



SEQUENTIAL ANALYSIS OF METALS IN MUNICIPAL DUMPSITE COMPOSTS OF KANO METROPOLIS, NIGERIA

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ABSTRACT

The heavy metals contents (Pb, Cu, Fe, Cr, Cd, Zn, Mn and Ni) in Municipal dumpsite compost were determined by the sequential extraction method. Chemical parameters such as pH, conductivity, and organic carbon contents of the samples were also determined. Analysis of the extracts was carried out by atomic absorption spectrophotometer machine (Buck Scientific VPG 210). Results of these analyses showed that Pb, Ni, Cr, Mn and Fe were largely associated with residual fraction (53.06%, 56.26%, 58.15%, 59.14% and 64.10% respectively). Cu, Cd and Zn were largely associated with non-residual fractions (71.42%, 54.44%, and 54.15% respectively). Calculated mobility and bioavailability factors of Cd, Zn and Cu were also high (54.54%, 54.16%, 53.06% and 0.54, 0.54, 0.53 respectively), moderate for Pb, Cr, Ni, Mn, and Fe (46.94%, 41.86%, 43.74%, 40.85%, 35.90% and 0.46, 0.41, 0.43, 0.40, 0.35 respectively). Mean percentage recoveries were ranged from 79.75%-100%.

Keywords: Municipal dumpsite, compost, sequential extraction, mobility factor, bioavailability factor.

INTRODUCTION

Metals are present in municipal dumpsites composts in different chemical forms, which influence their reactivity and hence their mobility and bioavailability. Apart from the sites of mineral extraction and application of sludge, uncontrolled Municipal dumpsites are increasingly seen as a source of soil pollution. These dumpsites are places where various products are stored (Ostman *et al.*, 2006). Wastes degradation leads to the pollution of soil by many pollutants through leachate seepage. The composts around the dumpsites are therefore subjected to different types of pollution including those caused by heavy elements. Metals such as cadmium, mercury and arsenic are the most hazardous (Park and Shin, 2006). The risks associated with the presence of heavy metals are varied and depend on their chemical forms (metal, oxide, salt and organometallic) (Kashem *et al.*, 2007). The impact of these metals in composts is their possible transfer into water or plants which is defined in terms of bioavailability. Cd and Pb are considered as the most important environmental pollutants in agricultural soils because of the potential harmful effects they may have on food quality and health of soil (Onweremadu and Duruigbo, 2007).

Metal in soils can be divided into two fractions (Rachou and Sauve, 2008): (1) Inert fraction, assumed as the non-toxic fraction, and (ii) the labile fraction, assumed to be potentially toxic. To assess the availability of heavy metals, only the soil labile fraction is taken into account because it is often called by extension, the bioavailability fraction (Gray *et al.*, 2004). However, the bio available 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, (oxy) metal hydroxides, organic matter and silica.

The sequential extraction was used to highlight the relationship between the compartments of compost and metals, and to assess the mobility, bioavailability and the potential threat of heavy metals to the environment.

MATERIALS AND METHODS

Study Area and Sample Collection

The composts samples were collected from twelve different – sampling points (0-15cm depth) in Kano metropolis into polyethylene bags with plastic spoon. Samples were immediately taken to the laboratory, extraneous materials were removed; the samples were air-dried, crushed and grinded to a fine powder in a mortar passed through a 0.20mm sieve. The compost samples were homogenized and stored in clean polyethylene bags in a dessicator till the analysis. Precautionary measures were taken to avoid contamination during sampling, grinding, sieving and storage (Tokalioglu *et al.*, 2003).

Reagents: Analytical reagent grade chemicals and de ionized water were used for preparing all solutions. Stock solutions containing 1000mgL⁻¹ of the analytes were prepared from nitrate salts of Pb, Cu, Fe, Cr, Cd, Zn, Mn and Ni in 1% of HNO₃ into calibrated flasks.

Working standard solutions were prepared by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents in equal quantities as described in the analysis procedure throughout the experiments. **Total Metal Analysis:** To check the accuracy of the sequential extraction procedures used in the analysis of municipal dumpsite compost samples, the recovery values (%) were investigated using total metal analysis.

Exactly, 0.25g of the samples was weighed and digested with 6ml of an acid mixture (HNO₃ + HF + H₂O₂) at ratio of 3:2:1. All the analyses Recovery

$$\sum n = \left[\frac{\text{sequential extraction procedure}}{\text{Single digestion with strong acid}} \right] \times 100, \text{ ranged from } 79.75 - 100\%$$

Heavy Metal Fractions: In this study, four different extraction procedures were used according to the modified Tessier's method (Blanchard, 2000), to establish the distribution of metal in the compost. The extraction was carried out at room temperature. After each extraction, the mixture was centrifuged (15min, 3000rpm) and the supernatant was filtered through no. 41 whatman filter paper.

Water soluble Fractions: Each sample was extracted with 50cm³ of deionized water. The mixture was shaken for 5h at 23°C and left to stand overnight.

Reducible Fractions: Metals bound to iron and manganese oxide were extracted by adding 50cm³ of 0.1M Hydroxylammonium chloride (adjusted to pH 2 with 2 molL⁻¹ nitric acid) onto the residue from the water soluble fraction.

Oxidizable Fractions: Exactly 50cm³ of 1.0M ammonium acetate solution (adjusted to pH 2 with 2 molL⁻¹ nitric acid) was added on to the residue from the reducible fraction.

Residual Fractions: The residue from oxidizable fractions after drying in the dessicator for 7days, 0.25g was weighed and digested in a platinum crucible with 3cm³ HNO₃, 2cm³ HF and 1cm³ H₂O₂ on a hot plate. The mixture was evaporated to the dry ness, 40cm³ of 0.25M of HNO₃ was added. The resulting solution was heated for about 10minutes, and then filtered into 60ml plastic bottles. Finally, the extracts collected were analyzed using AAS (Bulk scientific VPG 210) to determine the concentrations of Pb, Cu, Fe, Cr, Cd, Zn, and Ni metals in each of the fractions.

Mobility Factor

The mobility of metals in compost samples may be assessed on the basis of absolute and relative content of fractions weakly bound to components. The relative index of metal mobility was calculated as a "mobility factor." (MF; Kabala and Singh, 2001; Narwal *et al.*, 1999; Salbu *et al.*, 1998) on the basis of the following equation:

$$MF = \frac{(F_1 + F_2 + F_3)}{(F_1 + F_2 + F_3 + F_4)} \times 100$$

Where,

- F₁ = water soluble fraction
- F₂ = reducible fraction
- F₃ = Oxidizable fraction
- F₄ = Residual fraction

Bioavailability Factor

The bioavailability factor is expressed as the ratio of the available concentration of a metal in compost to its total concentration. It shows the potential of a particular metal from the soil matrix to enter the soil solution from which it can be absorbed by plants.

were run in triplicate analysis and recoveries of the eight metals were calculated by using the formula below (Tokalioglu *et al.*, 2003).

$$\text{BF} = \frac{\text{Available concentraion of a metal in compost}}{\text{Total concentration}}$$

Where, available concentration of a metal in compost is the concentration in non – residual fractions.

Total concentration is the concentration in residual and non – residual fractions.

RESULTS AND DISCUSSION

The mean percentage recoveries of metals are presented in Table 1. The mean percentage recoveries of metals ranged from 79.75% - 100%.

The results of total metal contents of compost samples are presented in Figure.1. The total concentrations of Zn ranged from 52.18 to 547.82mg/kg; while Cu concentrations varied from 34.50 to 262.06mg/kg and Cr level was from 30.76 to 107.68mg/kg. The Fe level ranged from 18.18 to 109.08mg/kg and the concentrations of Ni was varied from 9.52 to 76.19mg/kg. The level of Mn ranged from 12.40 to 73.45mg/kg, while a concentrations of Pb and Cd was ranged from 13.80 to 62.07mg/kg and 2.5 to 7.5mg/kg respectively. All the compost samples showed highest Zn concentration followed by Cu concentrations. The Cd concentrations were found to be the least as compared to other metals in all the compost samples. The predominance of Zn in the composts may be attributed to the stabilization of Zn oxides in the composts, as it was reported that Zn oxides in soils have high stability constant (Ma and Rao, 1997). While in the case of Cd may be due to the weak adsorption nature of Cd in the soils (Mido and Satake, 2003).

Irrespective of sampling points, the distribution of metals in Municipal dumpsites composts samples generally followed the order below for the various metal studied.

- Pb: residual>oxidizable>reducible>water soluble
- Cu: oxidizable>residual>reducible>water soluble
- Fe: residual>oxidizable>reducible>water soluble
- Cr: residual>oxidizable>reducible>water soluble
- Cd: residual>reducible>oxidizable>water soluble
- Zn: residual>reducible>oxidizable>water soluble
- Mn: residual>reducible>oxidizable>water soluble
- Ni: residual>oxidizable>reducible>water soluble

The difference in distribution patterns can be inclined towards possible mobilization of the metals. Lead was predominantly in the residual fraction (Figure 1). The amount of Pb in the residual fraction is 53.06%. The highest Pb content found in the residual fraction in this work is in agreement with the finding of Osakwe and Egharevba (2008) and Asagba *et al.*, (2007). Amongst the nonresidual fractions oxidizable and reducible were found to be the highest (Figure 1).

Some researchers have also found Pb to be highly associated with oxidizable form (Tokalioglu *et al.*, 2003). The good percentage of Pb in the reducible form may be due to ability of Fe/Mn oxides to scavenge metals from the soil solution that would normally not precipitate (Asagba *et al.*, 2007). However, water soluble fractions of Pb were found in a very small percentage. This suggested that Pb in these composts may not be bio available because water soluble fractions consist of metals species found in the soil solution. The highest percentage of Cu was found in oxidizable fraction amongst the non residual portion (46.95%). The major association of Cu with oxidizable fraction in these composts may be attributed to the high formation constant of organic-Cu complexes (Stumm and Morgan, 1981). This result is consistent with that of Harrison (1981) who found significant amount of Cu associated with oxidizable fractions. The second highest concentration of Cu was associated with residual fraction 28.58%, followed by reducible fraction 23.47% and the least percentage of Cu was associated in water soluble 1.02%. The poor presence of Cu in water soluble fraction may be as a result of high stability of Cu in the Cu organic complexes. Under oxidizing conditions copper can be leached into the environment (Venkateswaran *et al.*, 2007). Because of this copper may be considered as mobile element and bioavailable for plant uptake. Iron, manganese and chromium were predominantly in the residual fractions (Figure. 1).

The amount of Fe, Mn and Cr in the residual fractions are (64.10%), (59.14%) and (58.15%). The highest percentages of Fe, Mn and Cr in this study are in agreement with the finding of Tokalioglu (2003). Because of this, Fe, Mn and Cr can be considered as partially mobile and bioavailable for plant uptake, due to the greater percentages of these elements in the residual fraction (aqua regia). This implies that, these metals are strongly bound to minerals and resistant components, and do not represent environmental risk (Petit and Rucanido, 1999). Cadmium is distributed more in residual fraction, with around (45.45%) (Figure. 1). The second most concentrated fraction was reducible with about 36.37%, followed by oxidizable (18.18%). The low percentage of Cd in the organic fraction is consistent with the low adsorption constant of Cd on organic matter (Baron *et al.*, 1990; Chlopecka *et al.*, 1996) and the fact that Cd does not to form stable organic complexes (Keefer *et al.*, 1984). Cd was found to be the most mobile element because 54.55% of its total concentrations were in second and third fractions. This high amount of Cd associated with the non-residual phases, shows that it may be easily transferred into the food chain through uptake by plants growing in the soils. Zinc was predominantly in the residual fraction (Figure. 1). The amount of Zn in the residual fraction was (45.85%). The reducible fraction among the non-residual fractions contained the highest concentration of Zn

metal, followed by the oxidizable fraction. The highest amount of Zn in the reducible fraction could be attributed to the high stability of Zn oxides; (Ma and Rao, 1997). Several other researchers such as Ramos *et al.*, (1994) and Xian, (1989) have also found Zn associated with the reducible fraction. With the high percentages of Zn in non-residual portion (54.15%), Zn metal may be considered as mobile and thus bioavailable for plant uptake. The majority of the Ni concentrations were in residual fraction (56.25%). The oxidizable was the second most concentrated fraction followed by reducible fraction. The reducible fraction was also important for non residual fractions in the composts. This may be due to the ability of Fe²⁺ and Fe³⁺ species to scavenge metals from soil solution that would normally not precipitate (Asagba *et al.*, 2007). The appreciable percentage of Ni in the non-residual fractions of the composts suggested the potential mobility and bioavailability of Ni into plant. The results of mobility factor of the studied metals are presented in Table 2.

The MF gave values less than 50% for Pb, Fe, Cr, Mn and Ni, which is a symptom of moderate stability of the above metals in the compost samples. This could be linked to the high organic matter content in the compost which can lead to the formation of insoluble complex compounds which may be limiting the mobility of heavy metals. The MF_{Cu} is 53.06%, the index for Zn is 54.16% and for Cd is 54.54%. The high MF values have been interpreted as symptoms of relatively high liability and biological availability of heavy metals in soils (Kabala and Singh, 2001; Narwal *et al.*, 1999). Many soil factors such as pH, organic matter content, amounts and forms of oxides and carbonates, charge characteristics, as well as mineral composition influence the bioavailability and transport of heavy metals in the soil and within the agroecosystem (Fageria *et al.*, 2002).

The BF values were found to be moderate; this could be linked to the high organic matter content, which may lead to the formation of insoluble complex compounds limiting the bioavailability of heavy metals. These findings are in agreement with Sauve *et al.* (1998), that heavy metals are capable of forming insoluble complex compound with soil organic matter.

The results showed BF of Cd (0.54), Zn (0.54), Cu (0.53), Pb (0.46), Ni (0.43), Cr (0.41), Mn (0.40) and Fe (0.35). The sequence of BF was; Cd = Zn > Cu > Pb > Ni > Cr > Mn > Fe. Water soluble and exchangeable fractions are considered to be bioavailable, oxide, carbonate and organic matter bound fraction may be potentially bioavailable, to either plants or microorganisms (He *et al.*, 1995). Thus, for the compost samples studied, the residual fraction seems to contain more heavy metals than the bioavailable fraction. Besides, the high BF for Cd, Zn and Cu suggests that the bioavailable fraction contains more of Cd, Zn and Cu than the residual fraction.

Table 1: Mean percentage recoveries obtained from the original sample.

Metals	Mean percentage recoveries (%)
Cu	91.42
Pb	79.75
Fe	92.17
Cr	92.33
Cd	100.00
Zn	89.25
Mn	84.59
Ni	84.75

*Values are mean of triplicate analyses

Table 2: Mobility and Bioavailability Factors of Heavy Metals in dumpsite composts samples

Heavy Metal	Mobility Factor (%)	Bioavailability Factor
Lead (Pb)	46.94	0.46
Copper (Cu)	53.06	0.53
Iron (Fe)	35.90	0.35
Chromium (Cr)	41.86	0.41
Cadmium (Cd)	54.54	0.54
Zinc (Zn)	54.16	0.54
Manganese (Mn)	40.85	0.40
Nickel (Ni)	43.74	0.43

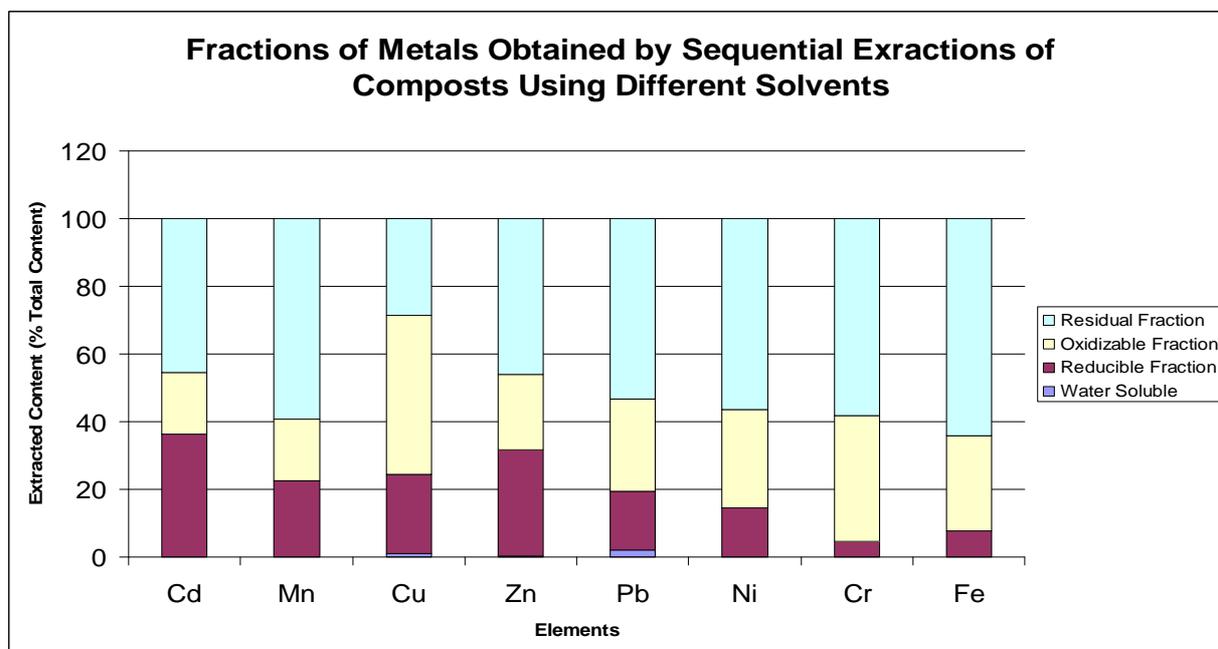


Fig 1: Fractions of Metals Obtained by Sequential Extractions of Composts using different solvents

CONCLUSION

The increasing amount of total metals (Pb, Cu, Fe, Cr, Cd, Zn, Mn and Ni) contents in the compost could be due to human activities. The main source is by the disposal of solid wastes. The residual fraction was the most abundant pool for all metals in the compost examined. However, in most of the composts, a significant percentage of total metals was associated with non residual fractions, which could be possible absorbed by plants. Significant amount of Cd, Zn and Cu were associated with the non-residual fractions in the composts, which indicated that these metals were potentially bioavailable. These may pose a real threat as Cd, Zn and Cu are transferred into the food chain from compost contaminated by these metals.

Recommendations

In Nigeria, there are little or no information available on the levels of heavy metals in municipal dumpsite composts. In contrast, extensive works have been directed to the characterization and prediction of mobility and bioavailability of heavy metals in municipal dumpsite composts in Europe and U.S.A, since composts generated in Nigeria may be considerably different from those of Europe and U.S.A, it is therefore necessary for Nigerian researchers to pay more attention to this field. Specifically more effort should be in the following directions.

- i. Interactions between organic components and heavy metals.
- ii. Development of specific guidelines and standards for application of composts in agricultural lands.
- iii. Phase association of heavy metals in composts.
- iv. Correlation between extractability and bioavailability.

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