metal to another and from one receptor to another. Mobility refers to the capacity of an element to move within fluids after dissolution. It is difficult to predict element mobility quantitatively in environments. Rather, mobility should be considered in a relative sense by empirically comparing the behavior of elements under changing environmental conditions, such as at geochemical barriers.

Chemical fractionation is affected strongly by variations in pH, redox state, organic content, and other environmental factors. The sequential extraction has been used to highlight the relationship existing between these compartments, and also to assess the bioavailability and the potential threat of heavy metals to the environment. The bioavailability is related to solubility of the metals which decreases in order: exchangeable > carbonate > Fe-Mn oxide > organic > residual

(Ma & Rao, 1997). This study was carried out to check the mobility and bioavailability of heavy metals in the soil near the selected metal dumpsites at Dambo, Agoro and Yankarfe in Zaria, Nigeria.

Materials and Methods

All the chemicals and Reagents used were of analytical grade (AR) and de-ionized water was used throughout the research work.

Study areas

Three areas in Zaria, Nigeria (11º 07' 51" N; 7º 43' 43" E) were selected for the research work because of the activities that involve disposal of metal containing materials into the biosphere, which may lead to increase in the amount of toxic metals entering the environment: Agoro, Dambo and Yankarfe in Zaria metropolis, and each dumpsite occupies an estimated area of 70 x 100 m.

Sample collection

Twenty soil samples from each study area were collected from the surface to a depth of 20 cm using hand trowel and then mixed together. Background soil (150 g) samples were also obtained as control from an area 5 km distance away from the metal dumpsites. The collection was done by dividing the experimental and control sites each into four quadrants, five soil samples were collected from each quadrant in a diagonal basis following the methods of Nuonom *et al*. (2000). The samples were cleaned from stones and twigs, packed in polyethylene bags and properly labeled and then taken to the laboratory.

Sample treatment and analysis

The collected soil samples were air-dried at room temperature for three days. The soil samples were ground and sieved through 2 mm sieve and kept in clean polythene bags for further analysis. The physicochemical parameters of the soil: pH, particle-size distribution, cation exchange capacity, organic matter (wet digestion method) and the moisture content were determined using standard methods as described by Agbenin (1995). The soil samples were subjected to sequential extraction using a modified Tessier's procedure as reported by Masa *et al*. (2013) to determine the bioavailable metals and those bound to different fractions.

Sequential extraction

Sequential extraction was carried out on the principle of selective extraction using a modified Tessier's procedure as

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reported by Masa *et al*. (2013): Water soluble was first of all extracted and then, $Mg(NO_3)_2$ was used instead of $MgCl_2$ to extract exchangeable fraction because the chloride ion can complex metals and increase the solubility of several heavy metals within the soil. Also, the extraction of the oxidizable phase was undertaken after the extraction of the exchangeable phase. This method allows the destruction of organic matter, which entraps the mineral materials and then provides a better extraction of the following phases. For the residual fraction, a combination of aqua regia/hydrofluoric acid ($HCl/HNO_3/HF$) was used.

The concentration of the heavy metals was determined by Atomic absorption spectrometry (AAS), for each fractionation sequence.

Results and Discussion
Physicochemical parameters of the soil
Table 1 shows the results of the physicochemical parameters of the soil analysed. The pH values obtained for the test soils ranged from 6.78±0.02 to 6.86±0.01, that is, slightly acidic, and slightly alkaline (7.50) for control soil. The pH of farmlands ranged from 4.5 to 8.4. The pH of soil affects the bioavailability of metals in the soil solution. Bioavailability of metals in soils decrease above pH 5.5 – 6 (Prasad, 2003). The present study showed that the soils were sandy loam which agreed with report of Shehu *et al*. (2015) that the soils of

Kaduna – Zaria area are sandy clay loam to sandy clay with sandy loam mainly on topsoil. When moisture content reached more than 4%, it could only cause the erosion of sandy loam soil to reduce by a small degree (Chen *et al*., 1996).

The percentage organic matter (% OM) ranged from 4.02±0.06 (at Yankarfe) to 5.10±0.05 (at Agoro) but still higher than the values found in soils of the Nigerian savannah which range from 0.8 to 2.9% (Sharu *et al*., 2013). The OM component of soil has negative charges on the surfaces which adsorbed and hold positive ions (cations) by electrostatic force. This electrical charge is critical to the supply of cations to the plants. Cation exchange capacity (CEC) ranged from 9.8±0.10 to 15.6±0.17 cmol/kg^{-1}; normal CEC ranges in soils would be from < 3 cmol/kg, for sandy soils low in OM, to > 25 cmol/kg for soils high in certain types of clay or organic matter (OM). The CEC represents the ability of the soils to absorb or release cations and, consequently, is an important parameter in sites contaminated by heavy metals. Organic matter and clay minerals are responsible for the CEC (Ashraf *et al*., 2012).When pH decreases (acidic) more H^+ ions are attached to the colloids and push the other cations from colloids into the soil solution. Soil OM will cause a greater CEC at near-neutral pH than under acidic conditions (Donald, 2000).

Table 1: Physicochemical parameters of the soil

Physicochemical parameters	Dambo	Agoro	Yankarfe	Control
Particlesize(%): Clay	12	10	15	11
Silt	18	17	7	18
Sand	70	73	78	71
Soil texture	Sandy loamy	Sandy loamy	Sandy loamy	Sandy loamy
Soil pH	6.80±0.02	6.86±0.01	6.78±0.02	7.50±0.03
Moisture content (%)	4.80±0.05	3.90±0.03	4.50±0.03	4.00±0.02
Organic matter (%)	4.53±0.07	5.10±0.05	4.02±0.06	4.87±0.05
CEC, (cmol/kg^{-1})	9.80±0.10	12.80±0.07	10.20±0.15	15.60±0.17

Total heavy metals in the soil
Figure 1 shows that the soil at Dambo had the lowest values in Co (8.30±0.04 mg/kg) and Pb (69.30±0.04 mg/kg), but highest in Cd (8.00±0.03 mg/kg), Cu (6.50±0.03 mg/kg) and Zn (55.93±0.11 mg/kg) as compared to their corresponding values at Agoro and Yankarfe soils. The soil at Agoro showed lowest value of Cu (5.30±0.03 mg/kg) only, but highest in Co (9.90±0.05 mg/kg) and Ni (84.93±0.07 mg/kg). The soil at Yankarfe showed lowest values of Cd (6.00±0.02 mg/kg), Ni (47.90±0.06 mg/kg) and Zn (25.58±0.06 mg/kg), but highest in Pb (76.90±0.05 mg/kg) when compared with those of Dambo and Agoro. The total concentration of the studied metals in the soil at the study area were higher than the control and also higher than the standard regulatory limits as reported by Akpoveta *et al*., 2010. Using one-way ANOVA, there was a significant difference ($P < 0.05$) between the metal level at the experimental site and the control. This implies that the dumping of scrap metals on the soil has contributed significantly to the heavy metals contamination of the soil and can be of health risk since crops are planted on nearby farmlands.

Fractionation
The mobility and bioavailability of heavy metals in soils depend on how the metals are associated with the components of the soil, and the measure of the mobility and bioavailability of metals serves to predict the behavior of heavy metals in the soil. The metals are bound to the solid component of the soil through phases such as water soluble, exchangeable, carbonate, oxide and hydroxide, and organic matter. The

selective sequential extraction of heavy metals provides detailed insight on how the metals are associated with the components of the soil (Achi *et al*., 2011).
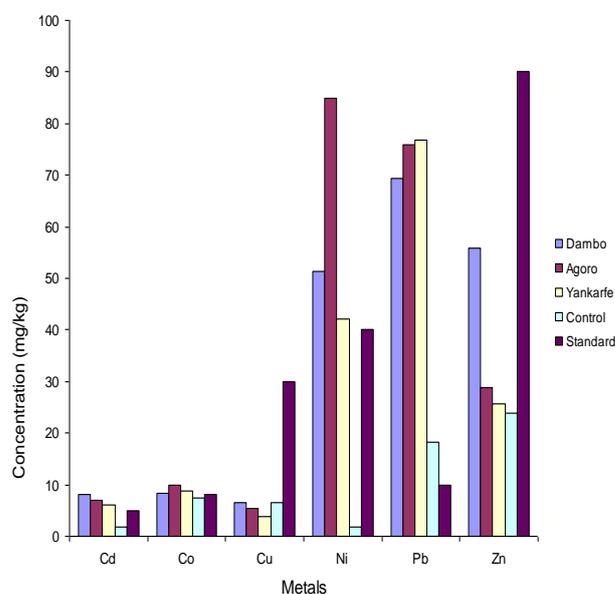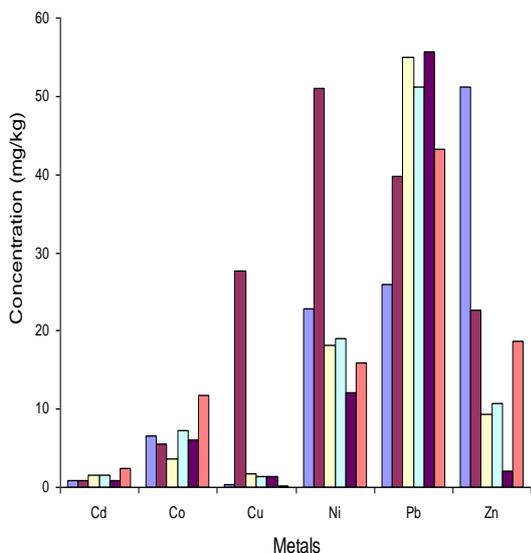

Fig. 1: Total concentration of the studied metals in the soil at the study areas

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Figure 2 shows the results of the sequential extraction of metals in different fractions of the soil at Dambo. The bioavailable fractions (F1 + F2 + F3) constitute about 40% Cd, 39% Co, 91% Cu, 66% Ni, 42% Pb and 73% Zn. The residual fraction (F6) has the highest level of Cd (31%) and Co (29%), while the Pb (21%) was highest in organic fraction (F5).

At Agoro study area (Fig. 3), the bioavailable fractions (F1+F2+F3) for Cd, Co, Cu, Ni, Pb and Zn were 39, 48, 74, 59, 41 and 60%, respectively. The highest percentage of Cd (36%) was found in the residual fraction (F6), Co was found to be 18, 20 and 19% in F3, F5 and F6, respectively. The percentage of Cu found in F5 was 16%. For Pb, 18 – 21% were found in other fractions (F4 – F6). The organic fraction (F5) contains about 22% Zn, while the Fe – Mn oxides had 16% Zn.

Yankarfe study area (Fig. 4) showed that Co, Cu, Ni and Zn were highest in the exchangeable fraction (F2), while Cd (32%) and Pb (20%) were highest in residual (F6) and organic fraction (F5), respectively. The predominant form of Cd (32%) available in the entire fractions is the residual fraction. A good proportion of Cu (27%) was found in the organic fraction (F5). The bioavailable fractions (F1+ F2+F3) constitute about 36% Cd, 47% Co, 50% Cu, 60% Ni, 44% Pb and 79% Zn.

At the Control site, the different fractions contain various metal levels as shown in Figure 5. The percentage bioavailability (F1+ F2+F3) of the studied metals were: Cd - 38%, Co – 36%, Cu – 59%, Ni – 50%, Pb – 39% and Zn – 44%. The highest percentage of Cd (32%) was found in the residual fraction (F6), Co was 19% and 14% in F5 and F6 respectively. The percentage of Cu found in F4 and F5 were 18 and 43%, respectively. For Pb, 14 – 23% were found in other fractions (F4 – F6). The organic fraction (F5) contains about 1% Zn, while the Fe – Mn oxides (F4) had 33% Zn, the residual (F6) fractions had 21% Zn.

Fig. 3: Concentrations (mg/kg) of metals in different fractions of the soil at Agoro

Fig. 4: Concentrations (mg/kg) of metals in different fractions of the soil at Yankarfe

F1= water soluble Fraction, F2 = Exchangeable Fraction, F3 = Carbonate bound Fraction, F4 = Fe and Mn oxides bound Fraction, F5 = Organic matter bound Fraction, F6 = Residual Fraction.

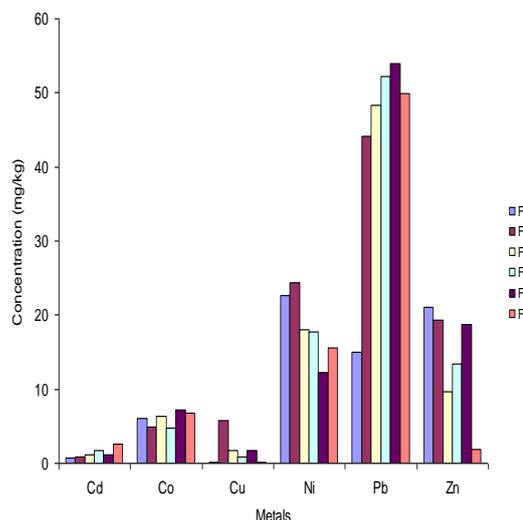**Fig. 2: Concentrations (mg/kg) of metals in different fractions of the soil at Dambo**

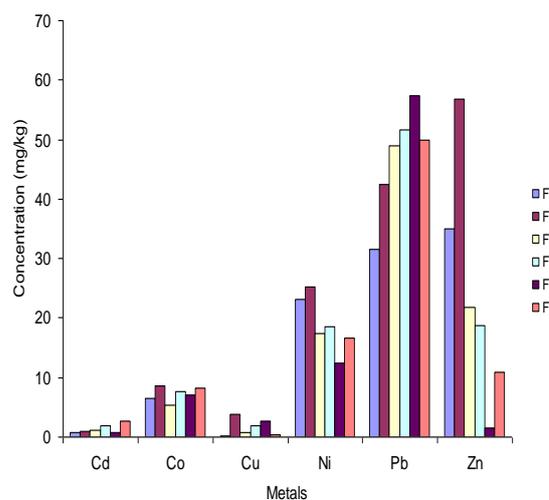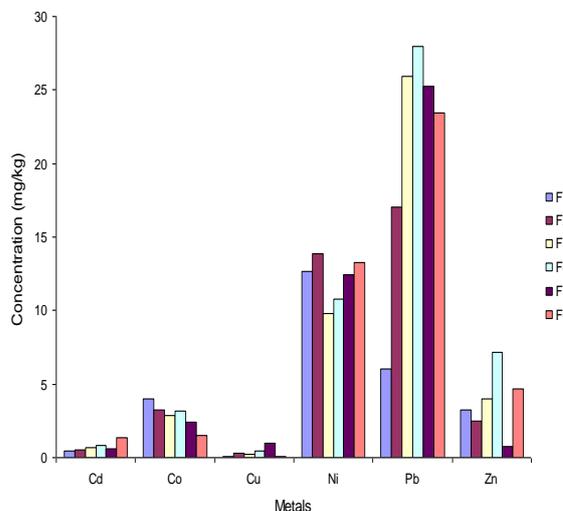**Fig. 5: Concentrations (mg/kg) of metals in different fractions of the soil at control site**

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The results of this study indicated that the unavailable Cd was mostly bound to the residual fraction (F6). This fraction typically contained within the silicate crystal matrix of the minerals and represents the relatively immobile fraction of metals in soil (Borgese *et al*., 2013). Co was bound to organic matter (F5) and residual (F6) fractions, Cu was mostly bound to oxides (F4) and organic matter (F5) fractions, Ni was found in oxides (F4) fractions, Pb was mostly found bound to oxides (F4) and organic matter (F5) fractions, while Zn was bound to organic matter (F5) and Residual (F6) fractions. The distribution patterns varied among the six studied metals, and were similar for a certain metal among most of sample sites. For Cd in most of the samples, residual fractions (F6) accounted for more than 30% of their total concentrations; whereas about 20% of Pb present in organic fraction (F5). A good proportion of Cu was found in the organic fraction (F5). The higher stability constant of copper complexes with organic matter leads to high organic fraction. Only under oxidizing conditions, can copper be leached into the environment (Venkateswaran *et al*., 2007).

Li & Thornton (2001) reported a significant association of Pb with the soil carbonate, while Kabata-Pendias & Pendias (2001) stated that there is a strong association of Pb with organic matter. Kabala & Singh (2001) and Ashraf *et al*. (2012) found that Zn was mostly concentrated in the residual fraction for agricultural calcareous soil. Different distribution patterns have been investigated by other authors, depending on the soil and contamination types (Kos *et al*., 2003). Tessier *et al*. (1979) reported that exchangeable Cd, Co, Cu, Ni, Pb, Zn and Fe are generally found to represent a minor fraction of the total metal concentration of the solid.

The results obtained for Fe and Mn oxides bound Fraction (F4) and organic matter bound Fraction (F5) indicated that these phases have a scavenging action for heavy metals that is far out of proportion to their own concentration. Only metals associated with water soluble (F1), exchangeable (F2) and carbonate (F3) fractions are readily available for plant uptake (Lasat, 2000). To assess the availability of heavy metals, only the soil labile fraction is taken into account because this fraction is often called, by extension, the bioavailable fraction (Gray *et al*., 2004). However, the bioavailable fraction can differ from one metal to another and from one receptor to another. The availability of metals for plants and micro-organisms in soil depends on the composition of the different compartments of soil such as carbonates, oxides, organic matter and silica. The partitioning of trace elements between soil and the soil solution governs their mobility and availability for uptake by plants and other organism (Allen *et al*., 2002). The sequential extraction has been used to highlight the relationship existing between these compartments, and also to assess the bioavailability and the potential threat of heavy metals to the environment. The disposition of cadmium and lead in F1, F2 and F3 fractions constitutes serious environmental problems because of their high mobility (Yang *et al*., 2013). The distribution of a given metal between various fractions does not necessarily reflect the relative scavenging action of discrete soil phases, but rather should be considered as operationally defined by the method of extraction (Tessier *et al*., 1979).

Considering the concentrations of the studied metals in the various fractions of the soil, the percentage bioavailability (F1+ F2 + F3) of the metals at the three different study areas were in the order: Dambo:- Cu > Zn > Ni > Pb > Cd > Co; Agoro :- Cu > Zn > Ni > Co > Pb > Cd and Yankarfe:- Cu > Ni > Zn > Pb > Cd >Co. Prasad (2003) reported that the most readily bioavailable metals are Ni, Zn, Cd and Cu, moderately bioavailable metals are Co, Mn and Fe, while the nonbioavailable are Pb, Cr and U. Lead (Pb) is notorious for its lack of soil mobility, primarily due to metal precipitation

as insoluble phosphates, carbonates and hydroxides which have low solubilities in natural water. Bioavailability of metals in soils decrease above pH 5.5 – 6. The result of this study indicated that the bioavailabilities of the studied metals at the test sites (Dambo, Agoro and Yankarfe) were higher than those at the control site except that of Co. There was no significant difference (P > 0.05) between the Co level in both the dumpsites and the control; hence Co is from natural lithogenic origin. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic or lithogenic ones (Kuo *et al*., 1983; Kaasalainen & Yli-Halla, 2003; Kumar *et al*., 2011). Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected landfills, leaded gasoline and lead-based paints, land application of fertilizing animal manures, biosolids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals and atmospheric deposition (Raymond & Felix, 2011). It is projected that the anthropogenic emission into the atmosphere, for several heavy metals, is one-to-three orders of magnitude higher than natural fluxes (Sposito & Page, 1984).

The low bioavailability of Cd, Co and Pb metals may be related to weak acidic soil property of the Dambo, Agoro and Yankarfe. Previous studies have reported that when pH reached 7.5, Cd will be hardly dissolvable. At higher pH (6.5 or higher), water soluble Cd would enter the soil, existing mainly in state combining with clay mineral and oxide as well as residual fraction (Dai, 2006). In addition, Cd ion adsorption will be greatly enhanced at higher pH than at lower pH due to hydrolysis (Ali & Dzombak, 1996; Fijalkowski *et al*., 2012). It is also widely accepted that water soluble fractions of other metals, such as Pb, were rather low in alkaline soil (Wu, 2011).

Conclusion

The bioavailability of the metals at the three different study areas is in the order: Dambo:- Cu > Zn > Ni > Pb > Cd > Co ; Agoro:- Cu > Zn > Ni > Co > Pb > Cd and Yankarfe:- Cu > Ni > Zn > Pb > Cd >Co. The distribution patterns varied among the six studied metals, and were similar for a certain metal among most of sample sites. The result of this study indicated that the bioavailabilities of the studied metals at the test sites (Dambo, Agoro and Yankarfe) were higher than those at the control site except that of Co. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic or lithogenic ones.

Authors' Contributions

This work was carried out by author ZIY under the supervision of authors EBA, CEG and SOI. All authors read and approved the final manuscript.

Competing Interests

No competing interests exist among the authors.

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