

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

Author details: Nanven D. Nimyel

nimyelnanven@yahoo.com

Department of Science, School of Science and Technology

Plateau State Polytechnic, Barkin Ladi.

Egila J.N. and Y.N Lohdip

Department of Chemistry, Faculty of Natural Sciences

University of Jos,

nimyelnanven@yahoo.com, nimyelnanven@yahoo.com

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 Pd. The results also showed that there were low tendency of bioavailability and reactivity in the environment. The results of the newly introduced extractants (BeCl₂, mixture of BeCl₂/BaCl₂ and CaCl₂/NH₄Cl), revealed that these reagents could be used for the leaching of the exchangeable fraction in speciation analysis. BeCl₂ extracted 0.6499mg/kg of the exchangeable Cd while the conventional MgCl₂ extract 0.010mg/kg (Cd). The results also revealed that the mixture BeCl₂/BaCl₂ extracted 0.4384mg/kg of Cd. The use of the mixture of BeCl₂/BaCl₂ and CaCl₂/NH₄Cl extractants leached exchangeable Ni more than the conventional single extractants. BeCl₂, **NH₄Cl** and the mixture of BeCl₂/BaCl₂, reagents were better extractants for the exchangeable Mn in soil samples.

Keywords: Speciation, bioavailability, extractants, dumpsite, heavy metals, exchangeable fraction.

INTRODUCTION

The presence of heavy metals in urban solid waste raises serious concern about the adverse environmental impact as a result of the use 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

37 partitioning among the various geochemical phases is more useful than measurements of total heavy metals
38 contents [6]. The chemical speciation of heavy metals allowed the assessment of heavy metal bioavailability
39 and is related to the different natures of the metals, their bonding strength, and either in free ionic form or
40 complexed by organic matter, or incorporated in the mineral fraction of the sample [7, 8]. In addition,
41 speciation will determine metal mobility and hence potential contamination of ground water following
42 dumpsite soil application. Therefore, chemical speciation can be defined as the process of identifying and
43 quantifying different species, forms or phases present in a material [9, 10].

44 Today, speciation science seeks to characterise at least some of the most important forms of an
45 element, in order to understand the transformation between forms which can occur, and to infer from such
46 information the likely consequences for example in terms of risk assessment, toxicity or biological activity
47 [11]. As such, it is a discipline which is of relevance to scientists with many different backgrounds:
48 Chemists, toxicologists, biologists, soil and sediment scientists, physicists and specialists in various aspects
49 of nutrition and medicine; all require this type of information.

50 Selective sequential extraction procedures have been commonly used for studying metal mobility and
51 availability in soils. Numerous extraction schemes for soils and sediments have been described [12, 13, 14,
52 15]. Despite uncertainties as to the selectivity of the various extractants and to possible problems due to
53 readsorption, extraction procedures provide qualitative evidence regarding the forms of association of heavy
54 metals and ultimately, of their bioavailability [16]

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

58 **MATERIALS AND METHODS**

59 **Study Area**

60 The farm (F1 and F2) in this study are located about 200m from Kuru Jantar dumpsite on longitude
61 $08^{\circ} 53'E$ and latitude $09^{\circ} 42' N$ (Garmin GPS model etrex 20). See figure 1

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63 **Sample Collection and Treatment**

64 Top soil samples were also collected randomly from twenty different locations in the farms that used
65 manure from the dumpsites and control farm. The soil samples collected were air-dried, crushed and passed
66 through a 2mm sieve. The sieved samples were kept in cellophane bags for laboratory analysis.

67 **Total Heavy Metal Analysis**

68 Triplicate samples (3.0g) of the sieved soil samples were digested with 25ml of aqua regia ($HCl +$
69 HNO_3 , 3:1 v/v) at $120^{\circ}C$ on a water bath in a fume cupboard. The digested samples were filtered into a
70 100ml volumetric flask and made up to the mark with distilled/deionised water.[15, 16, 17] The
71 concentration of the metals in the digested soil sample solutions were determined using Buck Scientific
72 model 210VGP atomic absorption spectrophotometer at wavelengths and slits specific to each metal. The
73 metals analysed were lead (Pb), copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), cadmium (Cd)
74 and manganese (Mn).

75 **Sequential Extraction of Metals**

76 **Exchangeable fractions [F1]**

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

81 **Acid Soluble (bound to carbonate fractions) [F2]**

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

84 **Easily reducible fractions (bound to Fe-Mn Oxides) [F3]**

85 Easily reducible fraction was extracted from the residue of [F3] with a mixture of hydroxylamine
86 hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) and 0.2M trioxonitrate (V) acid (HNO_3) and agitated at room temperature for 1
87 hour [18].

88 **Reducible Fraction [F4]**

89 Reducible fraction was extracted from the third residue [F3] with a mixture of hydroxylamine
90 hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) and 25% ethanoic acid (CH_3COOH) and agitated at room temperature for 15
91 hours [19, 20].

92 **Oxidizable (bound to Organic fractions) [F5]**

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

95 **The Residual fractions (bound to Silicates)[F6]**

96 The residual fraction was extracted with 25ml of aqua regia ($\text{HCl} + \text{HNO}_3$, 3:1 v/v) at 120°C on a
97 water bath in a fume cupboard [22, 23]. Metal levels in each fraction were determined using the calibrated
98 Buck Scientific model VGP 210).

99 **Results and Discussion**

100 The speciation study was conducted for a farm using dumpsite soil as manure to ascertain the forms
101 of the heavy metals in soil. The findings of past researchers had implicated mobility and bioavailability of
102 metals for plants uptake with the form of the metal (speciation) in the soil [9, 24, and 25]. The results of the
103 six chemical fractions [26] for seven heavy metals (Cu, Mn, Fe, Cd, Ni, and Zn & Pb) are presented in
104 Figure 1. The percent of each fraction associated with the total extractable metal is also presented in Figure
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Figure 1: A Farm [F1] in Kuru Jantar using the Kuru Jantar Dumpsite Soil as manure



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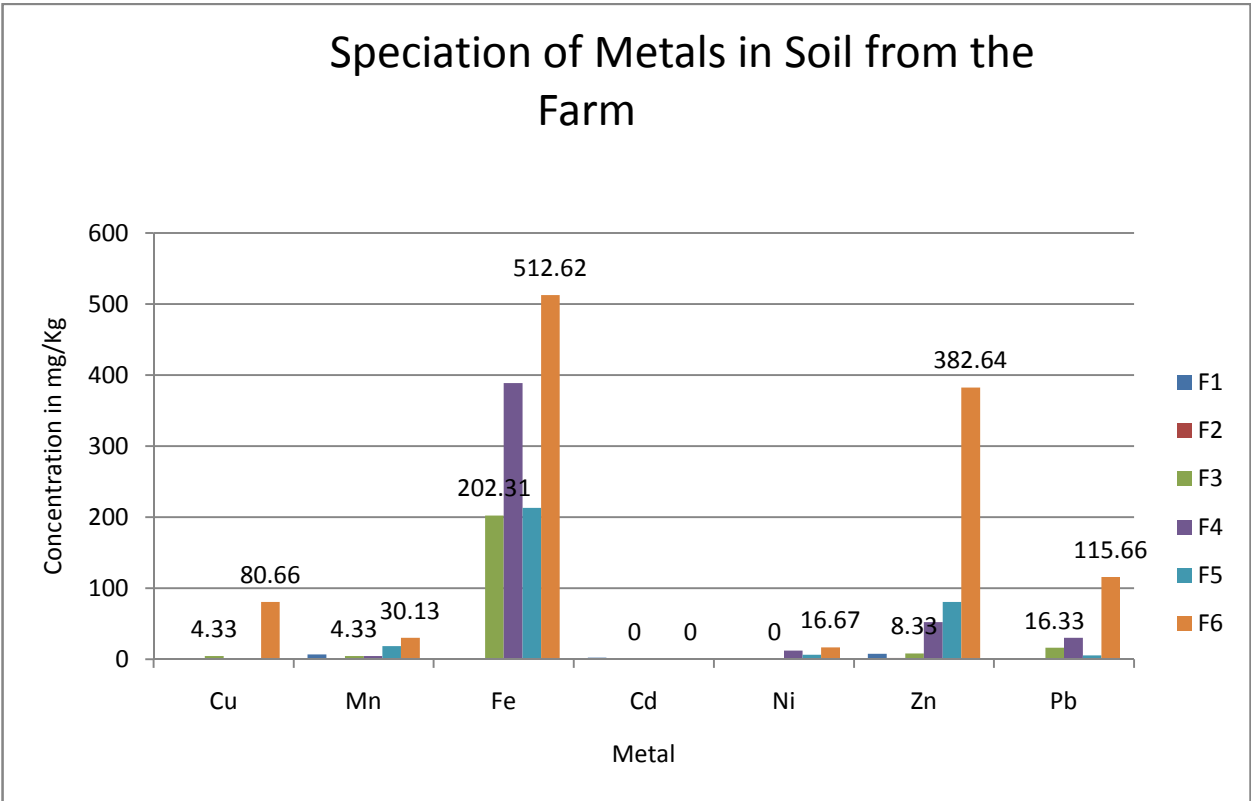
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Figure 2: A Farm [F2] in Kuru Jantar using the Kuru Jantar Dumpsite Soil as manure

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

125 **Figure 3: The Speciation of Heavy Metal in the Soil Samples Collected from the Farm**
126 **Using Manure from Kuru Dumpsite**
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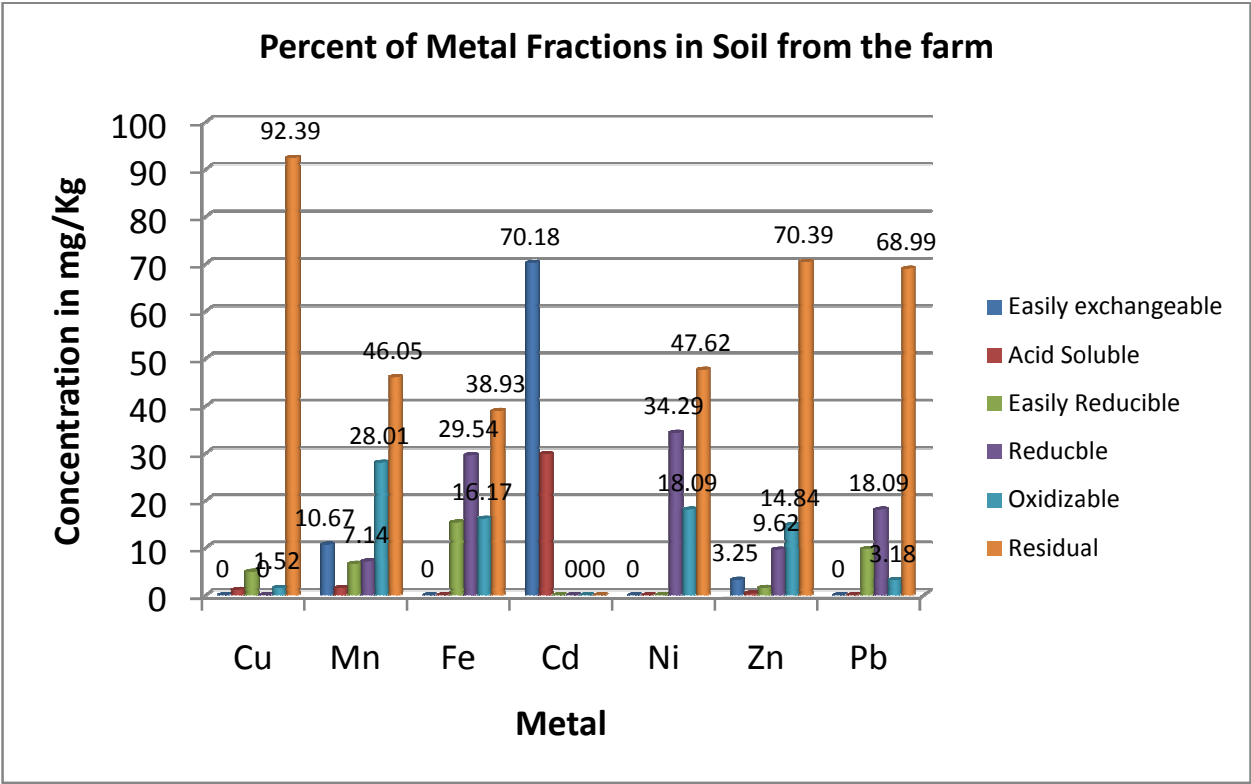


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133 F1 = Easily exchangeable F2 = Acid soluble F3 = Easily reducible F4 = Reducible
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 135 F5 = Oxidizable F6 = Residual
 136 ND = Not Detected

137 **Figure 4: Percent of Trace Metal Chemical Fractionation of Soil Samples Collected**
 138 **from the Farm Using Manure from Kuru Dumpsite**
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143 Manganese was found to be associated with all the fractions with the residual and oxidizable fractions
 144 dominating. The residual fraction had 46.05% while the oxidizable fraction had 28.01% of the total
 145 extractable metal. These results are comparable to those of [16] who reported Mn, to be mostly associated
 146 with the residual fractions. These findings could be linked to the preferential incorporation of Mn into
 147 silicate lattice. Also, the high Mn level in the organic matter bound fractions may be connected to the ease of
 148 complexation and peptization between the metal and natural organic matter like humic and fulvic acids [29].
 149 Relatively high levels of manganese in this fraction have been reported [1, 9]. The association of manganese
 150 with residual fraction implies partitioning into crystalline oxides [9].

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

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

165 Cadmium was predominantly associated with the mobile fractions (easily exchangeable and acid
166 soluble) with 70.18% and 29.82% respectively. Similarly, [21] reported the association of cadmium with the
167 easily exchangeable and acid soluble in waste soils in Port-Harcourt. The high percentage of the total
168 extractable fraction in the mobile phase suggests that cadmium in this soil was potentially more bioavailable
169 for plant uptake [36 and 37]. Contrary to this result, [38] reported Cd in the unpolluted oasis soil to be
170 associated the residual fraction. Cadmium was not detected in the easily reducible, reducible, oxidizable and
171 residual fractions which were the non mobile fractions of the metal.

172 Nickel was not detected in the easily exchangeable, acid soluble and easily reducible fractions but
173 nickel was predominantly bound to the residual and reducible fractions with 47.62% and 34.29%
174 respectively. Similarly, the predominance of Ni in the residual fraction has reported [39 and 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 of 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 and 42]. This result was also in agreement with previous findings by [10 and 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.

Generally 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 and 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.

198 The extractions or leaching of the metals bound to the exchangeable fraction using BeCl_2 ,
199 $\text{BeCl}_2/\text{BaCl}_2$ mixture (1:1) and $\text{CaCl}_2/\text{NH}_4\text{Cl}$ mixture (1:1) were investigated in this study. The results of the
200 extraction efficiencies were compared with the conventional reagents MgCl_2 , CaCl_2 , BaCl_2 and NH_4Cl ,
201 reported by other researchers. The results are presented in Figure 5.

202 The main goal of operational speciation is to convert the metals bound in the solid phase into soluble
203 forms with the extractant used at each step. Hence the abilities of BeCl_2 , MgSO_4 , a mixture of $\text{BeCl}_2/\text{BaCl}_2$
204 and a mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ to leach the exchangeable fractions were assessed.

205 **BeCl_2 reagent:** From the results, the newly tested extracting reagent BeCl_2 , extracted 0.6499mg/kg
206 of the exchangeable cadmium (Cd) which was much higher than the conventional MgCl_2 , (0.010mg/kg),
207 CaCl_2 (0.1010mg/kg) and BaCl_2 (0.5539mg/kg) extracts. BeCl_2 extracted 0.2952mg/kg of the exchangeable
208 nickel (Ni) which was very comparable to the concentration in the conventional CaCl_2 which was
209 0.3221mg/kg, NH_4Cl was 0.1783mg/Kg and BaCl_2 was 0.2488mg/kg. From the results in Figure 5, BeCl_2
210 extracted 0.4363mg/kg exchangeable fraction of lead (Pb) which was again higher than the conventional
211 extractants. For manganese (Mn), the mixture of $\text{BeCl}_2/\text{BaCl}_2$ extracted the highest concentration in this
212 fraction which was 0.6667mg/kg. The result of Mn extract using BeCl_2 had the concentration of
213 0.4245mg/kg, which was also higher than the conventional extractant ($\text{MgCl}_2 = 0.0650$, $\text{CaCl}_2 = 0.0272$,
214 $\text{BaCl}_2 = 0.0401\text{mg/kg}$, $\text{NH}_4\text{Cl} = 0.3163\text{mg/kg}$). The concentration of Zn in BeCl_2 extract was 1.4032mg/kg
215 which was also very comparable with other leaching reagents.

216 **Mixture of $\text{BeCl}_2/\text{BaCl}_2$ (1:1vv):** A higher concentration was also observed with the mixture of
217 $\text{BeCl}_2/\text{BaCl}_2$ (0.4384mg/kg) than the conventional extractant except BaCl_2 which was 0.5539mg/kg. The
218 concentration of nickel in the mixtures of $\text{BeCl}_2/\text{BaCl}_2$ was 0.4131mg/Kg which was higher than the
219 concentrations of MgCl_2 , CaCl_2 , BaCl_2 and NH_4Cl (see Figure 4). The concentration of Pb in the mixture of
220 $\text{BeCl}_2/\text{BaCl}_2$ was 0.3452mg/kg which was very comparable to the concentration in BaCl_2 which was
221 0.3581mg/Kg. The concentration of Mn in the mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ was 0.5136mg/Kg which was still
222 higher than the conventional reagents ($\text{MgCl}_2 = 0.0650\text{mg/Kg}$, $\text{CaCl}_2 = 0.0272\text{mg/Kg}$, $\text{BaCl}_2 =$

0.0401mg/Kg). The result of the extraction of Zn showed that, the concentration of the exchangeable Zn was highest in the mixture of $\text{BeCl}_2/\text{BaCl}_2$ with a concentration of 3.120mg/kg.

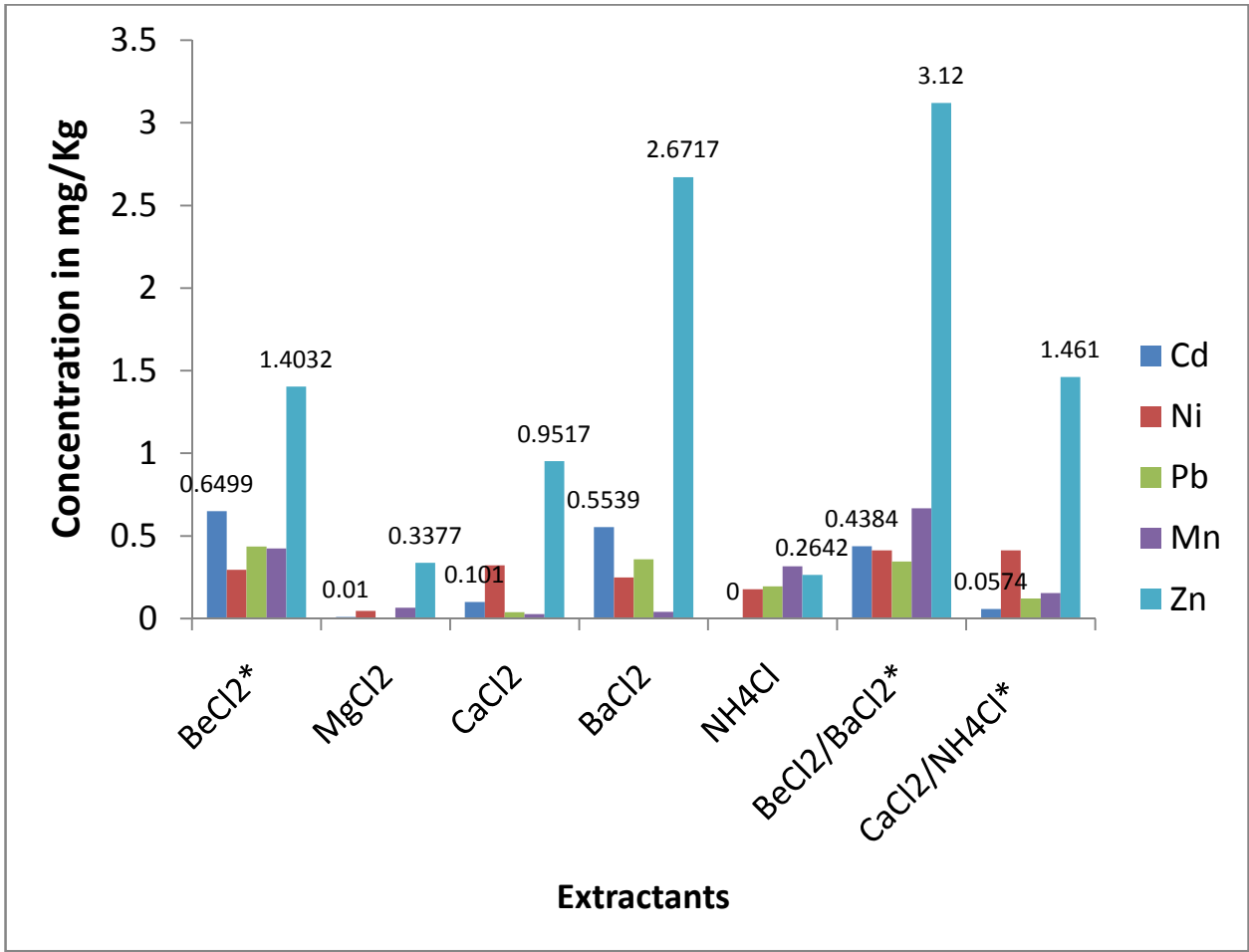
Mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ (1:1vv): The concentration of Cd in the mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ extract of 0.0574mg/kg was lower than CaCl_2 (0.1010mg/Kg) and BaCl_2 (0.5539mg/Kg) extracts. The concentration of nickel in the mixtures of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ (0.4132mg/kg) was also higher with the concentrations of MgCl_2 , CaCl_2 , BaCl_2 and NH_4Cl (see Figure 4). Thus, the use of the mixture of the extractants leached exchangeable Ni more than the single extractants. The concentration in the mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ was 0.1218mg/Kg which was also very comparable to the conventional extracting reagent NH_4Cl (0.1948mg/Kg). The mixture $\text{CaCl}_2/\text{NH}_4\text{Cl}$ extracted 0.1536mg/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 $\text{BeCl}_2/\text{BaCl}_2$, (1:1) reagents were better extractants for the exchangeable Mn in soil samples. The concentration of Zn in the mixture of $\text{CaCl}_2/\text{NH}_4\text{Cl}$ extract was 1.4610mg/kg. The result was very comparable to the value in BeCl_2 extract (1.4032mg/Kg). Thus, the concentrations of zinc in the newly introduced extractants were higher than the conventional extractants (see Figure 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].

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Figure 5: The Concentration of Metals in the Exchangeable Fraction Using Different Extractants



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Conclusion

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

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