Heavy Metal Speciation in Some Selected Farms Treated with Urban Solid Waste, in Jos South, Plateau State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author NDN designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors JNE and YNL managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Original Research Article	

ABSTRACT

The speciation of metals in environmental samples is a serious factor in appraising the potential environmental impacts, before their disposal. The six step extraction procedure previously proposed by Obasi et al. was used with modification to systematically study the speciation of Cd, Cu, Mn, Pb, Zn, Fe and Cr in a farm treated with the dumpsite soils. The speciation study revealed higher distribution of the metals in the residual fractions except Cd which had 70.18% in the exchangeable fraction. The results also showed that there were low tendency of bioavailability and reactivity in the environment. The results of the newly introduced extractants ($BeCl_2$, mixture of $BeCl_2/BaCl_2$ and $CaCl_2/NH_4Cl$), revealed that these reagents could be used for the leaching of the exchangeable fraction in speciation analysis. $BeCl_2$ extracted 0.6499 mg/kg of the exchangeable Cd while the conventional $MgCl_2$ extract 0.010 mg/kg (Cd). The results also revealed that the mixture $BeCl_2/BaCl_2$ extracted 0.4384 mg/kg of Cd. The use of the mixture of $BeCl_2/BaCl_2$ and

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CaCl$_2$/NH$_4$Cl extractants leached exchangeable Ni more than the conventional single extractants. BeCl$_2$, NH$_4$Cl and the mixture of BeCl$_2$/BaCl$_2$, reagents were better extractants for the exchangeable Mn in soil samples.

1. INTRODUCTION

The presence of heavy metals in urban solid waste raises serious concern about the adverse environmental impact as a result of the use of dumpsite soil as manure in agricultural lands. High and excessive accumulation of heavy metals in the soil may eventually contaminate both human and animal food chain [1,2]. It is widely recognized that to assess the environmental impact of soil pollution, the determination of total heavy metals concentration does not provide useful information about risk of bioavailability, toxicity, capacity for remobilization of heavy metals in the environment and chemical forms of a metal in which they are available in the soil [3,4,5]. Therefore, in geo-environmental studies of risk assessment, chemical partitioning among the various geochemical phases is more useful than measurements of total heavy metals contents [6]. The chemical speciation of heavy metals allowed the assessment of heavy metal bioavailability and is related to the different natures of the metals, their bonding strength, and either in free ionic form or complexed by organic matter, or incorporated in the mineral fraction of the sample [7,8]. In addition, speciation will determine metal mobility and hence potential contamination of ground water following dumpsite soil application. Therefore, chemical speciation can be defined as the process of identifying and quantifying different species, forms or phases present in a material [9,10].

Today, speciation science seeks to characterise at least some of the most important forms of an element, in order to understand the transformation between forms which can occur, and to infer from such information the likely consequences for example in terms of risk assessment, toxicity or biological activity [11]. As such, it is a discipline which is of relevance to scientists with many different backgrounds: Chemists, toxicologists, biologists, soil and sediment scientists, physicists and specialists in various aspects of nutrition and medicine; all require this type of information.

Selective sequential extraction procedures have been commonly used for studying metal mobility and availability in soils. Numerous extraction schemes for soils and sediments have been described [12,13,14,15]. Despite uncertainties as to the selectivity of the various extractants and to possible problems due to readsorption, extraction procedures provide qualitative evidence regarding the forms of association of heavy metals and ultimately, of their bioavailability [16]

Therefore, the aim of this present study was to evaluate the chemical speciation of heavy metals in a farm treated with urban solid wastes and to assess the leaching of the exchangeable fraction using some reagents.

2. MATERIALS AND METHODS

2.1 Study Area

The farm (F1) in this study is located about 200m from Kuru Jantar dumpsite on longitude 08°53'E and latitude 090 42 N (Garmin GPS model etrex 20) along Jos – Barkin Ladi road.

2.2 Sample Collection and Treatment

Top soil samples were collected randomly from twenty different locations in the farms that used manure from the dumpsites (see Fig. 1). Soil samples were also collected from a control farm. The soil samples collected were air-dried, crushed and passed through a 2mm sieve. The sieved samples were kept in cellophone bags for laboratory analysis.

2.3 Total Heavy Metal Analysis

Triplicate samples (3.0 g) of the sieved soil samples were digested with 25 ml of aqua regia (HCl + HNO$_3$, 3:1 v/v) at 120°C on a water bath in a fume cupboard. The digested samples were filtered into a 100 ml volumetric flask and made up to the mark with distilled/deionised water [15,16,17]. The concentration of the metals in the digested soil sample solutions were determined using Buck Scientific model 210VGP atomic absorption spectrophotometer at wavelengths and slits specific to each metal. The metals analysed were lead (Pb), copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), cadmium (Cd) and manganese (Mn).

2.4 Sequential Extraction of Metals

2.4.1 Exchangeable fractions [F1]

The exchangeable fraction was extracted using 1M NH_4Ac, (instead of $MgCl_2$), pH7, in stoppered polyethylene bottles at room temperature [6]. The fraction was also extracted using the new extractants ($BeCl_2$, $MgSO_4$, a mixture of $BeCl_2/BaCl_2$ (1:1vv) and $CaCl_2/NH_4Cl$ (1:1) following the same procedure with stirring on a magnetic stirrer.

2.4.2 Acid soluble (bound to carbonate fractions) [F2]

The carbonate fraction was extracted from the residue of [F1], using acetic acid, CH_3COOH, with buffering by CH_3COONa, pH5, in a stoppered polyethylene bottle at room temperature [11,18].

2.4.3 Easily reducible fractions (bound to Fe-Mn oxides) [F3]

Easily reducible fraction was extracted from the residue of [F3] with a mixture of hydroxylamine hydrochloride (NH_2OH. HCl) and 0.2M trioxonitrate (V) acid (HNO_3) and agitated at room temperature for 1 hour [18].

2.4.4 Reducible fraction [F4]

Reducible fraction was extracted from the third residue [F3] with a mixture of hydroxylamine

hydrochloride (NH_2OH. HCl) and 25% ethanoic acid (CH_3COOH) and agitated at room temperature for 15 hours [19, 20].

2.4.5 Oxidizable (bound to organic fractions) [F5]

The oxidizable fraction was extracted from the forth residue [F4] with a mixture of 30% $H_2O_2/0.02M$ HNO_3 at 85°C on water bath for 5 hours [21].

2.4.6 The residual fractions (bound to Silicates)[F6]

The residual fraction was extracted with 25 ml of aqua regia (HCl + HNO_3, 3:1 v/v) at 120°C on a water bath in a fume cupboard [22,23]. Metal levels in each fraction were determined using the calibrated Buck Scientific model VGP 210).

3. RESULTS AND DISCUSSION

The speciation study was conducted for a farm using dumpsite soil as manure to ascertain the forms of the heavy metals in soil. The findings of past researchers had implicated mobility and bioavailability of metals for plants uptake with the form of the metal (speciation) in the soil [9,24,25]. The results of the six chemical fractions [26] for seven heavy metals (Cu, Mn, Fe, Cd, Ni, and Zn & Pb) are presented in Fig. 2. The percent of each fraction associated with the total extractable metal is also presented in Fig. 3.

Fig. 1. A farm [F1] in kuru jantar using the kuru jantar dumpsite soil as manure

The results of the study showed that copper was not detected in the easily exchangeable and reducible fractions. This could mean that copper does not exist in these forms in the soil analyzed or it was present in concentration below the detection limit of the AAS used. Copper was associated predominantly with the residual fraction with 92.39% of the total extractable metal in the oil (see Fig. 3). The predominant associations of copper with the residual fraction have been reported in waste soils [16, 26]. Similarly, [27] have reported copper in the residual fraction and oxidizable fraction because of its affinity to organic matters. On the other hand, [28] reported that Cu was bound with reducible and oxidizable fractions in the tannery sludge. The high percentage of copper in this fraction (non-mobile fraction) suggests that it may not be readily available for plant uptake even though it was present in the soil analyzed. The results showed that copper was also associated with the acid soluble, easily reducible and oxidizable fractions (see Fig 2 and 3). The availability of this metal in the sequentially extracted fractions follows the order: residual>easily reducible> oxidizable> acid soluble.

Manganese was found to be associated with all the fractions with the residual and oxidizable fractions having 30.13 and 4.33 mg/Kg respectively. The residual fraction had 46.05% while the oxidizable fraction had 28.01% of the total extractable metal. These results are comparable to those of [16] who reported Mn, to be mostly associated with the residual fractions. These findings could be linked to the preferential incorporation of Mn into silicate lattice. Also, the high Mn level in the organic matter bound fractions may be connected to the ease of complexation and peptization between the metal and natural organic matter like humic and fulvic acids [29]. Relatively high levels of manganese in this fraction have been reported [1,9]. The association of manganese with residual fraction implies partitioning into crystalline oxides [9].

In this analysis, the easily exchangeable fraction and acid soluble accounted for 12.18% of the total extractable manganese. The easily exchangeable fraction and acid soluble fraction constitute the mobile fractions that are readily available for plant uptake [30]. The presence of Mn in these fractions suggests that the metal could be bioaccumulated to some extent. The availability of this metal in the sequentially extracted fractions follows the order: residual> oxidizable> easily exchangeable> reducible> easily reducible> acid soluble.
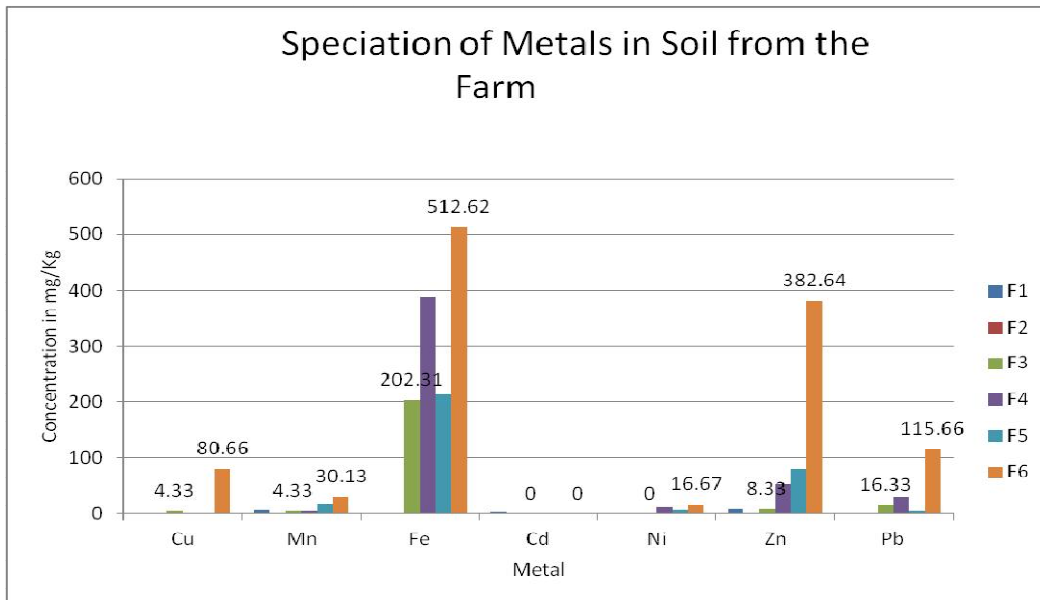

Fig. 2. The speciation of heavy metal in the soil samples collected from the farm using manure from kuru dumpsite

F1 = Easily exchangeable F2 = Acid soluble F3 = Easily reducible F4 = Reducible
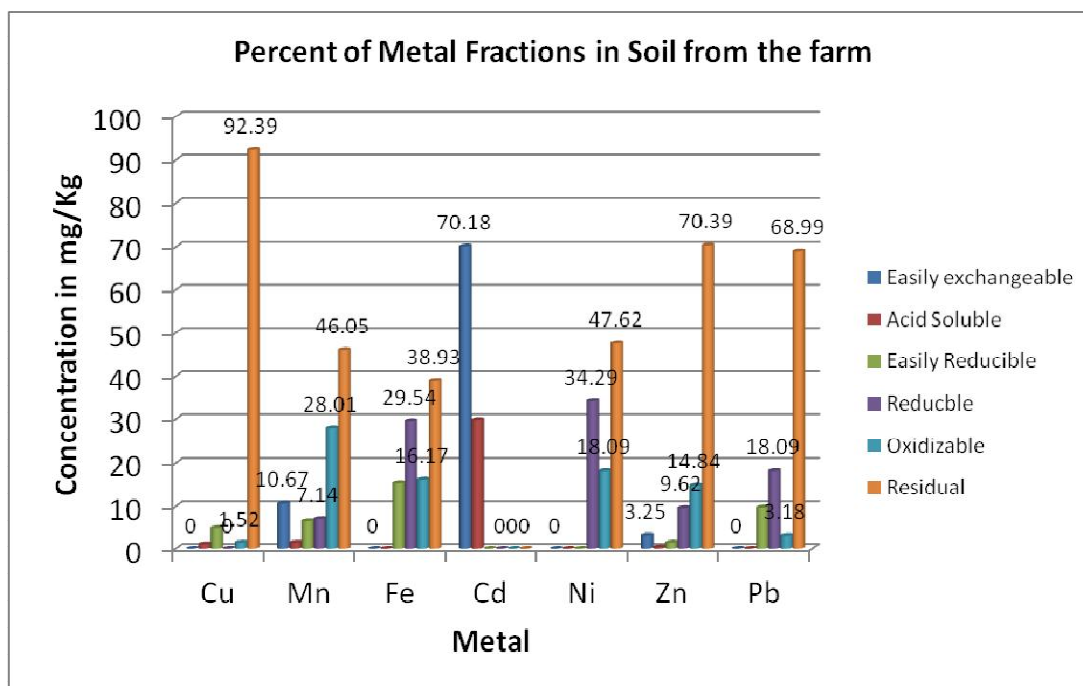*F5 = Oxidizable F6 = Residual ND = Not Detected*

Fig. 3. Percent of trace metal chemical fractionation of soil samples collected from the farm using manure from kuru dumpsite

Iron was not also detected in the easily exchangeable and acid soluble fractions. Iron was however, predominantly associated with the residual and reducible fractions having 38.93% and 29.54% respectively (see Fig. 3). Such findings have been reported in previous research [31,32]. The high percentage of iron in the residual fraction is also consistent with the results of [33,34]. The residual fraction can be taken as a guide to the degree of pollution of the soil. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area [35]. The high percentage of iron found in residual fraction in this study is an important repository of iron in the soil. The availability of iron in the sequentially extracted fractions follows the order: residual> reducible> oxidizable> easily reducible.

Cadmium was predominantly associated with the mobile fractions (easily exchangeable and acid soluble) with 70.18% and 29.82% respectively (see Fig. 3). Similarly, [21] reported the association of cadmium with the easily exchangeable and acid soluble in waste soils in Port-Harcourt. The high percentage of the total extractable fraction in the mobile phase suggests that cadmium in this soil was potentially more bioavailable for plant uptake [36,37]. Contrary to this result, [38] reported Cd in the unpolluted

oasis soil to be associated with the residual fraction. Cadmium was not detected in the easily reducible, reducible, oxidizable and residual fractions which were the non mobile fractions of the metal.

Nickel was not detected in the easily exchangeable, acid soluble and easily reducible fractions but nickel was predominantly bound to the residual and reducible fractions with 47.62% and 34.29% respectively. Similarly, the predominance of Ni in the residual fraction has been reported [39,40]. The order of Ni in the different fractions is: residual> reducible> oxidizable. The high association of Ni in the non mobile fraction may be attributed to the alkaline stabilization process of the soil [21].

The results of the sequential extractions of zinc in the farm soil showed that the mobile phase contained 0.37% to 3.25%, indicating a slight availability for plant uptake. Zinc was predominantly associated with the residual fraction having about 70.39% of the total extractable metal. The association of zinc with the residual fraction has been reported [41,42]. This result was also in agreement with previous findings by [10,43]. In the contrary, non-residual fraction has been reported the most abundant fraction for zinc at Zaria across the seasons [44].

The order of zinc in the different fractions of soil from the farm is: residual> oxidizable> reducible> easily exchangeable> easily reducible> acid soluble.

Lead was not detected in the exchangeable and acid soluble fractions but was predominantly associated with the residual fraction with 68.99%. The dominance of lead associated with this fraction has been reported by other researchers [3,21]. The residual fraction has been considered as the most stable, less reactive and less bioavailable [26]. This suggests that the leaching of the metal to the environment is not possible from the studied samples sites [45]. The order of the geochemical fractions of lead in the soil is: residual> reducible> easily reducible> oxidizable.

The results showed that, all the metals except cadmium were associated with the residual and oxidizable fractions (non-mobile fraction). This agreed with the findings of other researchers [42,44]. The presence of the metals in the residual fraction suggests that the metals may not be readily bioaccumulated by the plants grown on the contaminated area [19,20]. However the soluble component of cadmium (70.18%) and manganese (10.67%) in the soil samples are of major concern since they are known to biaccumulate as they journey through the environment and biological system [45]. There is therefore the need to pay more attention to the level of hygienic sourcing and handling of such soil when used for agricultural purposes. The risk associated with the presence of metals in soil is the ability of their transfer in water or plants.

The extractions or leaching of the metals bound to the exchangeable fraction using $BeCl_2$, $BeCl_2/BaCl_2$ mixture (1:1) and $CaCl_2/NH_4Cl$ mixture (1:1) were investigated in this study. The results of the extraction efficiencies were compared with the conventional reagents $MgCl_2$, $CaCl_2$, $BaCl_2$ and NH_4Cl, reported by other researchers. The results are presented in Fig. 4.

The main goal of operational speciation is to convert the metals bound in the solid phase into soluble forms with the extractant used at each step. Hence the abilities of $BeCl_2$, $MgSO_4$, a mixture of $BeCl_2/BaCl_2$ and a mixture of $CaCl_2/NH_4Cl$ to leach the exchangeable fractions were assessed.

3.1 $BeCl_2$ Reagent

From the results, the newly tested extracting reagent $BeCl_2$, extracted 0.6499 mg/kg of the

exchangeable cadmium (Cd) which was much higher than the conventional $MgCl_2$, (0.010 mg/kg), $CaCl_2$ (0.1010 mg/kg) and $BaCl_2$ (0.5539 mg/kg) extracts. $BeCl_2$ extracted 0.2952 mg/kg of the exchangeable nickel (Ni) which was very comparable to the concentration in the conventional $CaCl_2$ which was 0.3221 mg/kg, NH_4Cl was 0.1783 mg/Kg and $BaCl_2$ was 0.2488 mg/kg. From the results in Fig. 4, $BeCl_2$ extracted 0.4363 mg/kg exchangeable fraction of lead (Pb) which was again higher than the conventional extractants. For manganese (Mn), the mixture of $Becl_2/Bacl_2$ extracted the highest concentration in this fraction which was 0.6667 mg/kg. The result of Mn extract using $BeCl_2$ had the concentration of 0.4245 mg/kg, which was also higher than the conventional extractant ($MgCl_2$ = 0.0650, $CaCl_2$ = 0.0272, $BaCl_2$ = 0.0401 mg/kg, NH_4Cl = 0.3163 mg/kg). The concentration of Zn in $BeCl_2$ extract was 1.4032 mg/kg which was also very comparable with other leaching reagents.

3.2 Mixture of $BeCl_2/BaCl_2$ (1:1vv)

A higher concentration was also observed with the mixture of $BeCl_2/BaCl_2$ (0.4384 mg/kg) than the conventional extractant except $BaCl_2$ which was 0.5539 mg/kg. The concentration of nickel in the mixtures of $BeCl_2/BaCl_2$ was 0.4131 mg/Kg which was higher than the concentrations of $MgCl_2$, $CaCl_2$, $BaCl_2$ and NH_4Cl (see Fig. 4). The concentration of Pb in the mixture of $BeCl_2/BaCl_2$ was 0.3452 mg/kg which was very comparable to the concentration in $BaCl_2$ which was 0.3581 mg/Kg. The concentration of Mn in the mixture of $CaCl_2/NH_4Cl$ was 0.5136 mg/Kg which was still higher than the conventional reagents ($MgCl_2$ =0.0650 mg/Kg, $CaCl_2$ = 0.0272 mg/Kg, $BaCl_2$ = 0.0401 mg/Kg). The result of the extraction of Zn showed that, the concentration of the exchangeable Zn was highest in the mixture of $BeCl_2/BaCl_2$ with a concentration of 3.120 mg/kg.

3.3 Mixture of $CaCl_2/NH_4Cl$ (1:1vv)

The concentration of Cd in the mixture of $CaCl_2/NH_4Cl$ extract of 0.0574 mg/kg was lower than $CaCl_2$ (0.1010 mg/Kg) and $BaCl_2$ (0.5539 mg/Kg) extracts. The concentration of nickel in the mixtures of $CaCl_2/NH_4Cl$ (0.4132 mg/kg) was also higher with the concentrations of $MgCl_2$, $CaCl_2$, $BaCl_2$ and NH_4Cl (see Fig. 4). Thus, the use of the mixture of the extractants leached exchangeable Ni more than the single extractants. The concentration in the mixture of $CaCl_2/NH_4Cl$ was 0.1218 mg/Kg which was also very comparable to the conventional extracting
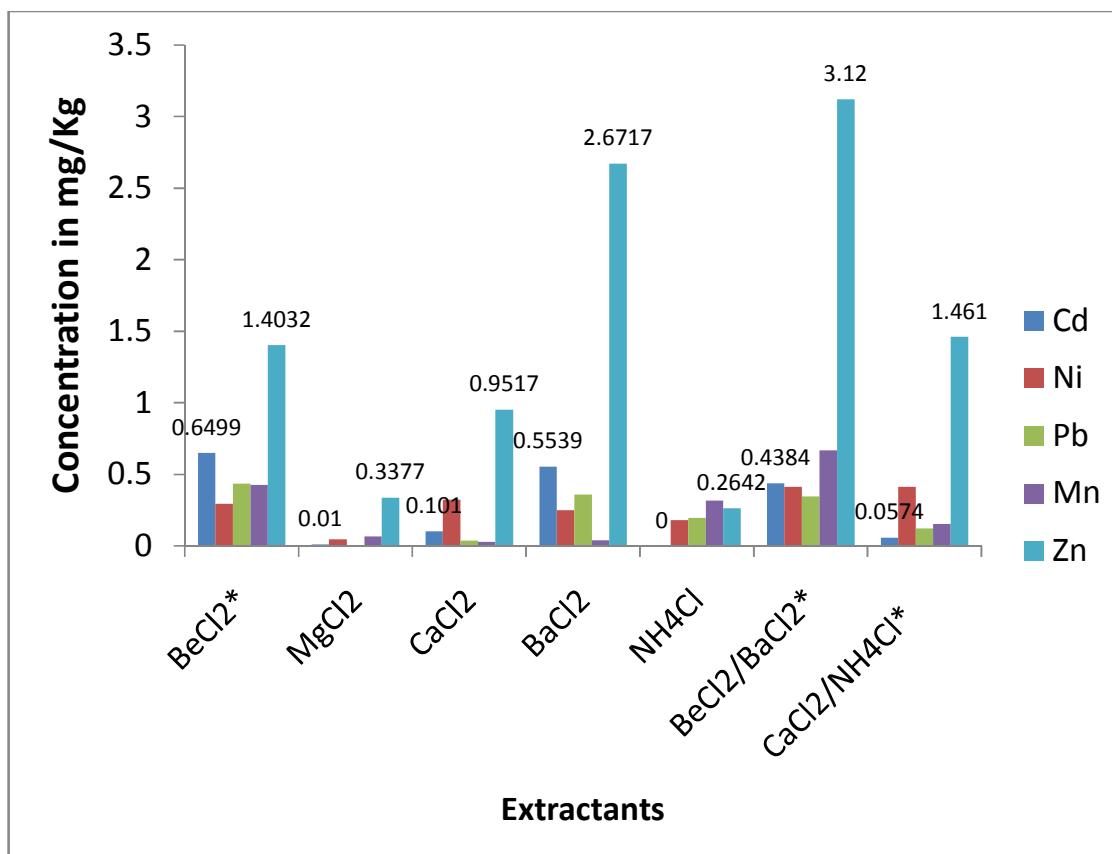
Fig. 4. The Concentration of metals in the exchangeable fraction using different extractants

reagent NH4Cl (0.1948 mg/Kg). The mixture $CaCl_2/NH_4Cl$ extracted 0.1536 mg/Kg of Mn which was higher than the concentrations of $MgCl_2$ (0.0650 mg/Kg) $CaCl_2$ (0.0272 mg/Kg) and $BaCl_2$ (0.0401 mg/Kg). Thus, from the results, the same quantity of $BeCl_2$, NH_4Cl and the mixture of $BeCl_2/BaCl_2$, (1:1) reagents were better extractants for the exchangeable Mn in soil samples. The concentration of Zn in the mixture of $CaCl_2/NH_4Cl$ extract was 1.4610 mg/kg. The result was very comparable to the value in $BeCl_2$ extract (1.4032 mg/Kg). Thus, the concentrations of zinc in the newly introduced extractants were higher than the conventional extractants (see Fig. 4).

Generally, the newly introduced extractants have proven to be good leaching agents of the exchangeable fractions in speciation studies. However, the chloride salts, apart from leaching the exchangeable fraction, enhance the extraction of transition metals as a result of their complexing action [46].

4. CONCLUSION

Generally all the metals except cadmium were associated with the residual and oxidizable fractions (non-mobile fraction). The presence of the metals in the residual fraction suggests that the metals may not be readily bioaccumulated by the plants grown on the contaminated area. However the soluble component of cadmium (70.18%) and manganese (10.67%) in the soil samples are of major concern since they are known to biaccumulate as they journey through the environment and biological system. There is therefore the need to pay more attention to the level of hygienic sourcing and handling of such soil when used for agricultural purposes. The newly introduced extractants have proved to be good leaching agents of the exchangeable fractions in speciation studies.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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