

## CHAPTER FOUR

## METALS DISTRIBUTION IN SOLID AND SOLUTION PHASES OF THE SOIL

## 4.1 Introduction

The bioavailability and metabolism of heavy metals and their availability to plants are related to the content of such metals in the soil solution and to the solid phase adsorbed forms that can be made available through the soil reaction. It is mandatory to understand and quantify the distribution of heavy metals partitioned in the solid and solution phases of the soil and to understand the factors, processes and reactions that govern their distribution in the different soil phases. The natural processes and mechanisms of a soil involving the distribution of heavy metals are related to the soil type, metal kind and their chemical form in the distribution of cadmium (Cd), lead (Pb), zinc (Zn) and nickel (Ni) in the solid and solution phases of each soil type.

# CHAPTER FOUR

## 4.2 Objective

The distribution of cadmium in the soil solid and solution phases in the three soils was determined in the four years application (1997). The results are presented below.

## CHAPTER FOUR

### METALS DISTRIBUTION IN SOLID AND SOLUTION PHASES OF THE SOIL

#### 4.1 Introduction

The leachability and mobility of heavy metals and their availability to plants are related to the content of such metals in the soil solution and to the solid phase adsorbed metals that can be made available through the soil solution. It is mandatory to understand and quantify the distribution of heavy metals contaminant in the solid and solution phases of the soil and to understand the factors, reactions and processes that govern their distribution in the different soil phases. The natural properties and components of a soil determine to a large extent its tendency for adsorption and desorption of metals into its system. To estimate the potential and residual risk of heavy metal contaminants in the soil environment it is important to focus on the length of time the soil is exposed to a specific metal contaminant. This chapter will discuss the influence of soil type, metals level and their residence time on the distribution of cadmium (Cd), lead (Pb), nickel (Ni) and zinc (Zn) in the solid and solution phases of each soil type.

#### 4.2 Cadmium

The distribution of cadmium in the soil solid and solution phases in the three soils was examined at the four metal application rates. The results are as showed below

#### 4.2.1 Effect of soil type and metal amendment level on Cd distribution between the solid and solution phases of the soils

The Cd concentration in the solutions of soil I, II and III varies from 2.47, 1.85, 1.14 to 29.07, 14.34 and 6.84 mmol/kg respectively as the mass loading increased from 5 to 40 mmol/kg. The amount of Cd adsorbed onto soil I, II and III particles ranges from 0.96, 0.91 and 2.08 to 6.30, 6.34 and 16.36 mmol/kg as the Cd amendment level increases from 5 to 40 mmol/kg. Table 4.1 presents the average concentration of Cd in solution form and that adsorbed by the solid phase of the soils.

Table 4.1: The distribution of added Cd in solution and solid soil phases

Soil type	Cd amendment level (mmol/kg)	Solution Cd (mmol/kg)	Adsorbed Cd (mmol/kg)	Recovery (%)
Soil I	5	02.49 $\pm$ 0.37	00.99 $\pm$ 0.15	69.4
	10	05.42 $\pm$ 0.30	01.78 $\pm$ 0.20	72.0
	20	11.23 $\pm$ 0.30	03.18 $\pm$ 0.03	72.0
	40	29.07 $\pm$ .052	06.30 $\pm$ 0.09	88.0
Soil II	5	01.85 $\pm$ 0.07	00.91 $\pm$ 0.21	75.1
	10	02.97 $\pm$ 0.13	01.64 $\pm$ 0.07	66.1
	20	05.90 $\pm$ 0.19	03.14 $\pm$ 0.04	85.2
	40	24.34 $\pm$ .038	06.34 $\pm$ 0.29	90.7
Soil III	5	01.14 $\pm$ .052	02.08 $\pm$ 0.21	82.4
	10	01.73 $\pm$ 0.09	04.08 $\pm$ 0.57	78.0
	20	03.52 $\pm$ 0.15	08.26 $\pm$ 0.49	68.0
	40	06.84 $\pm$ 0.27	16.36 $\pm$ 0.39	83.0

$\pm$  Standard deviation

The outcome of adding the cadmium to the three soils was that substantial adsorption took place in solid phase, but as the Cd amendment level increase the Cd amount in soil solution increases. The results showed that in general the metal distribution is a function of the metal concentration and soil type. Figures 4.1a and 4.1b below exhibit the influence of Cd amendment level and concentration of Cd in the soil solution and solid phases respectively.

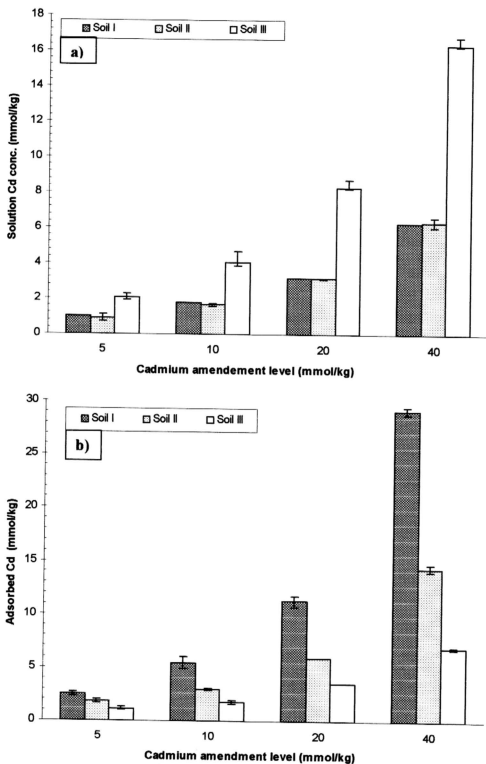


Figure 4.1: Effect of Cd amendment level on Cd distribution between the solid and solution phases of the soils.

a) Cd solution concentration

b) Adsorbed Cd



In the three soils, Cd adsorption by the solid phase was found to increase with the level of Cd amendment. The total adsorption value of Cd onto soil particles in the three soils showed an increase in each increment of their amendment level. This situation is clearly demonstrated in sandy clay loam (soil III). The solution concentration of Cd increases with the intensification of the Cd amendment level. This may attributed to that soils reach their maximum soil sorption capacity and virtually most of the added amendment will remain in the soluble phase. This is in agreement with the findings of many researchers (Linda and Chang, 1992; Andreu and Gracia, 1996; Percival, 1999 and Krishnamurti *et al.*, 1997).

On closer investigation on the effect of soil type on the Cd adsorption and desorption characteristics, Figures 4.2a and 4.2b illustrate the overall outcome of adding Cd to the three soils at the lowest and highest amendment level (5 and 40 mmol/kg). The charts show the starting level of the added Cd, the solution concentration and the adsorbed Cd respectively. Soil type has significant effect on Cd adsorption and solution concentration. Cd adsorbed more by the sandy clay loam (soil III), while it was less adsorbed by the sandy loam (soils I and II). This may be attributed to the pH and cation exchange capacity, both of which soil III has the highest values (Table 3.1). These two factors are important governing the Cd distribution in soils (Bolton and Evans 1996; Hickey and Kittrick 1984 Frost and Griffin, 1977). In agreement with this result Cavallaro and McBride 1979; Elliott (1983); Kuo *et al.*, (1983); Mench *et al.*, (1994); Merrington, & Alloway (1994) and Boekhold *et al.*, (1993), reported positive correlation between soil pH and Cd adsorption. Further support to the present result was the findings of Campbell *et al.*, (1987); Cowan *et al.*, (1992); Wilkens and Loch (1995); McBride, 1989 and Bolton and Evans (1996), who investigated the positive role of clay content and CEC of soils in their Cd adsorption.

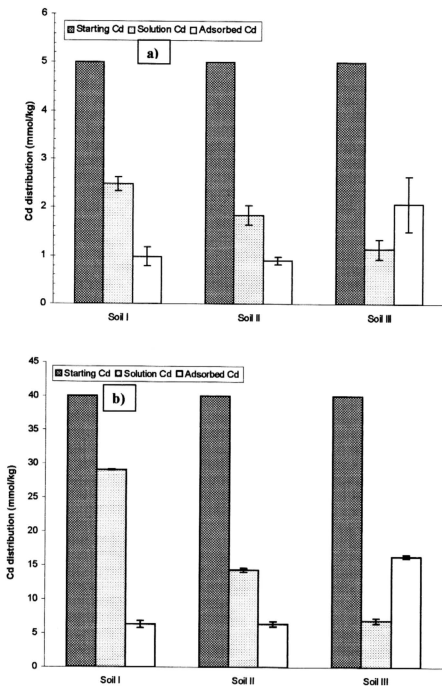


Figure 4.2: Effect of soil type on Cd distribution between the solid and solution phases of the soils

- a) Cd distribution at level 5 mmol/kg
- b) Cd distribution at level 40 mmol/kg

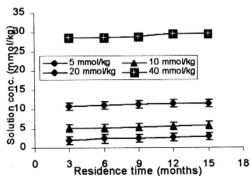
Although soil I and II are about the same type the amount of Cd adsorbed by soil I is slightly higher than that in soil II. This may be due to the relatively higher Fe and Al content of soil I

compared to that of soil II (Jenne, 1968; Elliott *et al.*, 1986 and Zachara *et al.*, 1992). Cd concentration in solution phase also varies among soils, soils I and II reported highest solution concentration than that of soil III. The differences between soils I and II are not significant. This supported by the fact that desorption or remobilization is the process by which sorbed species are released back to the solution phase and it is also pH dependent. Fischer *et al.*, (1991); Krishnamurti *et al.*, (1997) and Miner *et al.*, (1997) concluded that at lower the pH-value more Cd was found in solution.

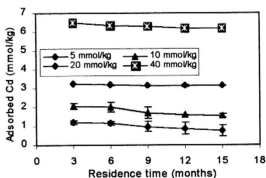
#### 4.2.2 Effect of residence time on Cd distribution between the solid and solution phases of the soils

The equilibrium Cd concentration in soil solution and the amount adsorbed onto soil surface were determined after incubations for up to 3,6, 9, 12 and 15 months. The adsorbed Cd was reported to be highest in the first three months and decreases as the residence time increases. The mean Cd concentration in solution of the three soils at the lowest Cd amendment level respectively varied from 1.96, 1.76 and 1.12 to 2.90, 1.93 and 1.12 mmol/kg as the residence time increased from 3 to 15 months ( $R^2 = 0.970, 0.822$  and  $0.149$ ). Fig 4.3 shows the results obtained for the concentration of Cd in solution and the adsorbed Cd concentration in five successive extraction times with three months interval. Results showed a slightly steady increase in soil I and II while in soil III there is a dramatic elevation in Cd concentration in the first six months of incubation followed by slightly steady increase in solution concentration and steady elimination in the adsorbed amount was recorded. At the lowest Cd amendment level, the adsorbed Cd of the three soils was reported to vary from 1.1584, 1.196, and 1.859 to 0.728, 0.7464 and 1.994 mmol/kg as the residence time increased from 3 to 15 months ( $R^2 = 0.925, 0.832$  and  $0.117$ ) respectively. Cd concentration in the soil I and II solutions of the four level

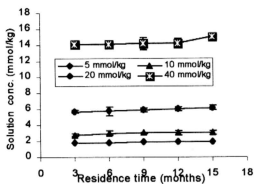
amended soils showed a positive correlation with the residence time ( $R^2 = 0.976, 0.992, 0.992$  and  $0.906$  for soil I and for  $0.947, 0.746, 0.970$  the four levels respectively).



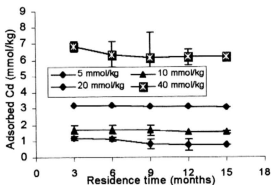
a) Soil I solution Cd concentration



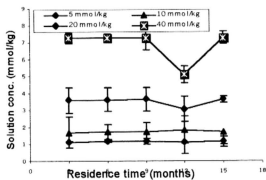
b) Soil I adsorbed Cd



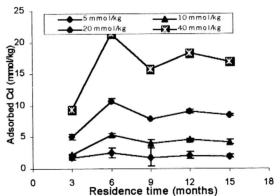
c) Soil II solution Cd concentration



d) Soil II adsorbed Cd



e) Soil III solution Cd concentration



f) Soil III adsorbed Cd

Figure 4.3: Distribution of cadmium in the three soils as influenced by residence time

On the other hand there was no significant correlation between the Cd concentrations in the solution of soil III treated by four Cd amended levels. The significant elevation of the Cd concentration in soil solution of soil I and II is due to that the number of exchangeable sites available for adsorption in these soils is less than that of soil III based on the measurement of the CEC (Table 3.1). When all these sites are exhausted through time soils reach their maximum soil sorption capacity and most of the added amendment will remain in the soluble phase

The amount of Cd adsorbed by soil II and I showed a steady decrease as the residence increases. Significant negative correlation was reported between the adsorbed amount of Cd and time at the four amendment levels in soil I and II ( $R^2 = 0.984, 0.925, 0.875$  and  $0.916$  for soil I and  $0.873, 0.939, 0.890$  and  $0.628$  II respectively). While soil III showed insignificant correlation between the Cd adsorption and residence time in soils that treated by the four Cd amended levels. The elimination in the adsorbed amount of Cd in soils can be explained by the exhaustion of the negatively charged sites on soil particles, which are available for adsorption of metal over (Brady and Weil 1999). The present results are in a good agreement with the findings of Street *et al.*, (1978); Schultz *et al.*, (1987); McLaren *et al.*, (1986); McGrath and Cegerra (1992); Comans, (1985); Ainsworth *et al.*, (1995); Martin and Kaplan, (1998) and Kookana *et al.*, (1999)

### 4.3 Lead

The following results illustrate the effect of the soil type, Pb level and the residence time on the distribution of the Pb added to the three soils at the four different rates between the solid and solution phases.

### 4.3.1 Effect of soil type and metal level on Pb distribution between the solid and solution phases of the soils

Table 4.2 presents the mean values obtained for the solution and the adsorbed Pb throughout the residence time. The solution Pb concentration in varies from 2.65, 2.32 and 0.93 to 18.236, 17.26 and 8.50 mmol/kg in soil I, II and III respectively as the Pb amendment level increased from 5 to 40 mmol/kg. The amount of lead adsorbed onto soil particles varies from 2.29, 2.67 and 3.94 to 20.24, 21.43 and 31.04 in soil I, II and III respectively as the Pb mass loading increased from 5 to 40 mmol/kg.

Table 4.2: The distribution of added Pb in solution and solid soil phases

Soil type	Pb amendment level (mmol/kg)	Solution Pb (mmol/kg)	Adsorbed Pb (mmol/kg)	Recovery (%)
Soil I	5	02.63 ± 0.50	02.29 ± 0.49	98.3
	10	05.25 ± 0.58	04.58 ± 0.45	98.3
	20	10.50 ± 0.62	09.15 ± 0.62	98.3
	40	18.24 ± 0.89	20.24 ± 0.79	96.2
Soil II	5	02.32 ± 0.50	02.68 ± 0.35	100.0
	10	03.64 ± 0.56	05.36 ± 0.33	89.9
	20	08.37 ± 0.33	10.72 ± 0.55	95.4
	40	17.26 ± 0.65	21.43 ± 0.56	96.7
Soil III	5	00.93 ± 0.73	03.94 ± 0.59	97.3
	10	02.13 ± 0.65	06.79 ± 0.83	89.1
	20	04.02 ± 0.46	15.75 ± 0.53	98.9
	40	08.50 ± 0.58	31.04 ± 0.65	98.9

± Standard deviation

The outcome of adding lead to the three soils was that metal adsorption increases as the amendment level increases and the concentration of Pb in soil solution slightly increased. The Figures 4.4a and 4.4b below exhibit the effect of soil type and lead content both in soil solution and adsorbed phases respectively.

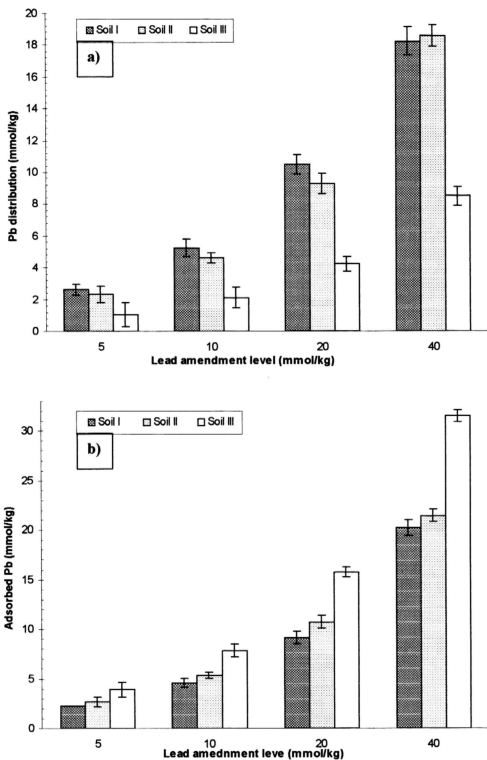


Figure 4.4: Effect of Pb amendment level on Pb distribution between the solid and solution phases of the soils.

a) Pb solution concentration

b) Adsorbed Pb

In the three soils both of the solution concentration and adsorption of Pb by the solid phase was found to increase with the level of Pb amendment. This is in agreement with the findings of Andreu *et al.*, (1996) and Percival (1999). Figure 4.5a and 4.5b illustrates the overall distribution of Pb added to the three soils at the lowest and highest amendment level (5 and 40 mmol/kg). The charts show the starting level of the added Pb, the solution concentration and the adsorbed Pb as respectively. Pb adsorbed more by the sandy clay loam (soil III), while it was adsorbed to less extent by the sandy loam (soils I and II). The difference between soils Soil II and I is not significant.

The concentration of Pb in solution is higher in soils I and II compared to that of soil III. This supported by the fact that Pb is mobilized with pH decrease Pb (Kotuby-Amacher and Gambrell 1988). Pb adsorbed more by the soil III, while it was less adsorbed by soils I and II. There are several possible reasons for this. First because pH is controlling variable in adsorption and solubility of Pb in soils (Basta *et al.*, (1993); Mench *et al.*, (1994); and McBride *et al.*, (1997) reported significant positive correlation soil pH and Pb adsorption. Second, many Pb adsorption studies confirmed the significance of CEC in the Pb adsorption capacity of soils (Bolton and Evans 1996; Frost and Griffin, 1977). Third, the formations of relatively stable organo-metal complexes or chelates with the organic matter in soil (Lopes and Cox 1977). Furthermore, the adsorption of Pb by Fe oxide could possibly contribute on increase the amount of Pb adsorbed by soils (Papadopoulos and Rowell 1988). As it was shown in Table 3.1 Soil III has the higher soil pH cation exchange capacity, Fe and organic matter content compared to that of other two soils.



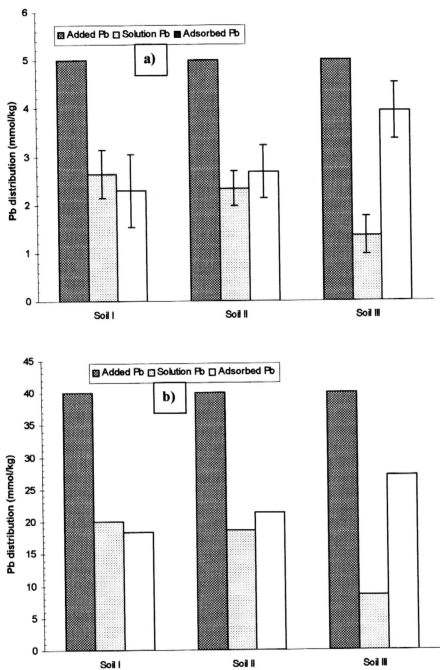


Figure 4.5: Effect of soil type on Pb distribution between the solid and solution phases of the soils

- a) Pb distribution at level 5mmol/kg
- b) Pb distribution at level 40 mmol/kg

#### 4.3.2 Effect of residence time on Pb distribution between the solid and solution phases of the soils

After incubations for up to 3, 6, 9, 12 and 15 months the values of the adsorbed Pb onto soil surface was observed to highest in the first three months and generally decreased as the residence time increase. Figure 4.6 shows the results obtained for solution concentration and the adsorbed Pb in the five successive extraction times. The results showed a slightly steady increase in the equilibrium Pb concentration in soil solution and in the three soils. At the lowest amendment level, the solution concentration of Pb for the three soils respectively were varied from 1.80, 1.74 and 0.85 to 2.84, 2.45 and 1.12. The values obtained for the adsorbed Pb in the same amended level are varied from 2.44, 2.84, and 4.09 to 1.70, 2.09 and 3.34 mmol/kg as the residence time increased from 3 to 15 months.

Positive significant correlations were found between the Pb concentrations in the solution of the three soils the Pb amendment level ( $R^2 = 0.986, 0.850, 0.986$  and  $0.986; 0.911, 0.894, 0.894$  and  $0.911; 0.916, 0.916, 0.854$  and  $0.916$  for soil I, II and III respectively). The amount of Pb adsorbed by the three soils showed a steady decrease as the residence increases. Significant negative correlation was reported between the adsorbed amount of Pb and time at the four amendment levels ( $R^2 = 0.990, 0.991, 0.990$  and  $0.991; 0.990, 0.991, 0.991$  and  $0.991$  and  $0.990, 0.990, 0.990$  and  $0.991$  for soil I, II and III respectively). Both of the significant elevation of the Pb concentration in soil solution and the elimination in the adsorbed amount of Pb can be explained by the exhaustion of the exchangeable sites through time by which soils reach their maximum soil sorption capacity and most of the added Pb amendment remains in the soluble phase (Brady and Weil 1999). The present results are in a good agreement with the findings of Schultz *et al.*, (1987); McKenzie, (1980); McGrath and Cegerra (1992) Menzies *et al.*, (1991) and Ainsworth *et al.*, (1995).

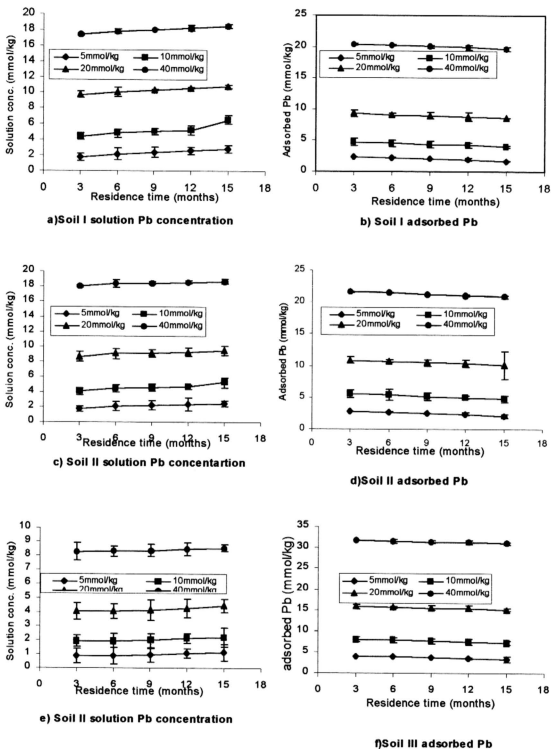


Figure 4.6: Distribution of lead in the three soils as influenced by residence time

#### 4.4 Nickel

The distribution of nickel (Ni) between soil solid and solution phases in the three soils was determined at the four metal rates. The results below illustrated the effect of the soil type, Ni level and the residence time on the distribution of the added Ni between the soil solid and solution phases.

##### 4.4.1 Effect of soil type and metal level on Ni distribution between the solid and solution phases of the soils

Table 4.3 presents the mean values obtained for the solution concentration and the adsorbed Ni throughout the incubation time ( 15 months).

Table 4.3: The distribution of added Ni in solution and solid soil phases

Soil type	Ni amendment level mmol/kg)	Solution Ni (mmol/kg)	Adsorbed Ni (mmol/kg)	Recovery (%)
Soil I	5	02.85 $\pm$ 0.54	01.66 $\pm$ 0.70	90.2
	10	05.97 $\pm$ 0.48	03.35 $\pm$ 0.25	93.2
	20	12.79 $\pm$ 0.70	06.70 $\pm$ 0.44	97.5
	40	26.35 $\pm$ 0.47	13.40 $\pm$ 0.31	99.4
Soil II	5	02.85 $\pm$ 0.49	02.01 $\pm$ 0.48	84.9
	10	05.80 $\pm$ 0.30	04.12 $\pm$ 0.08	99.2
	20	10.26 $\pm$ 0.55	08.24 $\pm$ 0.29	92.5
	40	23.04 $\pm$ 0.58	16.48 $\pm$ 0.53	98.8
Soil III	5	01.35 $\pm$ 0.33	03.43 $\pm$ 0.29	95.6
	10	02.90 $\pm$ 0.35	06.56 $\pm$ 0.32	94.6
	20	06.51 $\pm$ 0.59	13.12 $\pm$ 0.34	98.1
	40	11.24 $\pm$ 0.33	26.24 $\pm$ 0.50	93.7

$\pm$  Standard deviation

The overall distribution of Ni added to three soils was that substantial adsorption took place in solid phase, the estimated values of the adsorbed nickel were varied from 1.66, 2.01 and 3.43 to

13.40, 16.48 and 26.24 mmol/kg in soil I, II and III respectively as the Ni amendment level increased from 5 to 40 mmol/kg.

On the other hand as the Ni amendment level increases Ni in soil solution increased, the reported values are varied from 2.85, 2.85 and 1.35 to 26.35, 23.05 and 11.24 mmol/kg in soil I, II and III respectively as the Ni mass loading increased from 5 to 40 mmol/kg. The Figures 4.7a and 4.7b below exhibited the effect of Ni amendment level on the total content of Ni in the soil solution and solid phases respectively.

Results are in agreement with the findings of Hickey and Kittrick, (1984); Andreu *et al.*, (1996). Figures 4.8a and 4.8b illustrate the overall outcome of adding Ni to the three soils at the lowest and highest amendment level (5 and 40 mmol/kg). The charts show the starting level of the added Ni, the solution concentration and the adsorbed Ni respectively. Ni concentration in solution phase varies among soils, soil I and II reported highest solution concentration than that of soil III. The differences between soils and I are not significant. This is because under neutral and alkaline soil pH Ni is bound strongly by clays, soil organic matter and hydrous oxides of iron and manganese (Sadig and Enfield (1984a). The mobility of nickel in soils is enhanced by the formation of complexes of nickel with both organic and inorganic ligands.

The present result is in agreement with Fischer *et al.*, (1992) who reported a significant correlation between Zn concentration in soil solution and soil acidity. Soil III adsorbed larger amount of the added Ni compared with soils II and I. This may be justified by that among the studied soils soil III has the highest pH, CEC and Fe (Table 3.1)

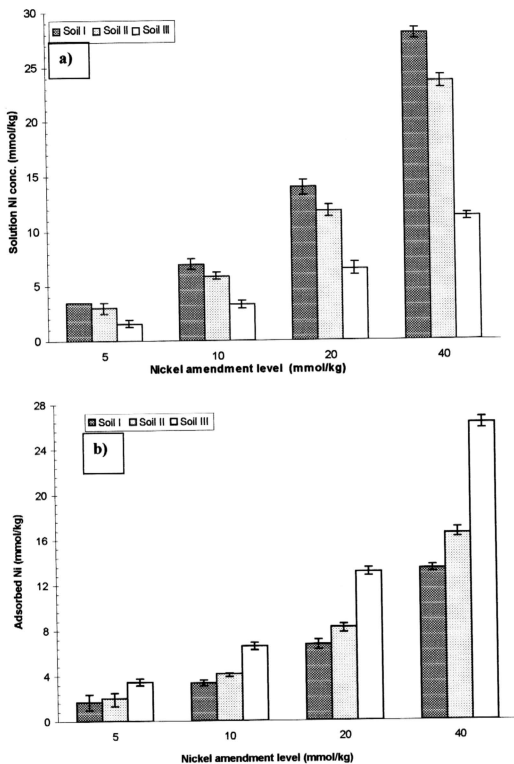


Figure 4.7: Effect of Ni amendment level on Ni distribution between the solid and solution phases of the soils.

- a) Ni solution concentration
- b) Adsorbed Ni

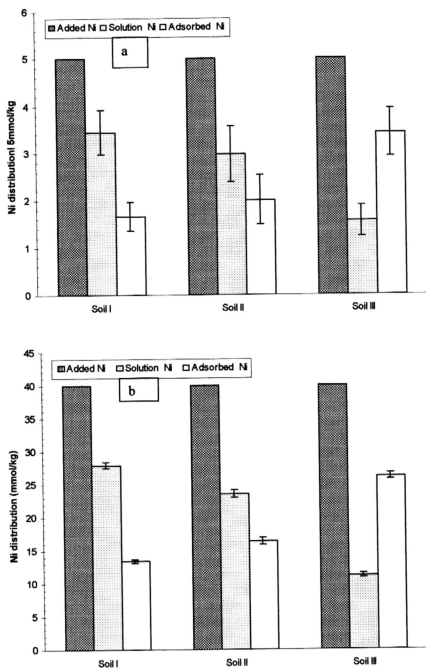


Figure 4.8: Effect of soil type on Ni distribution between solid and solution phases of the soils

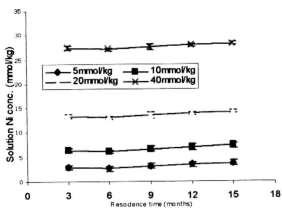
- a) Ni distribution at level 5 mmol/kg
- b) Ni distribution at level 40 mmol/kg

Based on the fact that the Ni occultation by the mineral lattice of the clay is largely dependent on CEC and hydrous oxides (Adriano, 1986; Uren, 1992; Ma and Lindsay, 1995 and Merrington and Alloway 1997). The present result is in agreement with the findings of Duke (1980); Ma and Lindsay (1995); Sadig and Enfield (1984a) and Sadig and Enfield (1984b), who reported significant amounts of nickel could be strongly bound to the surfaces of hydrous oxides. Further support for the results was found in the findings of Jenne (1968); Sadig and Zaidi (1981); Fischer *et al.*, (1992) and Wenzel *et al.*, (1992). Scheidegger *et al.*, (1997); Scheidegger *et al.*, (1998); Franz and Wenzel, (1999) reported that under neutral and alkaline soil pH Ni is bound strongly by clays, soil organic matter and hydrous oxides of iron and manganese.

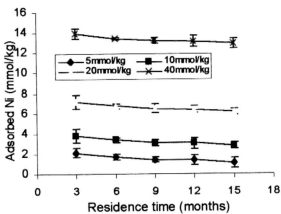
#### 4.4.2 Effect of residence time on Ni distribution between the solid and solution phases of the soils

Figure 4.9 present the Ni solution concentration and the adsorbed Ni of the three soils after soil incubation up to 3, 6, 9, 12 and 15 months. The recorded values for Ni concentration in soil solution for the three soils at the lowest Ni amendment level (5mmol/kg) were varied from 2.61, 2.15 and 0.73 to 3.78, 3.32 and 1.90 while the adsorbed Ni was varied from 2.30, 2.37, and 4.09 to 1.10, 1.44 and 2.86 mmol/kg as the residence time increased from 3 to 15 months. Positive significant correlations were found between the Ni concentrations in the solution of the three soils that treated by four Ni amended levels ( $R^2 = 0.821, 0.850, 0.821$  and  $0.821; 0.996, 0.697, 0.997$  and  $0.996$  and  $0.996, 0.996, 0.997$  and  $0.996$  for soil I, II and III respectively).

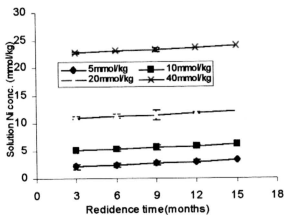




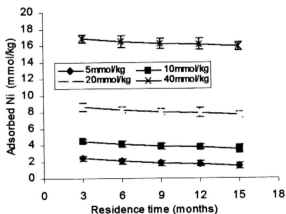
a) Soil solution Ni concentration



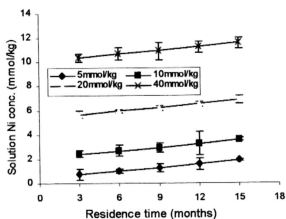
b) Soil I adsorbed Ni



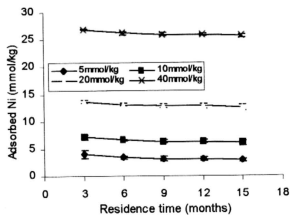
c) Soil II solution Ni concentration



d) Soil II adsorbed Ni



e) Soil III solution Ni concentration



f) Soil III adsorbed Ni

Figure 4.9: Distribution of nickel in the three soils as influenced by residence time

The amount of Ni adsorbed by the three soils a steady decrease as the residence increases. Significant negative correlation was reported between the adsorbed amount of Ni and time at the four amendment levels ( $R^2 = 0.937, 0.937, 0.990$  and  $0.937; 0.956, 0.956, 0.956$  and  $0.991$  and  $0.881, 0.904, 0.904$  and  $0.893$  for soil I, II and III respectively). Both of the significant elevation of the Ni concentration in soil solution and the elimination in the adsorbed amount of Ni can be explained by the exhaustion of the exchangeable sites through time by which soils reach their maximum soil sorption capacity and most of the added Ni amendment remains in the soluble phase (Brady and Weil 1999). The present results are supported by the findings of Brummer *et al.*, (1988); Scheidegger *et al.*, (1996)

## 4.5 Zinc

The distribution of zinc (Zn) between soil solid and solution phases in the three soils was examined at the four metal rates. The following results illustrate the effect of the soil type, Zn level and the residence time on the distribution of the added Zn between the soil solid and solution phases.

### 4.5.1 Effect of soil type and metal level on Zn distribution between the solid and solution phases of the soils

Table 4.4 presents the mean values obtained for the solution concentration and the adsorbed Zn throughout the amendment residence time in the three soils.

Table 4.4: The distribution of added Zn in solution and solid soil phases

Soil type	Zn amendment level (mmol/kg)	Solution Zn (mmol/kg)	Adsorbed Zn (mmol/kg)	Recovery (%)
Soil I	5	$3.45 \pm 0.53$	$00.82 \pm 0.51$	85.5
	10	$5.99 \pm 0.42$	$02.06 \pm 0.41$	80.4
	20	$11.97 \pm 0.44$	$04.12 \pm 0.50$	80.4
	40	$23.94 \pm 0.51$	$08.23 \pm 0.49$	80.4
Soil II	5	$03.87 \pm 0.55$	$00.94 \pm 0.39$	96.0
	10	$6.53 \pm 0.58$	$02.54 \pm 0.42$	90.7
	20	$12.99 \pm 0.12$	$05.07 \pm 0.57$	90.3
	40	$26.12 \pm 0.39$	$10.14 \pm 0.45$	90.7
Soil III	5	$02.75 \pm 0.53$	$01.26 \pm 0.48$	80.2
	10	$06.37 \pm 0.50$	$03.53 \pm 0.48$	98.9
	20	$13.24 \pm 0.40$	$06.03 \pm 0.53$	96.3
	40	$18.24 \pm 0.48$	$15.20 \pm 0.50$	83.7

$\pm$  Standard deviation

The outcome of adding zinc to three soils was that slight adsorption took place in solid phase but the greater proportions of the added metals remained in the soil solution. The solution concentration of the three soils was found to increase from 3.45, 3.87 and 2.75 to 23.94, 26.120 and 18.24 40 mmol/l as the zinc mass loading increases from 5 to 40 mmol/kg. While the adsorption onto soils is extremely low, the estimated adsorbed Zn is varied from 0.82, 0.94 and 1.26 to 8.23, 10.14 and 15.23 mmol/kg in soil I, II and III respectively as the Zn amendment level increased from 5 to 40 mmol/kg. Figures 4.10a and 4.10b below exhibited the effect of soil type and metal level on the total content of Zn in the soil solution respectively.

When Zn was introduced into the soil at it's higher mass loading (40 mmol/kg) high percent of the added Zn remains in the solution phase which varied from 68.9% to 73.5% in soil I and from 61.6% to 66.2% in soil II and from 56.2% to 61.2% in soil III. The result is supported by the findings of Frost and Griffen, (1977); Andreu *et al.*, (1996) and McBride *et al.*, (1997a).

Figures 4.11a and 4.11b illustrate the overall outcome of adding Zn to the three soils at the lowest and highest amendment level (5 and 40 mmol/kg).

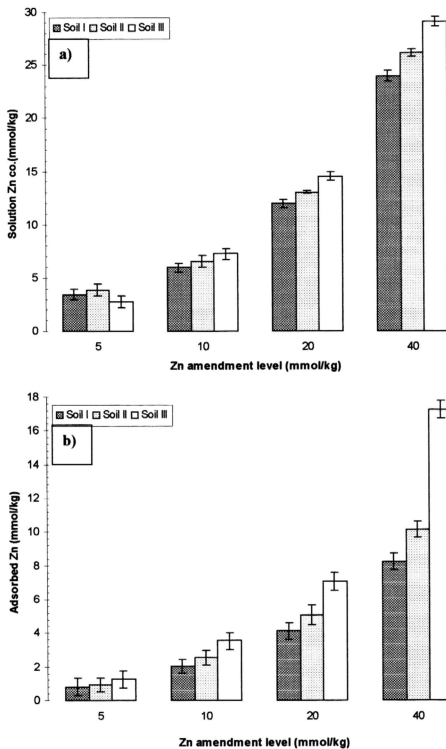


Figure 4.10: Effect of Zn amendment level on Zn distribution between the solid and solution phases of the soils.

- a) Zn solution concentration
- b) Adsorbed Zn

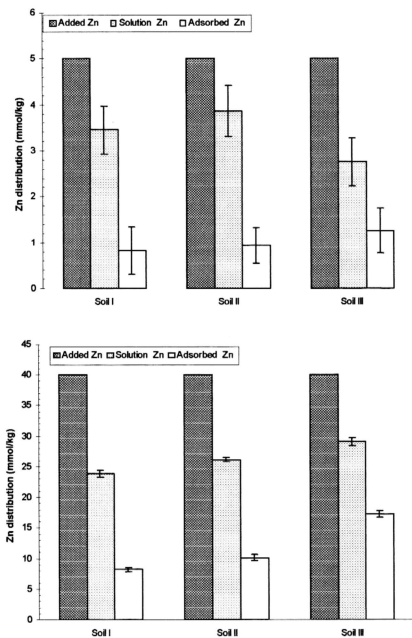


Figure 4.11: Effect of soil type on Zn distribution between the solid and solution phases of the soils

- Zn distribution at level 5 mmol/kg
- Zn distribution at level 40 mmol/kg

The charts showed the starting level of the added Zn, the solution concentration and the adsorbed Zn respectively. Zn concentration in solution phase varies among soils, soils I and II reported higher solution concentration than that of soil III. On the other hand soil III adsorbed relatively higher amount of the added Zn. This could possibly be due to that Zn is readily adsorb by clay minerals and iron oxide in soil III that contain both the higher clay and Fe content among the studies soils (Table 3.1). This supported by the fact that the chemical behavior of zinc is govern by soil pH, soil organic matter, and the interaction with amorphous hydroxides. (Kuo *et al.*, (1983; Mench *et al.*, (1994); and Reddy *et al.*, 1995). In agreement with present result Shuman, (1977); Tessier *et al.*, (1980); Kuo *et al.*, (1983) and Stahl and James, (1991) found that the greatest percent of zinc in soils was associated with iron and manganese oxides. Furthermore, this result is also in agreement with the findings Frost and Griffin, (1977); Robson, (1993); Wilkens and Loch, (1995); Reddy *et al.*, (1995) and McBride *et al.*, (1997a), who sated that the solution concentration of zinc decreases at higher pH

#### 4.5.2 Effect of residence time on Zn distribution between the solid and solution phases of the soils

Figure 4.12 shows the results obtained for solution concentration and the adsorbed Zn in five successive extraction after incubation up to 3, 6, 9, 12 and months. The equilibrium Zn concentration in soil solution and was lower in the first three months and generally increased as the residence time increase. While the amount of Zn adsorbed onto soil surface showed a slightly steady decrease with the residence time increase. At the lowest level of amendment the solution concentration of Zn was varied in the three soils from 1.84, 2.38 and 1.32, to 3.99, 4.19 and 3.08 on the other hand the adsorbed Zn was varied from 1.72, 1.83 and 2.15 to 0.82, 0.94 and 1.26 mmol/kg as the residence time increased from 3 to 15 months. Results of the three soils treated with the four levels of Zn amended showed positive correlations between the

solution concentration of Zn and residence time ( $R^2 = 0.992, 0.994, 0.994$  and  $0.993; 0.994, 0.994, 0.992$  and  $0.993; 0.995, 0.998, 0.994$  and  $0.998$  for soil I, II and III respectively

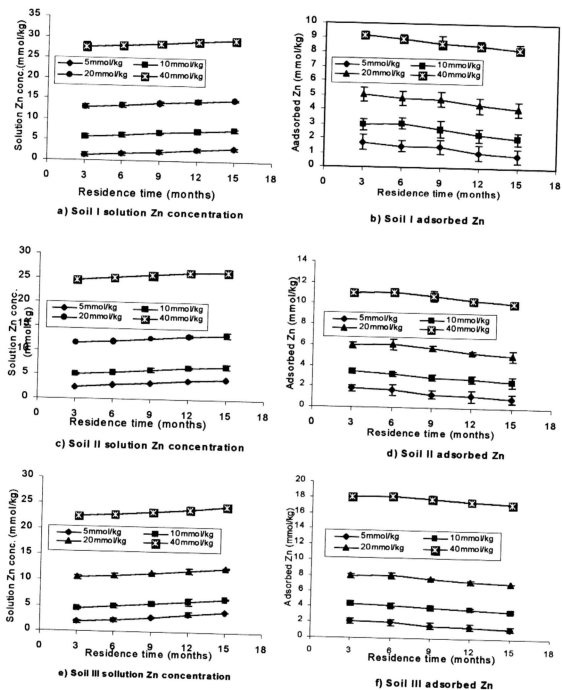


Figure 4.12: Distribution of zinc in the three soils as influenced by residence time

Significant negative correlation was also reported between the adsorbed amount of Zn and residence time for soils treated with the four levels Zn amendment ( $R^2 = 0.943, 0.890, 0.943$  and  $0.990$ ;  $0.981, 0.989, 0.890$  and  $0.990$  and  $0.981, 0.987, 0.890$  and  $0.890$  for soil I, II and III respectively). Both of the significant elevation of the Zn concentration in soil solution and the elimination in the adsorbed amount of Zn can be explained by the exhaustion of the exchangeable sites through time by which soils reach their maximum soil sorption capacity and most of the added Zn amendment remains in the soluble phase (Brady and Weil 1999). The present result is in an agreement with the findings of Brummer *et al.*, (1988); Kuo and Mikkelesn, (1980); Schultz *et al.*, (1987); McGrath and Cegerra (1992) and Daniel and Spark (1999).

#### **4.6 Comparative investigations on the distribution of cadmium, lead, nickel, and zinc in the three soils**

Metals are varied in their behavior, and their ultimate fate in the soil environment depends largely on their sorption reactions with the soil particles (Brian, 1980). Thus, the understanding of the variation between metals adsorption and desorption reaction mechanisms in the soil environment is critical to compare their fate and their potential hazards (Brady and Weil, 1999). This section will compare the experimental results of solution concentration and adsorption characteristics of heavy metal ions Cd, Pb, Ni and Zn onto the three experimental soils. At the lowest amendment level the equilibrium solution concentration of Cd, Pb, Ni and Zn in soil I were 2.49, 2.63, 3.45 and 3.45 mol/kg respectively while the adsorbed value at the same amendment level for the four metals are 0.99, 2.29, 1.66 and 0.94 respectively. In soil II solution concentrations of the four metals are 1.85, 2.32, 2.99 and 3.86 while their adsorbed values are 0.91, 2.67, 2.01 and 0.82 respectively.



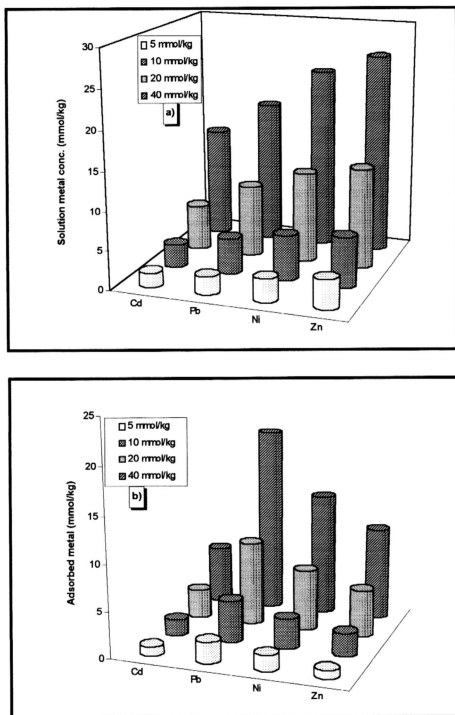


Figure 4.13: The outcome of adding cadmium, lead, nickel and zinc to soil I

- a) Soil solution metals concentration
- b) Soil adsorbed metals

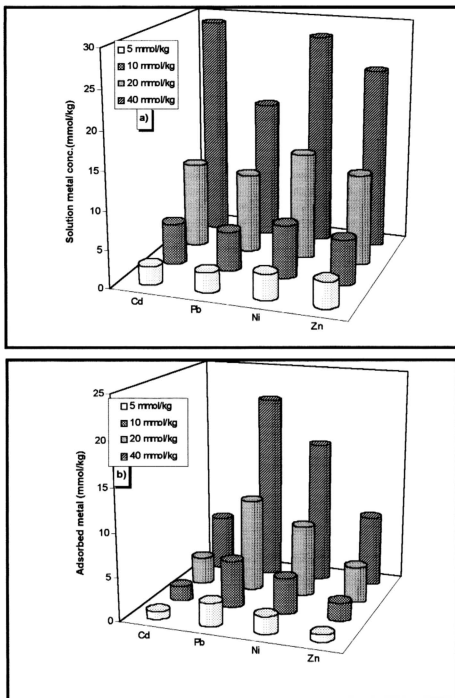


Figure 4.14: The outcome of adding cadmium, lead, nickel and zinc to soil II

- a) Soil solution metals concentration
- b) Soil adsorbed metals

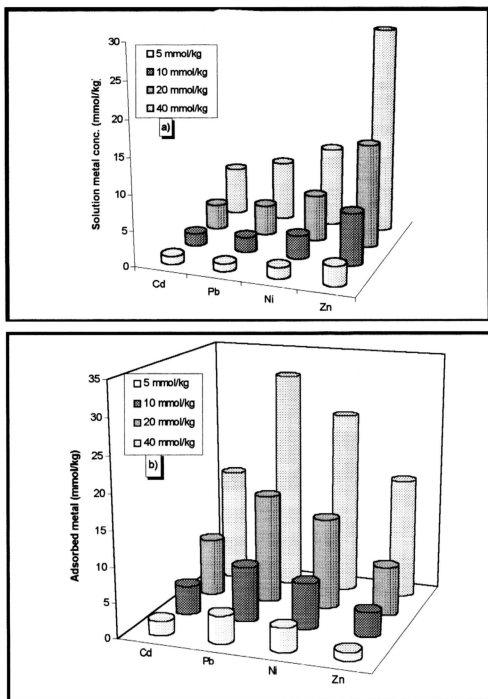


Figure 4.15: The outcome of adding cadmium, lead, nickel and zinc to soil III

- a) Soil solution metals concentration
- b) Soil adsorbed metals

For soil III the solution concentrations of the four studied metals respectively are 1.14, 1.06, 1.57 and 2.75 while their adsorption values are 2.08, 3.94, 3.43 and 1.26 mmol/kg. Figure 4.15 below illustrate the overall Cd, Pb, and Ni and Zn distribution in the three experimental soils. Results show that the most adsorbed metal is Pb followed in descending order are by Cd Ni and Zn. The experimental results of the four metals show that their adsorption value onto soil III particles is higher than that onto soil II and I (Figure 4.15). The concentration of Zn solution is the highest among the studies metals followed in descending manner by Ni, Cd and Pb in the three soils. This result is in agreement with what has been recorded by Tessier *et al.*, (1980) and Kuo *et al.*, (1983).

Under equal experimental conditions the different adsorption values of Cd, Pb, Ni and Zn are varied greatly. This has already been demonstrated by the considerable relevant research work (Aresen and Singh, 1998, Harry Percival 1999 and Andreu *et al.*, 1996). However, the present investigation has shown that, among the four studies metals lead was found to be more adsorbed than cadmium, nickel and zinc, which was in agreement with the findings of Nogales *et al.*, (1997); Aresen and Singh, (1998). Clay minerals show a preference for lead relative to cadmium, nickel or zinc, which adsorb potentially onto metal oxides. Another important feature is that it is not the total accumulation of heavy metals in soils that is important, but rather their bioavailability. Bioavailability is mostly related to the water-soluble fraction. Zinc concentrations in the soil solution is the highest followed by nickel and cadmium, while lead is the least, which was in agreement with the findings of pervious research (Nogales *et al.*, 1997; Aresen and Singh, 1998; Andreu, and Gimeno, 1996).