

EFFECT OF PARTICLE SIZE ON THE EXTRACTABILITY OF HEAVY METALS IN SOILS

¹James A. P., ¹Tanimu J., ¹Onwu, C.A., ²Ibrahim F.

¹Department of Soil Science and Land Resources Management, Federal University Wukari, Nigeria

²Department of Soil Science, Federal University of Agriculture, Makurdi, Nigeria.

Corresponding Author: clementonwu@gmail.com +2348032939662

Abstract: Heavy metals are natural component of the environment but are of concern because they are being added to the soil, water, and air in an increasing amount. As part of a much larger study, to systematically document the status of bioavailability and reactions of heavy metals in soils, this study aims at determining the effect of particle size on the extractability of Cu, Pb, and Zn in urban garden fields from Kaduna metropolis fertilized with municipal and industrial wastes. Samples were collected from Kakau, Kakuri, Trikania and Romi and were passed through a nest of sieves (2.00 – 0.5mm, 0.5 – 0.075mm and <0.075mm). The soil aggregate class collected from the sieves were used to determine the extractabilities of Cu, Pb, and Zn by three single extractants (1 M CaCl₂, 1M NH₄NO₃, and 0.05M EDTA). The relative contribution of the aggregate size fractions to the soil total extractable metals by 1M CaCl₂ indicated that the micro (0.5 – 0.075mm) aggregate class accounted for a larger percentage of exchangeable metals than either 2.00 -0.50mm and <0.075mm except for Romi where there was practically no exchangeable Cu. For all the sample sites, micro (0.5 -0.075mm) aggregate size class accounted for 57 to 67% of Cu. A similar trend was observed for Pb and Zn. The amount of Cu, Pb and Zn extracted by 1M NH₄NO₃ seemed related in all the sites. As also observed for 0.1M CaCl₂ there was no 1M NH₄NO₃ extractable Cu in any aggregate class in Romi and micro aggregate in Trikania. The distribution of potentially labile metals determined by EDTA among the aggregate size classes showed that the highest concentration occurred in the micro (0.5 -0.075mm) aggregate size class for Cu, the fine (<0.075mm) sized aggregate accounted for slightly greater percentage than micro aggregates in Romi and Kakau in contrast to other sites.

Keywords: particle size, micro aggregates, extractant, Copper, Lead, and Zinc.

1. INTRODUCTION

The term heavy metals refer to any metallic chemical element which has a relatively high density and is toxic or poisonous at low concentration. Some examples of heavy metals include Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Copper (Cu), Zinc (Zn) and Lead (Pb) (Adriano, 2001). Heavy metals are natural component of the earth crust. They cannot be degraded or destroyed. To a small extent, they enter our bodies via food, drinking water and air. Living organisms required trace amount of some heavy metals including cobalt, Copper, Manganese, Vanadium and Zinc, but excessive levels can be detrimental to the organism. Other heavy metals such as Mercury, Lead and Cadmium have known vital or beneficial effect on organisms, and their accumulation overtime in the bodies of mammals can cause serious illness (Cameron *et al.*, 1997).

Heavy metals are introduced into the soil by land application of sewage sludge, fertilizer, and other waste materials (Peng *et al.*, 2018). Heavy metals enrichment of agricultural soils may increase plant availability and movement of heavy metals through the food chain. The concentration of heavy metals in soils is associated with biological and geochemical cycles and is influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal. Heavy metals in soils may be inherited from the parent materials or added through use of organic and chemical fertilizers

and pesticides (Appel and Ma (2002)). The knowledge of both the total concentration and chemical speciation is necessary to characterize the behavior of heavy metals in soil. It is well known that these heavy metals are present in chemical forms, which influence their reactivity and hence their mobility (extractability). The extractability nature of heavy metals is influenced by some certain factors such as; soil pH, soil particle size distribution, soil organic matter and temperature.

Due to the growing concerns about heavy metals contamination of agricultural lands under say long term application of inorganic fertilizers and inorganic wastes makes periodic risk assessment of heavy metals extractability in arable lands imperative (Agbenin, 2003). As a part of much larger study to systematically document the status bioavailability and reactions of heavy metals in savannah soils, this study is aimed at determining the interaction of particle size in the extractability of heavy metals in savannah soils.

2. MATERIALS AND METHOD

Experimental Site

The research site were Kaduna State Environmental Protection Agency (KEPA) dump site within Kaduna metropolis, Kaduna- Abuja express way, Kakau 1 and Kakau 2, Trikania (sewage sludge), Arewa textile effluents (Kakuri 1 and Kakuri 2) and Peugeot and Tower galvanized plant effluent, Kaduna, Kaduna State. These were the dump sites soil samples were collected for this research work.

Soil Sampling and Analysis

The soil samples were collected at a depth of 0 – 10cm corresponding to the A- horizon. Composite samples were collected from each site using random sampling methods into sample bags. The bulk samples were air dried at room temperature and then screened through a 2mm-sieve. Fifty (50) grams of each sieved soil samples were then collected into the different labelled containers and kept for analysis. Particle size analysis was conducted using the bouycous (hydrometer) method (Gee and Bauder, 1986). Using the potentiometric method (McLean, 1982), pH was determined in water and 0.01M CaCl_2 at ratio 2:1. Soil organic carbon was determined by the Walkley and Black procedure by wet oxidation using chromic acid digestion (Nelson and Sommers, 1996). Total N was determined using micro-Kjeldahl digestion and distillation techniques (Bremner, 1996), available P was determined by Bray-1 extraction followed by molybdenum blue colorimetry (Frank *et al.*, 1998). Exchangeable K, Ca, Na and Mg were extracted with a 1 M NH_4OAc , pH 7 solution. Thereafter, K and Na were analysed with a flame photometer and Ca and Mg were determined with an atomic absorption spectrophotometer (Okalebo *et al.*, 2002). Cation exchange capacity (CEC) was determined using the procedures described by IITA (1979) and modified by Anderson and Ingram (1993). Exchangeable acidity was determined by titration method of Anderson and Ingram (1993). The following Cu, Zn, Ni, Cr, Pb and Cd metals were digested, washed into 50ml plastic containers and made up to mark with distilled water. The concentration of each metal solution was determined using Atomic Absorption Spectrophotometer (AAS).

Electrical conductivity determination

10g of the air – dried 2mm sieved soil samples were weighed separately into a 50ml plastic cups and 25ml of distilled water was added to each of the cups. The suspensions were stirred frequently for 30 minutes and allowed to stand overnight. The next day, the settled suspension was decanted and the extract was analyzed for electrical conductivity using a conductivity bridge.

Heavy metals extraction with Aqua – Regia

Each of the air-dried soil (0.2g) in the different particle sizes were weighed into a beaker and 25mls of the aqua-regia was added to each beaker and the solution was digested for 8 hours. The digest was then turned into a 50ml volumetric flask after allowed to stand for the digests was then poured into a container where Zn, Cu, Cd and Pb were determined using the Absorption Spectrophotometer (AAS).

Heavy metals extraction with 0.1M CaCl_2

Five gram (5g) each of the different particle size fraction were weighed into a 50ml centrifuge tubes and 20ml of 0.1M CaCl_2 solution was added to each tube. The suspension were shaken for 16 hours (overnight) on a reciprocating mechanical shaker and filtered through whatman No. 42 filter paper. The filtrates were then used to determined Zn, Cu, Cd and Pb using Absorption Spectrophotometer (AAS).

Heavy metals extraction with 1.0M NH₄NO₃

Five gram (5g) each of different particle size fraction were weighed into a 50ml centrifuge tubes and 20ml of 0.1M NH₄NO₃ solution was added to each tube. The suspension were shaken for 16 hours (overnight) on a reciprocating, mechanical shaker and filtered through whatman No.42 filter paper. The filtrates were then used to determined Zn, Cu, Cd and Pb using AAS.

Heavy metals extraction with 0.1M EDTA

Five gram (5g) each of the different particles size fraction were weighed into a 50ml centrifuge tubes and 20ml of 0.1M EDTA solution was added to each tube. The suspension were shaken for 16 hours (overnight) on a reciprocating mechanical shaker and filtered through whatman No.42 filter paper. The filtrates were then used to determined Zn, Cu, Cd and Pb using AAS.

3. RESULTS

Physico – chemical properties of the soil

Based on particle size distribution of the soils (Table 1), the textural class of Kakuri was clay loam, Kakau and Trikaniya were sandy loam while Romi was loam. The soil pH in H₂O was greater than pH in CaCl₂. The pH in water ranges from 4.2 in Kakuri to 6.2 at Trikaniya while in CaCl₂ it ranges from 4.0 at Kakuri to 5.9 at Trikaniya.

The percentage organic carbon of the soils ranged from 1.3 to 1.5%. The highest concentration of organic carbon was recorded in Kakau 5.3% and Kakuri 5.6% soil. Exchangeable acidity ranged from 30 mmol kg⁻¹ at Trikaniya to 105 mmol kg⁻¹ in Kakuri. Calcium (Ca) was the dominant cation in the exchange sites of soils, ranging from 46 mmol kg⁻¹ at Romi to as high as 206 mmol kg⁻¹ at Kakau. The dominance of cation at the exchange sites was in the order Ca> Mg> Na>K (Table 1). The effective cation exchange capacity (ECEC) of the soils was relatively high ranging from 68mmolKg⁻¹ in Romi to as high as 268mmolKg⁻¹ in Kakau.

Table 1: Selected physico-chemical properties of the soil

Site	Sand	Silt	clay	pH(H ₂ O)	pH(CaCl ₂)	Organic Matter %	Exch. Acidity gkg ⁻¹	Exchangeable Bases gkg ⁻¹				ECEC
								K	Na	Ca	Mg	
Kakuri	47.30	21.30	31.30	4.20	4.00	5.60	10.50	3.20	4.00	86.10	17.80	123.00
Kakau	62.30	23.00	14.70	4.90	4.80	5.30	7.00	7.00	7.90	206.00	39.30	268.00
Trikaniya	61.30	24.00	14.70	6.20	5.90	1.30	3.00	1.90	4.70	76.60	17.30	104.00
Romi	52.70	30.70	16.70	5.40	5.20	1.30	7.00	1.70	1.70	46.10	12.00	68.00

Distribution of aggregate class

The distribution of aggregate size fraction of the soils expressed as percentage of the total soil is given in (Fig.1). The micro aggregate size fraction (0.5 – 0.075) had the highest percentage ranging from 51 % at Romi to 65 % at Trikaniya followed by the macro aggregate size fraction (2.00 – 0.500) with values ranging from 17.9 % at Romi to 28.9 % at Trikaniya. The least aggregate size fraction (<0,075) was fine or silt + clay.

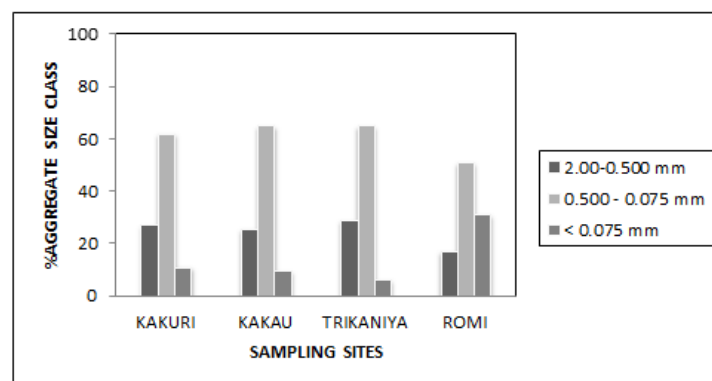


Figure 1: Distribution of aggregate size classes in soils sampled from urban garden field around waste dump sites in Kaduna Metropolis.

Total metal concentration in the soil

The total concentration of metals in soil shows that (Zn) has the highest concentration in the experimental soil followed by Pb and Cu in that order (Table 2). The concentration of Zn in the experimental soil has values ranging from 318mgKg⁻¹ at Kakuri to as high as 995mgKg⁻¹ in Romi. For Pb the concentration ranged from 76mgKg⁻¹ at Kakuri and 203mgKg⁻¹ at Kakau. The concentration of Cu was least at Romi and highest at Trikaniya (Table 2). The relative abundance of the metals was Zn > Pb > Cu.

Table 2: Total Concentration of Heavy Metals in the Experimental Soils

Site	Cu mg kg ⁻¹	Zn	Pb
Kakuri	21.40	318.00	75.70
Kakau	30.40	458.00	203.00
Trikanিয়া	38.80	533.00	97.10
Romi	10.30	995.00	179.00

Distribution of metals in aggregate size classes

The Distribution of metals in aggregate size classes is presented in figure 2. The relative contribution of the aggregate size fractions to the soil total metal concentration was higher in the micro aggregate size class for Cu, Pb, and Zn in all the sites except for Pb in Kakuri where the fine aggregate size (0.075mm) had slightly higher contribution to the total Pb concentration in the soil than the micro aggregate size class.

For Cu, Pb, and Zn the contribution of the fine aggregate size class to total concentration of metals in soils was greater than in the macro-aggregate in Romi, whereas the fine aggregate size class made slightly higher contribution to the total Pb concentration than the micro aggregate size in Kakau.

The macro aggregate contributed between 10 and 18% to the total Pb concentration in the soil, the fine aggregate size class between 11 and 49% across the sites while micro aggregate class accounted for between 39 and 77% of the total Pb in the soil. Similarly, the macro aggregate size class between 17 and 24% of the total Zn while the fine size aggregate class between 12 and 28% while micro aggregate accounted for up to between 55 and 71% of total Zn.

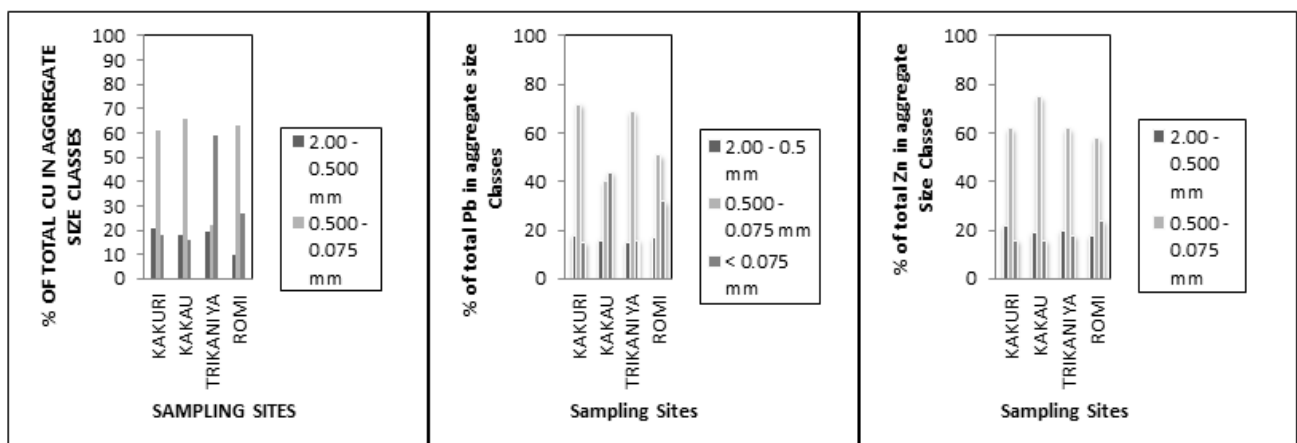


Figure 2: Distribution of Cu, Pb and Zn in aggregate size classes expressed as percentages

Extractability of metals in the soil and aggregate class by 0.1M CaCl₂

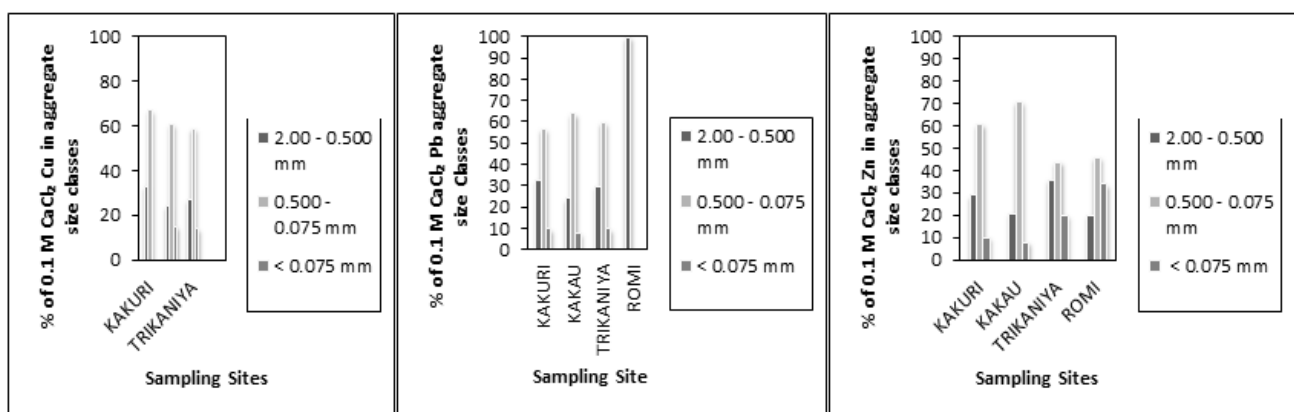
The 0.1M CaCl₂ extracted more of Zn than either of Pb and Cu (Table 3). The CaCl₂ extractable fraction of the metal is the portion that is readily exchangeable with Ca. The concentration of extractable Cu, Pb and Zn seemed to parallel the total concentration in the soil and in some cases use related to the soil pH, O.M, and ECEC. As can be seen in Table, the distribution coefficient (K_d) of Cu, Pb and Zn a measure of the extractability of Cu, Pb and Zn seemed to parallel the total concentration in the soil and in some cases use related to the soil pH, O.M, and ECEC. As can be seen in Table 3, the distribution coefficient (K_d) of Cu, Pb, and Zn a measure of the extractability of Cu, Pb and Zn was generally low, ranging from 0.004 to 0.015 for Cu, between 0.005 to 0.042 for Pb and between 0.007 and 0.064 for Zn.

Table 3: Total concentration of Heavy Metals Extracted with 0.1M CaCl₂ in the soils

Site	Cu		Zn		Pb	
	mg kg ⁻¹					
Kakuri		Kd		Kd		kd
	0.06	(0.003)	2.35	(0.007)	3.07	(0.040)
Kakau	0.46	(0.015)	20.6	(0.045)	5.12	(0.025)
Triyaniya	0.14	(0.004)	6.16	(0.012)	4.1	(0.042)
Romi	0.00	-	61.5	(0.064)	0.80	(0.005)

Values in parenthesis are the distribution coefficient (kd) derived as CaCl₂/ Total

The relative contribution of aggregate size fractions to the soil extractable metals by CaCl₂ is shown in Figure 3. Of the exchangeable Cu, Pb and Zn, the micro aggregate size class accounted for a larger percentage than either the macro aggregate or the fine – sized aggregate size class (<0.075). There was practically no exchangeable Cu in any aggregate class in Romi. Similarly, there was no exchangeable Pb in micro aggregate and fine- size aggregate class in Romi. For all other sites, micro aggregate size contributed between 57 to 67% of Cu, while macro aggregate accounted for a higher proportion than fine – size aggregate class. A similar trend was observed for Pb and Zn except that for Zn at Romi, the fine – size aggregate fraction accounted for a slightly higher concentration of exchangeable Zn than the macro aggregate size class.

**Figures 3: Distribution of 0.1 M CaCl₂ extractable Cu, Pb and Zn in aggregate size**

Extractability of metals in soil and aggregate class by 1.0M NH₄NO₃

The use of NH₄NO₃ is to extract mobile and weakly bound metals in soils (Table 4). The concentrations of mobile Cu, Pb and Zn in the soils are given in Table 4. Dilute ammonium nitrate solution extracted less Cu, Pb and Zn in the soils than 0.1M CaCl₂. Using the distribution coefficient (Kd) to assess the mobility of the metals, distribution coefficient (Kd) was generally low, less than 0.004 for Cu, between 0.003 and 0.051 for Zn and from 0.006 to 0.014 for Pb. Zn and Pb were generally in greater mobile forms than Cu in the soil, suggesting more of anthropogenic input for Zn and Pb than Cu. The amount of Cu, Zn and Pb extracted by 1M NH₄NO₃ seemed related to the total concentration in the soil.

Table 4: Total concentration of Heavy Metals Extracted with 1.0M NH₄NO₃ in the Soils

Site	Cu		Zn		Pb	
	mg kg ⁻¹					
Kakuri	0.08	(0.003)	1.31	(0.004)	0.92	(0.012)
Kakau	0.02	(0.001)	9.88	(0.022)	1.30	(0.006)
Triyaniya	0.05	(0.001)	1.41	(0.003)	0.97	(0.010)
Romi	0.00	-	49.1	(0.051)	2.47	(0.014)

Values in parenthesis are the distribution coefficient (kd) derived as NH_4NO_3 / Total

As also observed for 0.1M CaCl_2 , there was no extractable Cu in any aggregate size class in Romi and in micro aggregate in Trikaniya (Fig. 4).

In Trikaniya, almost 100% of NH_4NO_3 extractable Cu was accounted for by fine size aggregate whereas micro aggregate accounted for over 60% of the total mobile Pb in Kakuri soil. Other than these, the micro aggregate size class accounted for a greater proportion of mobile Pb and Zn across the sites. Surprisingly in Kakau, there was no detectable concentration of Cu in the micro aggregate size class. The mobile Cu in Kakau soil was equally contributed by micro aggregate and the fine aggregate classes (Figure 4).

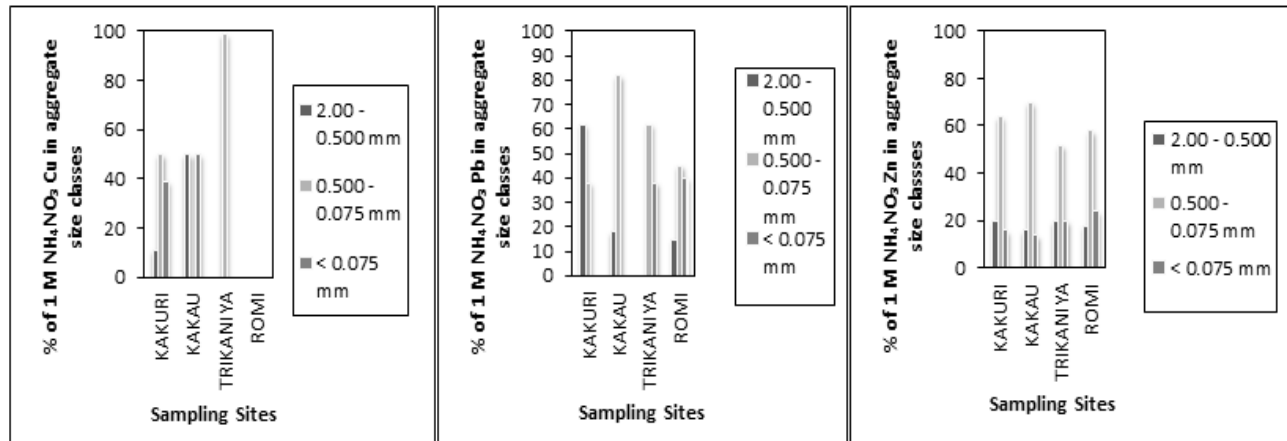


Figure 4: Distribution of 1 M NH_4NO_3 extractable Cu, Pb and Zn extractable Cu, Pb and Zn

Extractability of metals in soils and aggregate class by 0.05M EDTA

The concentration of Cu, Pb and Zn extracted with 0.05M EDTA is given in Table 5. The concentration of metals extracted by EDTA can be referred to as the potentially labile pool of metals in the soils. The concentrations extracted by EDTA were greater than the CaCl_2 and NH_4NO_3 extractable combined. The EDTA extractable Cu, Pb and Zn increased with increasing total concentrations in the soil and generally followed the order $\text{Zn} > \text{Pb} > \text{Cu}$. The proportion of the potentially labile pool as a function of total concentration in the soil indicated as Kd followed the order $\text{Cu} > \text{Pb} > \text{Zn}$ (Table 5).

Table 5: Total Concentration of Heavy Metals Extracted with 0.05M EDTA in the Soils

Site	Cu		Zn		Pb	
			mg kg ⁻¹			
Kakuri	10.51	(0.49)	59.54	(0.19)	26.33	(0.38)
Kakau	8.70	(0.29)	69.96	(0.15)	31.8	(0.16)
Trikaniya	15.38	(0.34)	76.5	(0.14)	19.04	(0.20)
Romi	5.12	(0.50)	90.5	(0.90)	45.53	(0.25)

Values in parenthesis are the distribution coefficient (kd) derived as EDTA/ Total

The distribution of potentially labile metals in the soil among the aggregate size classes showed that the highest concentration occurred in the micro aggregate size class (Fig. 5). For Cu, the fine size aggregate accounted for slightly greater percentage than macro aggregate in Romi and Kakau in contrast to the other sites. Similarly, the fine size aggregate class amounted for greater percentage of potentially labile Pb and Zn than macro aggregate in Romi in contrast to the other sites (Fig. 5).

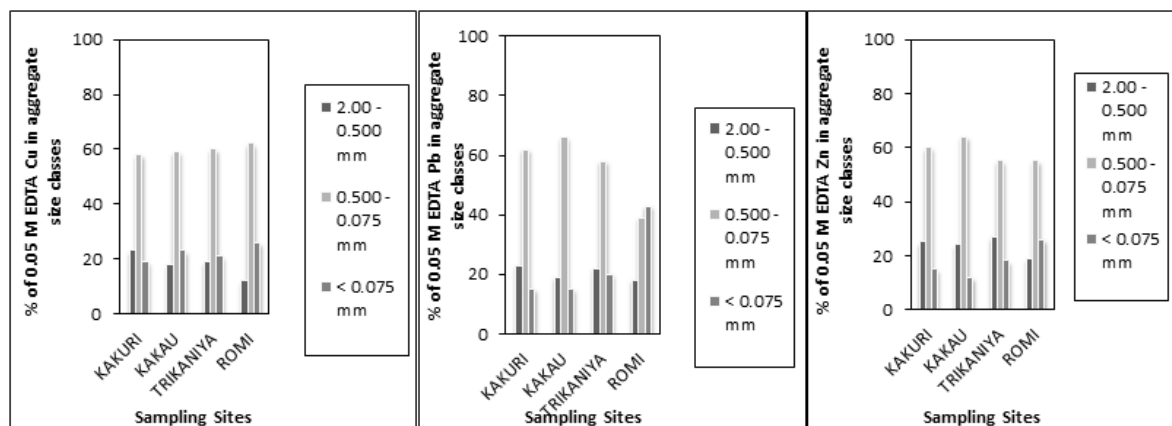


Figure 5: distribution of 0.05 M EDTA extractable Cu, Pb and Zn extractable Cu, Pb and Zn in aggregate size classes expressed as percentages of the Cu, Pb and Zn concentrations in the soils.

4. DISCUSSION

Heavy metal content at the study sites were generally higher than the concentration normally encountered in arable soils outside urban areas. Total Cu concentration ranged between 10.3 and 38.8 mg kg⁻¹. This is about 2 to 3 times greater than the concentration of 5 to 13 mg kg⁻¹ reported by Agbenin (2004) for cultivated arable soils. Total Zn concentration ranged between 318 and 995 mg kg⁻¹ this is about 9 to 10 times more than concentration of 28 to 57 mg kg⁻¹ reported by Agbenin (2003) for cultivated arable soils. Leads concentration ranged between 75.7 and 203 mg kg⁻¹ this is about 4 to 5 times more than the concentration of 28 to 45 mg kg⁻¹ reported by Agbenin (2002) for cultivated arable soils. The high concentration of these metals in the different sites is likely attributed to the anthropogenic metal inputs in the soil which have occurred at the sites. The concentrations of the metals in the soils as they relate to the threshold limits for agricultural soils are on the high side as reported by Kabata-Pendias (2010).

The relative contributions of aggregate size classes to the total metal concentration of the soil were such that micro-aggregates accounted for the highest concentration of Cu, Zn and Pb in all sites except for some minor variations. We could therefore deduce that there might have been high accumulation of anthropogenic contaminants in these garden soils. This is in agreement with other reports (Harmsen, 1977).

The most extractable metal from this experiment, using three extractants, was Zn followed by Pb and Cu in that order. The preferential extraction of Zn to, most especially, Cu could be due to strong affinity of Cu for soil colloids and organic matter than Zn. According to Cavallaro and McBride (1980), the preferential extraction of Cu to Zn, which makes Zn more extractable than Cu, could be explained by their differences in electronegativity. Whereas electronegativity of Cu is 2.0 that of Zn is 1. It could easily be deduced that when Zn is in competition with Cu it will be easily exchanged or substituted by Cu. This is in agreement with other reports (McBride and Blasiak, 1979; Gomes *et al.*, 2001).

The extractants used for this experiment (0.1M CaCl₂, 1M NH₄NO₃ and 0.05M EDTA) were to isolate and extract elements from particular soil phases. Concepts of metals in soil ecosystems indicate that they can occur in soluble, exchangeable, organically complexed, secondary (carbonates, hydroxides of iron and manganese sulphides) and primary mineral soil pools of different solubility (Viets, 1962). Each of the extractants with their different strength can access one or a few pools of a given metal. The experimental results for extractable Cu, Zn and Pb as percentages of total concentration in the soil showed that 0.05M EDTA extracted the highest concentration of Cu, Pb and Zn because it forms strong complexes with the metals removing both the exchangeable and organically complexed pools (Polesakova *et al.*, 2001; Singh *et al.*, 1998) than 0.1M CaCl₂ which extracts heavy metal only in the exchangeable fraction and 1M NH₄NO₃ which extracts metals only in the mobile fraction and weakly adsorbed (Ure, 1996).

5. CONCLUSION

The particle size is known to be one of the most important soil properties that influence the extractability of heavy metals in soil. The effect of particle size on heavy metal extraction is not only of agricultural importance but also of environmental significance. Experiments were carried out to determine the effect of aggregate size fraction(macro, micro and silt +clay) on the extractability of heavy metals in mildly polluted urban soils using three different extractants (0.1M CaCl₂, 1M NH₄NO₃ and 0.05M EDTA).

From my result, although the total Cu, Zn and Pb concentration were high in the study sites, only very small amounts of these metals were extractable. The concentration of these metals (Cu, Zn and Pb) in the study sites were over 6 times higher than concentrations obtained from other soils of the same region.

The percentage of 0.1M CaCl₂, 1M NH₄NO₃ and 0.05M EDTA extractable Cu showed that the highest concentration occurred in the micro aggregate size class, while the fine size aggregate accounted for slightly greater percentage than macro aggregates in Romi and Kakau in contrast to the other sites. The fine sized aggregate class accounted for greater percentage of partially labile Pb and Zn than macro aggregate in Romi in contrast to the other sites.

It could be maintained therefore that heavy metal accumulation due to increased anthropogenic activities within these study sites, was found in the micro aggregate size fraction of the soil than either the macro or finer aggregate classes. This study has implication for management of metal polluted soils in urban areas.

The management implication of my result is that maximum tillage practice involving ploughing and harrowing in urban contaminated soils might increase the mobility and availability of the metals to contaminate ground water table and plant uptake.

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