CHAPTER FIVE

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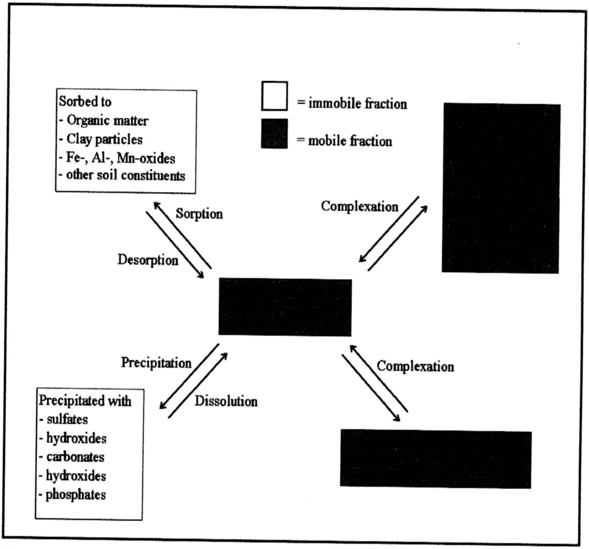
CHEMICAL SPECIATION OF HEAVY METALS IN THE STUDIED SOILS

5.1 Introduction

To design recovering techniques for heavy metals contaminated sites and to prevent future contaminations of other sites it is essential to assess the risk associated with their presence. The measurement of the total metal concentration of soils provides little indication of the metal's interactions in the environment; therefore, the assessment of the potential threat of heavy metals to ecosystem health requires knowledge of their chemical speciation. (Allen, 1993 and Ross and Ross, 1994).

The speciation of heavy metals, i.e. the way that a metal is distributed among its different chemical forms and physical phases, determines how it is distributed in the environment. In the soil environment a heavy metal ion can undergo a number of processes and reactions. These affect how the total metal content of a soil is distributed into fractions that can be found in the water phase, i.e. the mobile phase, or the solid phase, i.e. the immobile phase, respectively (Ross and Ross, 1994). This is illustrated in figure 5.1. The kinetics of metals and the phase transformation of these initial metal phases determine the further fate of the metals in the soil.

The accommodation, kinetics and release of the physiochemical species of heavy metals in the soil environment are largely affected by the soil properties and residence time (Allen, 1993 and Sager and Stoeppler 1992). The intention of this chapter therefore is to present and discuss the solid and solution speciation of metals added to soils and the influence of soil type and residence time on the metals distribution among the different chemical forms.



Adapted from Lindsay, (1979)

Figure5.1: Speciation of heavy metals in the soil environment

5.2 Solid phase speciation

The occurrence of heavy metals in soil theoretically includes the following pools: water soluble, exchangeable, complexed or adsorbed (exchangeable only by other cations with higher affinities), coprecipitated and held in the primary minerals (Viets 1962). Metal fraction in the solid phase is related to the intensity of metal release to the liquid phase. These chemical pools present decreasing degrees of metal availability ranging from ions in solution to ions in the soil crystal lattices.

Sorption processes including precipitation generally retain metals that are introduced in the soils. Thus information about the partitioning of heavy metal contaminants between the various solid phase fractions is critical in understanding their ultimate metal fate and availability. There are several sequential extraction procedures developed and used for the speciation of solid phase associated metals (Tack and Verloo 1995; Daniel and Sparks 1999).

The solid phase speciation of cadmium (Cd), lead (Pb), nickel (Ni) and zinc (Zn) for soil I, II and III was determined by sequential extraction procedure introduced by Warman and Thomas (1976) and modified by Soon and Bates (1982). Soils received an amendment level of 5mmol/kg are sequentially extracted with IM NH_4OAc to remove the water soluble and exchangeable metals, with 0.125 M Cu $(OAc)_2$ to remove complexed metals and with 1M HNO_3 to dissolve the precipitated and residual metals as described in 3.3.6.

5.2.1 Cadmium

Average extracted values for exchangeable, complexed and precipitated cadmium (Cd) in soil I, II and III were expressed as percentages are presented in Table 5.1 The sum-extracted metal was listed in the table as total extracted. The duplicate analysis deviated about the mean value by 0 to 30 percent. When the sum of the metal extracted by the three extractants is compared to the total initial cadmium amendment level (5mmol/kg) recoveries of extractable Cd in soil I, II and III are 85, 77 and 69 percent respectively.

Table 5.1: Percentage exchangeable, complexed, acid soluble and total extracted cadmium

Soil type	Extractants %			Total Extracted* (mmol/kg)	Recovery (%)
	Exchangeable	Complexed	Acid-soluble		
Soil I	37.55 ±0.15	40.42± 0.17	19.75± 0.32	4.25	85
Soil II	40.83± 0.078	44.18± 0.03	17.96± 0.10	3.85	77
Soil III	32.26± 0.29	40.54± 0.26	26.17± 0.54	3.45	69

±: Standard deviation

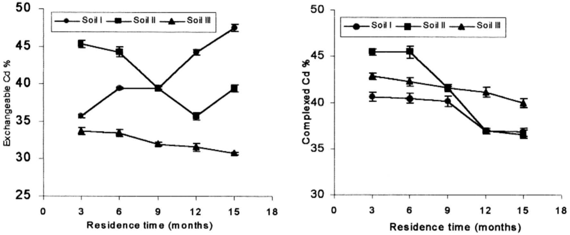
** Total extracted was obtained by summing the amount of Cd removed by the three extractants*

Although appreciable amounts of Cd in soil I, II and III were found in the exchangeable form (37.55, 40.83 and 32.26%) respectively yet the complexed pool was the prevailing fraction in the three tested soils (40.42, 44.18 and 40.54%) respectively. This may be attributed to the acidic nature of the extractant (Cu (OAc)$_2$ because in the first extraction with neutral NH_4OAc (pH 7) part of the easily soluble Cd could remain un extracted. It is reported that Cd may easily be complexed by soil organic matter and, as such is not strongly sorbed (Andersson 1977).

Less percentage of the added Cd was found in the precipitated and residual forms (19.75%, 17.96% and 26.17%). That was in partial agreement with the findings of Boon and Soltanpou, (1991); Jeng and Singh (1993) Liang et al., (1996) and Narwal et al., (1999). They reported relatively high percent of cadmium added to soils in the labile and exchangeable forms and less percentage in the residual fraction. Among the soils, soil II recorded the greatest percentage of Cd in the exchangeable form (40.83%). However, in soil III (sandy clay loam) the Cd distribution is quite different. Lower proportion of the added Cd was removed by the three extractants compare to that of soil I and II. Indicating that considerable amount of Cd remaining unrecovered. The greatest extracted percentage of Cd in the sandy clay loam was in the complexed form (40.54%) indicating higher amount of Cd was Fe and Mn oxides in the sandy clay loam (Forbes *et al.*, 1988). On the other hand the acid soluble fraction is recorded of lower percentage (26.17%), which represent the higher proportion among the three soils. The last aspect is in contrast with findings of, Liang and Schoenau. (1996), who proved the presence of great amount of Cd in clay loam soils in the weak acid soluble fraction. In general a recognizable amount of Cd added to the three soils was found in the exchangeable form, which considered more mobile and plant available (Dudka and Chlopeca, 1990). Greatest proportion of Cd was in the complexed pool that can be made available through soil chemical alteration.

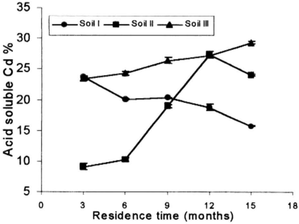
After incubation periods for up to 3,6, 9, 12 and 15 months exchangeable, complexed and precipitated Cd in the three soils may be able to provide information on how the speciation, binding and release of Cd changes with time. Figure 5.2 shows percentage of the extracted Cd after incubation periods for up to 3,6, 9, 12 and 15 months.

In soil I the percentages exchangeable, complexed and precipitated Cd were varied from 35.69%, 40.60% and 23.67% to 47.47%, 36.80% and 15.72%, soil II recorded percentages of exchangeable, complexed and precipitated Cd were varied from 45.36%, 45.48% and 20.11% to 39.40%, 36.58% and 24.01%, while soil III recorded values varied from 33.63%, 42.86% and 23.49% to 30.75%, 39.91% and 29.32% exchangeable, complexed and precipitated Cd as the residence time increased from 3 to 15 months.



a)Exchangeable cadmium %

b)Complexed cadmium %



c)Acid soluble cadmium

Figure 5.2: Cadmium species percentages as influence by soil type and residence time

The charts showed the variation in the percentages of exchangeable, complexed and precipitated Cd in the three soils throughout the residence time. The exchangeable fraction showed steady elevation as the residence time of Cd amendment increases. Both the complexed and precipitated Cd pools were higher in the first 3 months of incubation and gradually decreased as the incubation time increased that was due to the soil processes that govern the balance between accumulation and solubilization of Cd through time (Street et al., (1978); Schultz et al., (1987); McLaren et al., (1986); McGrath and Cegerra (1992); Comans, (1985) Ainsworth et al., (1995) and Merrington and Madden, (2000).

5.2.2 Lead

Table 5.2 presents the sequential extracted average values for exchangeable, complexed and precipitated lead (Pb) in soil I, II and III expressed as percentages, total amount of extracted metal in mmol/kg and percentage of total recovery. The duplicate analysis deviated about the mean value by 0 percent to 40 percent. When the sum of the metal extracted by the three extractants is compared to the total initial lead amendment level (5mmol/kg) recoveries of total extractable Pb in soil I, II and III are 76, 75 and 73 percent respectively.

Table 5.2: Percentage exchangeable, complexed, acid soluble and total extracted lead

Soil type	Extractant %			Total extracted* (mmol/kg)	Recovery (%)
	Exchangeable	Complexed	Acid-soluble		
Soil I	2.60± 0.43	15.42±0.25	81.97 ± 0.24	3.80	76
Soil II	3.13± 0.40	32.96±0.21	63.09 ± 0.21	3.75	75
Soil III	2.23± 0.44	64.22±0.28	35.55 ± 0.38	3.65	73

±: Standard deviation

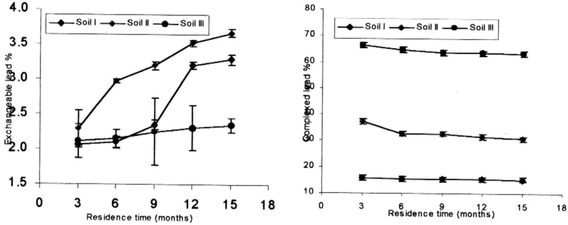
** Total extracted was obtained by summing the amount of Pb removed by the three extractants*

The distribution of Pb varied from soil to soil; generally extremely low detectable amount of Pb was extracted by IM NH_4OAc (exchangeable form) from any of the three soils (Table 5.2). In soil I and II (sandy loam) over 2.60 and 3.13 % of the added Pb was found in exchangeable form This supported by Sebsatien et al., (1997) conclusion about the low percentage of free ion in lead contaminated soils. The percentage of precipitated form was varying greatly among soils. The sandy clay loam (soil III) recorded the greatest percentage of the precipitated form. The result is in agreement with Robert *et al*., 1995 and Sposito *et al*., (1997) who reported significant amount of lead entered in clay soil systems will remain in the precipitate fraction. Greatest proportion of the extracted Pb in soil I and II was in the acid soluble form (81.97, 63.90%) respectively. In agreement to this result Liang *et al*., (1996); Legret, (1993) stated that most of the lead added to soils is associated with the acid soluble fraction and did not display a great availability in the soil at low soil pH. They also reported that at high soil pH only most of the added lead is associated with hydrated iron oxide, which supports the results obtained for precipitated fraction in soil III (64.22%).

Figure 5.3 below shows percentage exchangeable, complexed and precipitated Pb in the three soils as determined after incubation periods for up to 3,6, 9, 12 and 15 months. The exchangeable, complexed and precipitated Pb percentages in soil I were varied from 2.08, 15.79 and 82.14 to 3.29, 15.28 and 81.43 as the residence time increased from 3 to 15 months. In soil II recorded percentages of exchangeable, complexed and precipitated Pb varied from 2.30, 37.20 and 60.50 to 3.67, 30.67 and 65.66, while soil III recorded values varied from 2.11, 6.20 and 31.69 to 2.35, 63.40 and 34.25 for exchangeable, complexed and precipitated Pb as the residence time increased from 3 to 15 months.

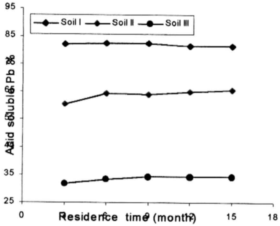
The exchangeable fraction showed a positive correlation with the residence time of Pb amendment, while both of the complexed and precipitated Cd pools showed a steady elimination throughout the incubation period that may justify the effect of the balance between adsorptions, sorption and solubilization process of Pb in soils through time (Brady and Weil 1999). The present results are in agreement with the findings of Schultz *et al*., (1987);

McKenzie, (1980); McGrath and Cegerra (1992) Menzies _et_ _al_., (1991) and Ainsworth _et_ _al_., (1995).



a)Exchangeable lead %

b) Complexed lead %



c)Acid soluble lead %

Figure 5.3: Lead species percentages as influence by soil type and residence time

5.2.3 Nickel

The results of the sequential extraction for nickel (Ni) as influenced by the soil types were expressed as percentages are presented in Tables 5.3. The triplicate analysis deviated about the mean value by 0 to 35 percent. The recoveries of total extractable Ni in soil I, II and III are 86, 80 and 76 percent respectively.

Table 5.3: Percentage exchangeable, complexed, acid soluble and total extracted nickel

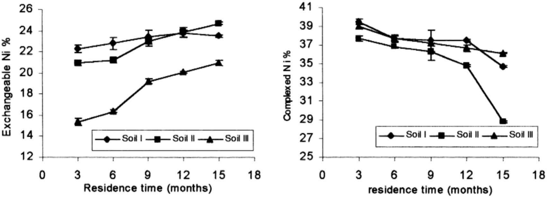
Soil type	Extractant %			Total extracted* (mmol/kg)	Recovery (%)
	Exchangeable	Complexed	Acid-soluble		
Soil I	23.19 ± 0.35	37.37 ± 0.32	39.48 ± 0.35	4.30	86
Soil II	22.73 ± 0.29	34.86 ± 0.25	42.39 ± 0.29	4.00	80
Soil III	18.38 ± 0.33	37.34 ± 0.34	44.27 ± 0.15	3.80	76

± Standard deviation

Total extracted was obtained by summing the amount of Ni removed by the three extractants

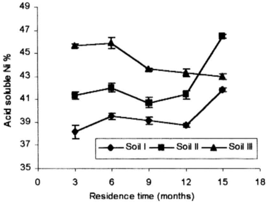
Nickel is distributed in the different chemical fractions in increasing order from exchangeable to the precipitated and residual form. Ahumada et al., (1999) and Adam et al., (1996) found that nickel is less mobile and they reported a small percentage of added Ni in the exchangeable form. Similar results were found in this study especially in soil III (sandy clay loam). That may be attributed to the greater association of nickel with Fe oxides, which is higher in soil III (Dudka et al., 1990; and 1996 Berti et al., 1996). Further support for this results was found in the findings of Narwal et al., (1999); Singh et al., (1995); Liang et al., (1996) who concluded that only a small percentage of the total soil nickel were found in mobile fraction, higher percentage was in complexed and precipitated forms.

After incubation periods for up to 3, 6, 9, 12 and 15 months the three soils were sequentially extracted as described in 3.3.6. Figure 5.4 shows the percentage exchangeable, complexed and precipitated Ni in the three soils. The exchangeable, complexed and precipitated Ni percentages in soil I have values ranging from 22.3 %, 39.51% and 38.18% to 23.5%, 34.67% and 41.83 as the residence time increased from 3 to 15 months.



a)Exchangeable nickel %

b) Complexed nickel %



c)Acid soluble nickel %

Figure 5.4: Nickel species percentages as influence by soil type and residence time

Soil II recorded percentages of exchangeable, complexed and precipitated Ni were varied from 20.95%, 37.7% and 41.35% to, 24.70%, 28.8% and 46.49%, while soil III recorded values that varied from 15.36, 39 and 45.64 to 20.93%, 36.13% and 42.94% for exchangeable, complexed and precipitated Ni respectively as the residence time increased from 3 to 15 months. The present results are in agreement with the findings of Brummer et *al,* (1988) and Scheidegger *et al*., (1996).

5.2.4 Zinc

Sequential extraction average percentages for exchangeable, complexed and precipitated as well as the total extracted zinc (Zn) in soil I, II and III are presented in Table 5.4. The duplicate analysis deviated about the mean value by 0 percent to 30 percent. When the sum of the metal extracted by the three extractants is compared to the total initial Zn amendment level (5mmol/kg) the percent recoveries of extractable Zn in soil I, II and III are 62, 63 and 66 respectively.

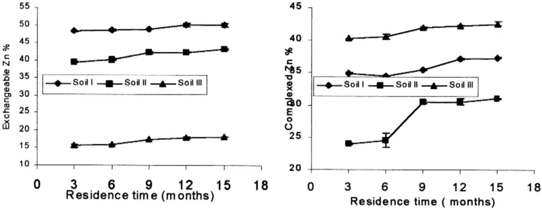
Table 5.4: Percentage exchangeable, complexed, acid soluble and total extracted zinc

Soil type	Extractants %			Total extracted* (mmol/kg)	Recovery (%)
	Exchangeable	Complexed	Acid-soluble		
Soil I	49.16 ± .057	35.84 ± 0.15	14.99 ± 0.55	3.10	62
Soil II	41.46± .095	28.10 ± 0.13	30.43± 0.32	3.15	63
Soil III	17.02 ± .369	41.53± 0.45	41.43 ± 0.65	3.30	66

± Standard deviation
**Total extracted was obtained by summing the amount of Zn removed by the three extractants*

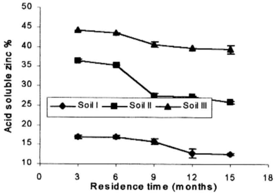
Soil I and II greatest percentages of the extracted zinc was in the soluble and exchangeable form (49.16% and 41.46%), Although zinc is considered as a very mobile metal it can also react with clay minerals and oxides thus a greater percentage of zinc extracted from soil III was in complexed form (41.53%). This is supported by the findings of Calvet et al., (1990); Boon and Soltanpou, (1991); Jeng and Singh (1993) and Robert et al., (1995) which stated that a high percentage of the Zn added to soils was readily found in exchangeable form. Several investigators have found the added zinc was associated with Fe and Mn oxides (Kuo et al., 1983). In general almost 35-40% of the added Zinc remained unrecovered and the differences in the total extractable Zn among the soils were generally small, yet a greater amount of Zn was extracted from soil III (sandy clay loam) that may attributed to that more Zn is adsorbed by negatively charged colloidal soil III particles. The result is on contrast with the findings of Narwal *et al.*, (1999) which recorded a higher total extracted Zn from sand loam soils than that of the clay loam. Figure 5.5 below shows the percentage of exchangeable, complexed and precipitated Zn in the three soils as determined after incubation periods for up to 3,6, 9, 12 and 15 months.

The exchangeable Zn fraction is positively correlated with the length of incubation time and it is generally higher in soil I and II than that of soil III. For soil I the percentages exchangeable, complexed and precipitated Zn were varied from 48.23, 34.87 and 16.89 to 50.10%, 37.30% and 12.60%, soil II recorded percentages of the exchangeable, complexed and precipitated Zn were varied from 39.5%, 24 and 36.5 to 43.2, 30.98 and 25.85, while soil III recorded values varied from 15.60%, 40.25% and 44.15% to 18.12%, 42.56% and 39.32% percent exchangeable, complexed and precipitated Zn respectively as the residence time increased from 3 to 15 months.



a)Exchangeable zinc %

b)Complexed zinc %



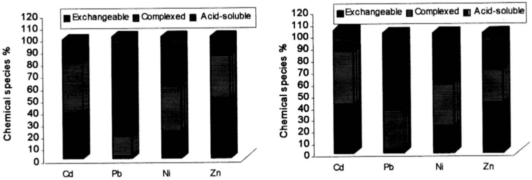
c) Acid soluble zinc %

Figure 5.5: Zinc species percentages as influence by soil type and residence time

The exchangeable fraction showed a steady elevation as the incubation time proceeds. The present result is in an agreement with the findings of Kuo and Mikkelesn, (1980); Schultz *et al.*, (1987); Brummer *et al.*, (1988) and McGrath and Cegerra (1992)

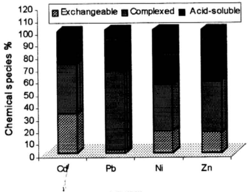
5.2.5 Comparative investigations on exchangeable and complexed Cd, Pb, Ni, and Zn in the three soils

Metals varied in the way they are distributed among their different chemical species. The existence of heavy metals in different chemical forms in the soil environment provides the conceptual basis of the varying ranges of their availability. To compare the availability and the environmental fate of different metals it is essential to look on their speciation. This section discusses the speciation variability among the four studied metals. The percentage of exchangeable, complexed and acid soluble pools of Cd, Pb, Ni and Zn are compared in each of the three soils (Figure 5.6). The charts showed that generally greatest percentages of Zn, Ni and Cd were in the exchangeable proportion while Pb is mostly associated with the acid soluble phase and did not display a great availability in exchangeable fraction (Legret 1993).



a) Soil I

b) Soil II



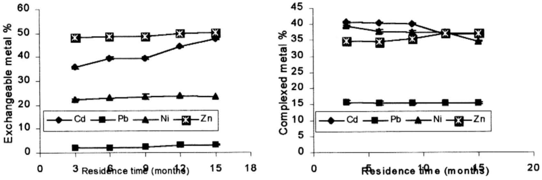
c) Soil III

Figure 5.6: Cadmium, lead, nickel and zinc species percentages in the three soils

Exchangeable extracted Cd, Pb Ni, and Zn form soil I and II was generally higher than that in soil III. The result is in agreement with results obtained for sandy loam and sandy clay loam soils (Soon and Bates, 1982). In the three soils the order of exchangeable pool was Zn> Cd > Ni >Pb. The order of the complexed pool was varied from soil to soil; in soil I it was Cd > Ni > Zn > Pb, in soil II Cd > Ni > Pb > Zn, while in soil III Pb showed the greatest percentage of complexed metal. Metals acid soluble fraction percentage in soil I was in the following order Pb > Ni > Cd > Zn, in soil II Pb > Ni > Zn > Cd and in soil III Ni > Zn > Pb > Cd. These are supported by the findings of Andreu et al., (1996) and Krishnamurti et al., (1997).

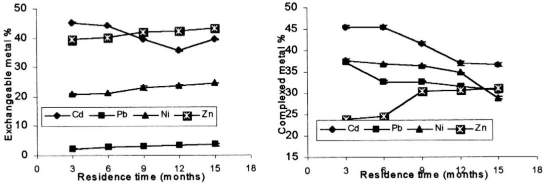
According to Viets (1962) the quantification of water soluble, exchangeable, and complexed and acid soluble pools of heavy metals in soil environment provides a useful approach to predicting their availability for plants. Based on that and on the results presented we may infer that in sandy loam soils (Soil I and II) Zn is the most bioavaiable metal, followed by Cd and Ni. In soil III (sandy clay loam) Cd is the most bioavailable followed by Zn and Ni, while Pb was primarily in strongly bound forms resulting in limited solubility and availability in the three experimental soils. Similar conclusion was reported by Percival, (1999).

Figure 5.7 compare the percentage of exchangeable and complexed species of Cd, Pb, Ni and Zn in the three soils as influence by the residence time. Simple regression analysis revealed the following correlations between the percentages of exchangeable and complexed chemical forms and the residence time in the three soils (Table 5.5 and 5.6)



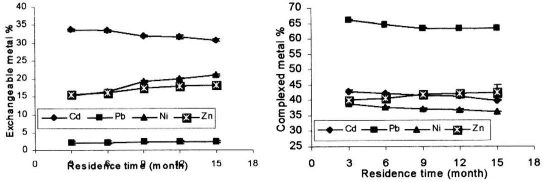
a)Soil I exchaneable metal

b) Soil Icomplexed metal %



c) Soil II exchangeable metal %

d) Soil II Complexed metal %



e) Soil III exchangeable metal %

f) Soil III Complexed metal %

Figure 5.7: Cadmium, lead, nickel and zinc species percentages as influenced by residence time

Table 5.5: Regression models for the exchangeable Cd, Pb, Ni and Zn chemical fraction as related to residence time

Soil Type	Heavy metal adjusted regression coefficient (R^2)			
	Cadmium	Lead	Nickel	Zinc
Soil I	0.95	0.87	0.81	0.92
Soil II	0.67	0.93	0.96	0.94
Soil III	0.96	0.98	0.95	0.91

Table 5.6: Regression models for the complexed Cd, Pb, Ni and Zn chemical fraction as related to residence time

Soil Type	Heavy metal adjusted regression coefficient (R^2)			
	Cadmium	Lead	Nickel	Zinc
Soil I	0.91	0.79	0.78	0.80
Soil II	0.97	0.77	0.95	0.91
Soil III	0.96	0.97	0.95	0.92

5.3 Solution speciation

Soil solution is the natural medium for plant growth; it plays a central role in many soil chemical processes and represents the chemical fraction immediately available in the environment. Dissolved ions in solution interact with each other (form complexes), interact with particulate surfaces (adsorb) and possibly form solid phases (precipitate) (Figure 5.1). Metals in the soil solution can be present in different physiochemical forms varying in size and charge (Lindsay, 1979). The behavior and transformation of heavy metals in soil solution is of importance in the understanding of their bioavailability in plants. The species of heavy metals present in the soil solution principally determine their mobility and bioavailability in the soil environment and consequently their influence on human health. In a typical natural soil solution, there may be 10 to 20 major chemical components dissolved species. Some of these chemical species may be biologically active or even toxic while others may be inert. All of this depends on factors like the total concentration of each component, the pH, pe, ionic strength and temperature. Several chemical fractionation techniques have been developed and applied for estimating the speciation of metals in the solution phase (Tack and Verloo 1995 and Allen et al., 1995). Recently a number of new, powerful and flexible computer software packages, based on soil chemical and thermodynamic data have been developed and applied for the speciation of heavy metals in the soil solution.

The visual MINTEQ program is a solution equilibrium model that calculates the speciation of chemical elements among the aqueous-solution and predicts ion activity in soil solutions (Appendix C). In this study MINTEQA is used to explore and predict the speciation of Cd, Pb, Ni and Zn in soil solution from the modeling of the equilibrium soil solution concentrations of Cd, Pb, Ni and Zn, chemical and thermodynamic data of the three experimental soils that receive an amendment level of 5mmol/kg. The method of calculation employed in this program is based on soil chemical thermodynamics properties. The program specifications and operation procedure have been illustrated in 3.3.7.

5.3.1 Cadmium

Cadmium in the soil solution can be present as free, hydrated cation or as species with organic and inorganic ligands (Helmke, 1999). The distribution of total dissolved Cd among the different chemical species as estimated by MINTEQA2 is as follows: the free Cd^{2+}, $CdCl^{+}$, $Cd(NO_3)_2$ $Cd(OH)^{+}$ and other miner concentrations like $CdSO_4$ and $CdPO_4$ Table 5.7 presents the percentage soluble species of Cd in the three experimental soils.

Table 5.7: Inorganic species of cadmium in solution phase

Soil type	Cadmium chemical species (%)				
	Cd^{2+}	$CdCl^+$	$Cd(NO_3)_2$	$Cd(OH)^+$	Other hydrated species
Soil I	98.795	0.084	1.056	0.058	0.007
Soil II	98.225	0.126	0.298	-	1.351
Soil III	92.274	7.259	0.259	0.122	0.086

Significant part of the total dissolve Cd in the three soils occurs as free hydrated cation. The free Cd^{2+}ion concentration accounted for 98.795, 98.225 and 92.274 in soil I, II and III respectively. Other measurable proportions Cd species are $CdCl^+$, $Cd(OH)^+$ and minor percentages of $Cd(OH)^+$ and other hydrated species. The percentages of the inorganic species are varying among the experimental soils. The highest percentage of the free Cd^{2+}ion was recorded in soil I. This is due to the effect of the pH. This is supported by the published fact that, the speciation of Cd in soil solution is markedly affected by the pH and stating the decreasing proportion of the free ions as the pH of the solution increased (Lindsay, 1979; Ma and Lindsay, 1990 Lorenz et al., 1997; McLaughlin et al., 1997 and Helmke, 1999). The percentage of the free Cd^{2+}ion reported in the present study is extremely higher than that reported by Jette et al., (1996), who estimate 50.9% of the Cd in leachate polluted groundwater samples as free ion. The percentages of other inorganic species reported by Jette et al., (1996) are comparable to the present results expect for $CdCl^+$ which was reported to represent 45.1% of the total dissolved Cd in polluted water samples. Jopony and Young, (1994) summarized the most significant inorganic species of the dissolved Cd as Cd^{2+} and $CdCl^+$, they reported the $Cd(NO_3)_2$, $Cd(OH)^+$ and other chlorocomplexes as minors species.

.5.3.2 Lead

The distribution of the dissolved Pb among the different inorganic species is a function of the total dissolved Pb and soil properties like the pH. As estimated by MINTEQA2. The major species in the three experimental soils are free Pb^{2+}, $PbCl^+$, and $Pb(NO_3)_2$ while the minor species are $Pb(OH)^+$ and $Pb(NO_3)_2$ Table 5.8 presents the percentage soluble species of Pb.

Table 5.8: Inorganic species of lead in solution phase

Soil type	Cadmium chemical species (%)				
	Pb^{2+}	$PbCl_2$	$Pb(NO_3)_2$	Pb (OH)	Other hydrated species
Soil I	95.37	1.41	2.55	0.59	0.08
Soil II	90.28	3.01	2.11	2.22	2.35
Soil III	87.12	0.96	2.03	0.22	9.66

Results above in are comparable to the findings of Jopany and Young, (1994), who listed the major inorganic Pb species in soil solution as Pb^{2+}, PbCl, and $Pb(NO_3)_2$ and the minor species as PbCl, $Pb(NO_3)_2$ and PbOH. Results indicted that the most dominant Pb species in the three soils is the free Pb^{2+}, which accounted for 95.370%, 90.277% and 87.123% of the total dissolved Pb in the three soils respectively. This is may be due to the effect of the pH (Sauve et al., 1997).

In partial consistence with this result, Jopany and Young, (1994) reported the free Pb^{2+}as be most significant Pb species in soil solution with neutral and alkaline pH with percentage range of 42-78. Further support for the results was found in the findings of Kalbasi et al., (1995). In contrast with this result Sauve et al., (1997), reported about 60-80% of the dissolved Pb as complexes. They also reported the decrease of this percentage in soils with low pH. The percentages of other inorganic species are also varying among soils; soil II recorded the highest PbCl and Pb (OH) (3.006% and 2.220) On the other hand soil III recorded the highest percentage of the hydrated species (9.664%). There is no obvious variation among the percentages of $PbNO_3$ in the three tested soils. Jopany and Young, (1994).

5.3.3 Nickel

Nickel in soil solution is mainly present as Ni^{2+}, NiCl, $NiCO_3$ $Ni\,(HCO_3)_2$, NiOH, Ni PO_4 and $NiSO_4$ depending on the soil pH and the levels of the SO_4 and PO_4 legends (McGrath, 1995 and Sposito and Page, 1984). The solution speciation of Ni is estimated by MINTEQA2 is as follows: the free Ni^{2+}, NiCl, $NiNO_3$ NiOH and other miner concentrations such as the hydrated forms of NiCl, Ni PO_4 and $NiSO_4$. Table 5.9 presents the percentages of soluble species of nickel in the three experimental soils.

Table 5.9: Inorganic species of nickel in solution phase

Soil type	Cadmium chemical species (%)				
	Ni^{2+}	NiCl	$NiNO_3$	$Ni\,(OH)_2$	Other hydrated species
Soil I	99.03	0.49	0.48	-	0.03
Soil II	99.34	0.45	0.41	0.02	0.00
Soil III	99.54	0.07	0.60	0.13	0.00

Significant part of the total dissolve nickel in the three soils occurs as free hydrated Ni^{2+}ion. The recorded percentages of the inorganic Ni species in soil I and II are comparable to each other, while soil III slightly differ mainly in the NiCl and $NiNO_3$ (0.069 and 0.260). Results are in agreement with the findings of Percival, _et al._, (1999) and supported by the findings of Jette _et al._, (1996), who summarized the most significant inorganic species of the dissolved Ni as Ni^{2+}, NiCl and NiCl (aq). The results obtained for soil I and II partially supported by the findings of McGrath, (1995), who reported the major inorganic species of dissolved Ni in acid soil solution as Ni^{2+}, NiOH, Ni PO_4. Results obtained for soil III are supported by the fact that under alkaline conditions, the hydroxy-complex Ni2^{+}, and NiOH ions are the most major forms in soil solution (Sposito and Page, 1984).

5.3.4 Zinc

The common aqueous forms of Zn in soil solution are: the free hydrated ion (Zn^{2+}), ZnCl, $ZnNO_3$ Zn (OH) and $CdSO_4$ (Robson, 1999). The distribution of Zn among it's soluble chemical species as estimated by MINTEQA2 is as follows: the free Zn^{2+}, ZnCl, $ZnNO_3$ and other miner concentrations of $CdPO_4$ and $CdSO_4$ Table 5.10 presents the percentage soluble species of zinc in the three experimental soils. Chemical speciation of Zn in the solutions of the three studied soils showed that the majority of Zn was present in the hydrated ionic form Zn^{2+}.

Table 5.10: Inorganic species of zinc in solution phase

Soil type	Cadmium chemical species (%)				
	Zn^{2+}	$ZnCl_2$	$ZnNO_3$	$Zn\ (OH)_2$	Others hydrated species
Soil I	98.59	0.08	0.56	0.74	0.02
Soil II	99.16	0.14	0.60	0.14	0.01
Soil III	98.41	0.13	0.47	0.95	0.04

The percentages of the free Zn^{2+} in the three soils are 98.589, 99.116 and 98.406. The proportions of other inorganic species including the $ZnCl_2$ and the $ZnNO_3$ are very low and that may be due to either the low concentrations of the ligands or the weak compexing strength (Robson, 1999).

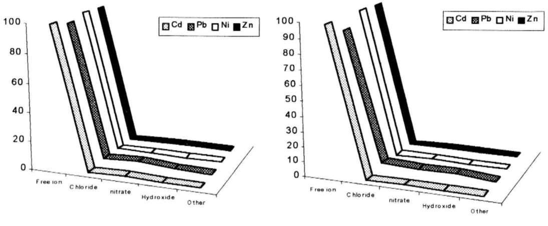
These results are consistent with the findings of Dang et al (1996); Fotovat and Naidu, (1997); Lorenz *et al*., (1997) and Percival, *et al*., (1999). The present results are corresponded broadly to those calculated using other programs like GEOCHEM (Mahler, 1980 and McGrath and Lane, 1989). MINTEQA2 and GEOCHEM speciation modeling of several soil types under normal conditions showed that $Zn\ (OH)_2$ and $CdSO_4$ might comprise up to 10% of the dissolved Zn (Robson, 1999).

5.3.5 Comparative investigations on soil solution chemistry of Cd, Pb, Ni, and Zn in the three soils

The soil solution chemistry of heavy metal is of great importance in assessing and comparing their bioavailability and estimates their toxicity (Allen *et al*., 1995 and Percival, *et al*., 1999). The chemical speciation trends of Cd, Pb, Ni, and Zn in the solution are similar for the three studied soils but differ in magnitudes and proportions of the different inorganic species. Figure 5.8 compare the percentage of inorganic species of Cd, Pb, Ni and Zn in each of the three soils. The proportions of the different inorganic species of metals in the soil solution vary among the studied metals and soil type Percival, *et al*., (1999). The majority of Cd, Pb, Ni and Zn in the three soil solutions were present in the free ionic Cd^{2+}, Pb^{2+}, and $Ni^{2+}$and Zn^{2+}forms, which represent the major source of bioavailable component of metals added to the soil.

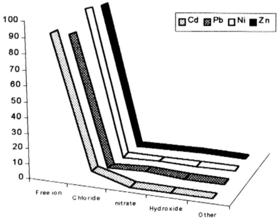
These findings on the speciation of Cd, Pb, Ni and Zn in the three soil solutions correspond broadly to those estimated by many researchers using computer implemented models such as GEOCHEM, MINTEQA2 and (Barak, 1990; Mahler, 1989; McGrath and Lane, 1989; Jette *et al*., 1996; Percival, *et al*., 1999 and Robson, 1999). The present results contrast with the findings of Hamon *et al*., (1999) in which they found that the amount of complexed Cd and Zn in solution could exceed the free ion concentration.

Within the studied metals nickel and zinc reported by the highest percent of the free ion and than that of cadmium and lead in the three tested soils. Results are consistent with the findings of Percival, (1999) and Percival, *et al*., (1999). The percentages of the free ion of the studied metals are varying with the soil type, generally soil III showed the lowest percentage. That is possibly due to the effect of soil pH as stated in Table 3.1 soil III has the highest pH among the experimental soils (Lindsay, 1979; Sposito and Page, 1984; Sauve *et al.*, 1997; Helmke, 1999 and Robson, 1999).



a) Soil I

b) Soil II



c) Soil III

Figure 5.8: The solution chemistry of Cd, Pb, Ni and Zn in the three soils.

The proportions of the other minor inorganic complexes of Cd, Pb, Ni and Zn are also varying within the studied metals and soil type (Jette *et al.*, 1996 and Jopony and Young, 1994). As noted above that the free metal is the predominant species in soils amended with the Cd, Pb, Ni and Zn that is considered as the major source for the bioavialable fraction of metal added to soils (Percival, 1999 and Percival, et al., (1999).