

*Full Length Research Paper*

# Levels and geochemical fractions of Cd, Pb and Zn in valley bottom soils of some urban cities in south-western Nigeria

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The valley bottom soils of urban cities are sink for municipal and industrial solid and liquid wastes. These valleys are used by urban farmers to grow vegetables for the consumption of urban dwellers. Knowledge of total content of heavy metals is not enough to fully assess the environmental impact of these soils. Therefore the determination of metal fractions in solution is very important to understand their behaviour and their mobility capacity to the vegetables grown on them. Sequential extraction procedure was used to speciate Cd, Pb and Zn from eleven locations from the cities of Lagos, Ibadan, Akure, Ikare, Ondo and Okitipupa in southern western Nigeria into seven operational defined geochemical species; available, carbonate, easily reducible, organic, amorphous Fe-Mn oxide, crystalline Fe-Mn oxide, and detrital (residual). All the metal investigated were significantly associated with non-residual fractions. The highest amounts of metals in non-residual fractions were found in organic fractions while the lowest were found in oxide species. The residual fractions contained on average 65 - 66% for Pb, 8 - 50% for Cd and 25 - 29% for Zn. Assuming that mobility and bioavailability of these metals are related to the solubility of the geochemical forms and that the decrease in the order of extraction sequence, the potential bioavailability of these metals were: Cd > Zn > Pb. The mobility indexes of the metals correlated negatively and significantly with total contents of the metals. Correlation among species of each metal indicates a dynamic equilibrium between labile and non-labile forms of the non-residual fraction.

**Key words:** Geochemical factions, levels, valley bottom, soils, urban cities.

## INTRODUCTION

Enrichment of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment. Heavy metals are introduced into the terrestrial environment and mostly, especially, into the soil from different sources such as industrial and municipal waste (Parry et al., 1981; Olajire and Ayodele; 1998; Olajire et al., 2003), automobile emissions (Olajire and Ayodele, 1997) mining activities (Culbard and Johnson 1984) and agricultural practices (Vulkan et al., 2002; Mo et al., 1999; Taylor, 1997).

Several soil related factors, namely pH, organic matter, Mn and Fe oxide, and clay content determine the chemical association of heavy metals and their availability to plant (Narwal and Singh, 1998). The sorption and precipitation of heavy metals are enhanced by increasing pH (Kiekens, 1995; Alloway and Jackson, 1991). These processes help to explain the decreased mobility normally found in soils with a basic pH.

Sequential extractions have been used to fractionate heavy metal in sludge (McGrath and Cegarra, 1992) or sludge amended soils (Morera et al., 2001). Speciation of metals is an important study since the behaviour of heavy metals in soils depend both on level of contamination as expressed by the total and on the form of origin of metals and the properties of the soils themselves. Sequential ex-

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traction procedures have been used to partition heavy metals in soils and sediment in order to assess the forms of heavy metals in contaminated soils and sediments (Morera et al., 2001). It provides information on potential mobility as well as bioavailability and plant uptake of trace elements (Singh, 1997). Study on the speciation of heavy metals in polluted soil using sequential extraction technique provides knowledge about metal affinity to the soil component and strength with which they are bound to the matrix (Narwal et al., 1999). Sequential extraction also provides information about both mobile and stable fractions of metals in soil which evaluates the actual and potential mobility of metals. Numerous fraction techniques have been used for sequential extraction of heavy metals in soil (Tessier et al., 1979; Shuman, 1985; Rasmussen et al., 1994; Krishnamurti and Naidu, 2000).

Sequential extraction techniques do not provide a direct characteristic of metal speciation but rather indication of chemical reactivity. Despite uncertainty related to the selectivity of various extractants and to potential problem due to reabsorption, redistribution of elements among phase during extraction, (Ahnstrom and Parker, 1999), the extraction procedures provide an indication regarding the forms of association of heavy metals and indirectly of their potential mobility to food and water sources. The separation of metal into species has been widely used in several environmental studies (Bunzl et al., 1999; Olajire et al., 2003).

However, the forms of heavy metals in valley bottom soils (wetland) of urban cities have only been investigated a little. This is despite the fact that the physiochemical properties of these soils are different from the urban upland soils. The use of valley bottom land of streams and rivers to grow vegetables during the dry season is wide spread in urban cities of sub-Saharan Africa. The valleys are rich in major plant nutrients and have high water table during this period to provide residual moisture for plant growth. Owing to the high fertility status, urban vegetable growers concentrate their activities on the valley bottom during the dry season. Furthermore, these land area are not affected by the land tenure problems because it is under the control of the municipal councils.

Urban soils have received much attention in recent years. Studies on metal enrichment of urban soils in Nigeria have been documented (Olajire and Ayodele, 1997; Onianwa and Adogbe, 1997). All these studies are concentrated to the dumping sites, automobile garages, road side drainage channels of industrial area. It is however, obvious that during rainfall event, these metals find their way year in year out to the streams and rivers through run-off and thence to the valleys during flooding.

The sinks of most urban waste (solid and liquid) are the valley bottom land. Urban development coupled with the presence of industrial activities within the cities leads to varying degree of contamination with metals. Toxic metals are present in domestic refuse in varying concentration. The frequently mixing of domestic and industrial waste

during rainfall events results in the enrichment of valley bottom (Oluwatosin et al., 2005).

Since the physiochemical properties of the valley bottom soils are different from upland soils, it is therefore necessary to characterize the metal species so as to understand the mobility of these metals to food and plant. This study was undertaken to investigate the distribution and chemical species of cadmium, lead and zinc in six urban cities of south western Nigeria using sequential extraction procedures developed by Tessier et al. (1979). It also set out to investigate the relationship between soil properties and chemical species of the effect of total metal concentration on metal partition into different fractions.

## MATERIALS AND METHODS

### Site description

The sampling was carried out in a dedicated valley bottom site of the cities of Lagos, Ibadan, Akure, Ikare, Ondo and Okitipupa in south western Nigeria (Figure 1). The sampling was done during the 2004/2005 dry season. The sites are the flood plains of rivers and streams that drains the cities and are being farmed as vegetable enterprise during the dry season when evapotranspiration is greater than the precipitation. The sites also received run-off loaded with domestic waste from the adjacent uplands during rainfall events of raining season. The soils are products of colluvial/alluvial deposits. The water table is often at the surface during the rainy season but goes down during the dry season. This allows farmers to crop the land when the water table is below 20 cm depth.

The soils are (Table 2) Entisols with sandy loam topsoils and pH ranged between 5.3 and 6.6, soil organic matter (SOM) ranged between 3.0 and 17 gkg<sup>-1</sup>, cation exchange capacity (CEC) ranged between 2.94 and 19.78 cmol kg<sup>-1</sup>, water table at the time of sampling ranged between 22 and 35 cm depth. The main vegetable crops grown during the 2004/2005 season were *Amaranthus cruentus* and *celocia*. The vegetables were sold to urban dweller for consumption.

### Sampling procedure

Sampling of topsoil was undertaken using four quadrats (0.25 m<sup>2</sup>) located in a grid pattern across individual field. The samples were taken to depth 20 cm using stainless steel auger; ten auger samples were taken, in a grid pattern, from within each quadrat. A valley bottom surface soil sample was collected from Alabata area (a peri-urban site), which does not suffer from urban city wash served as an uncontaminated reference point. Soil samples were spread in a thin layer on aluminium foils in rectangular wooden boxes for 7 days. The air dried samples were then sieved to <2.00 m prior to grinding for acid digestion.

### Analysis

The properties of surface soil samples investigated are listed in Table 2. Soil pH was determined using 1:2 ratio of H<sub>2</sub>O to soil according to Salbu et al. (1988). The soil organic matter was determined by thermal analysis (< 01) (Salbu et al., 1988), CEC was determined using the method of Matsue and Wada (1985).

Reagent grade chemicals and doubly de-condistilled water were used throughout the laboratory analysis. All the glasswares were

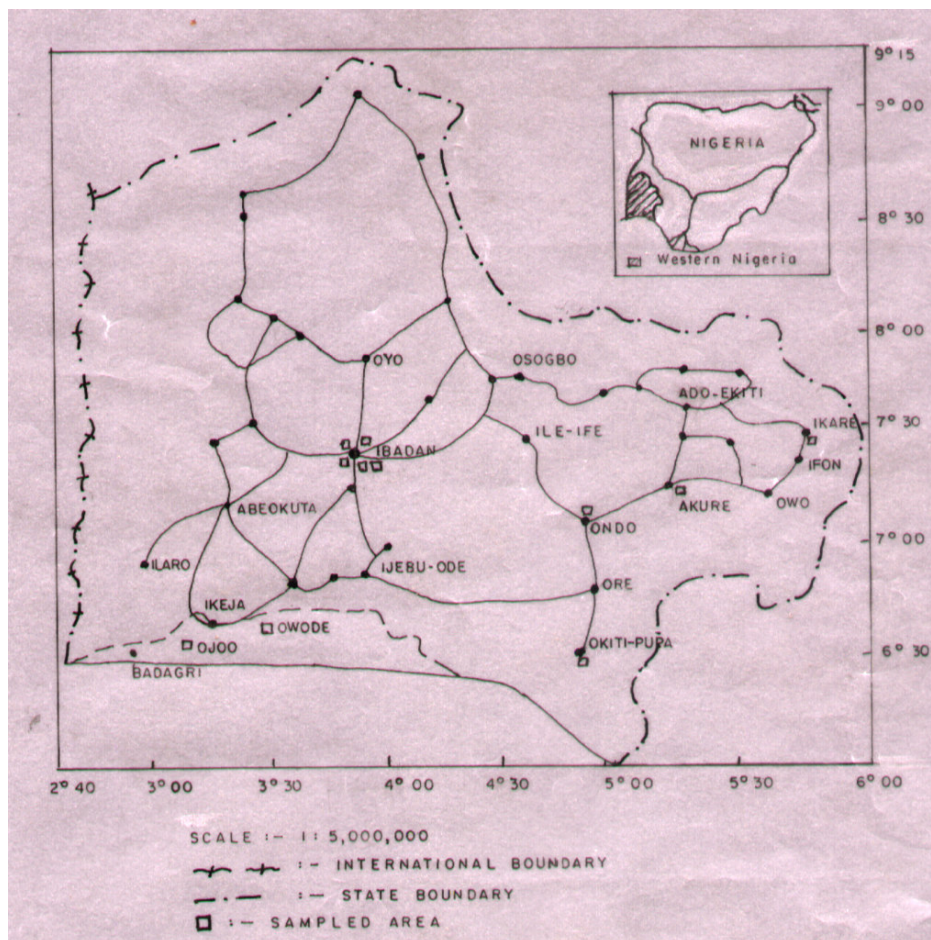


Figure 1. Map showing the cities and sampling locations.

soaked for 48 h in 10%  $\text{HNO}_3$ . All the containers were rinsed repeatedly and successively in  $\text{HNO}_3/\text{H}_2\text{O}$  (1:1) and  $\text{HCl}/\text{H}_2\text{O}$  (1:1) before use.

#### Metal extraction

The procedure of Krishnamurti and Nada (2000) which is a modified version of Tessier et al. (1979) was selected for this study. It was designed to separate heavy metals into seven operational defined fractions: exchangeable (F1), carbonate bound (F2), easily reducible metal-organic complex bound (F3), organic bound (F4), amorphous Fe-Mn oxide bound (F5) crystalline Fe-Mn oxide bound (F6) and Detrital (F7). A summary of the procedure is shown in Table 1. Following each successive extraction; the mixtures were centrifuged at  $14400 \times g$  for 30 min. The supernatants were removed with pipette, filtered with  $0.2 \mu$  pore poly carbonate membrane filters and analyzed for metals. Prior to the start of the next extraction step, samples were shaken for 30 min with  $8 \text{ cm}^3$  of de-ionized distilled water, centrifuged and the washed solutions discarded. All extractants were in triplicate.

#### Total metal determination

1 g of the soil samples were placed in a  $250 \text{ cm}^3$  round-bottomed quick-fit pyrex flask on a  $50 \text{ cm}^3$  mixture of hot concentrated nitric

acid (800 ml/L) and perchloric (200 ml/L) acid was added. The flask was then placed on digestive block mounted on an electric heating plate. The samples were digested until clear solutions were obtained. The solutions were cooled and filtered through acid washed Whatman No 1 filter papers and then made up to a volume of  $100 \text{ cm}^3$  using doubly distilled water (Olajire et al., 2003).

A reagent blank was prepared using a  $50 \text{ cm}^3$  mixture of nitric and perchloric acid in a  $250 \text{ cm}^3$  round-bottomed quick-fit pyrex flask, and the entire sequence of steps was followed as described for sample preparation.

All the analyses were in triplicate to verify precision of the method of digestion and recoveries of metals. The recoveries of the metals, calculated by the standard addition technique, were within  $\pm 11\%$ ; limits of detection range from  $0.25$  to  $2.79 \text{ mg/kg}^{-1}$  for Cd,  $1.00$  to  $6.98 \text{ mg/kg}^{-1}$  for Pb and  $2.25$  to  $7.00 \text{ mg/kg}^{-1}$  for Zn.

#### Analytical methods

Metal content of the seven fractions and total metal content in the filtered solution were analyzed by atomic absorption spectrophotometer using Buck scientific AGW AAS, AES MODEL 2004 operated according to the instrument manual. The instrument was calibrated using mixed calibration. Standard solutions for the metals were prepared for each extraction step in the same matrix as the extracting agents to minimize matrix effects. Results were corrected for reagent blanks and non-atomic absorption. The reproducibility of

**Table 1.** Procedure for sequential extraction of Cd, Pb and Zn in the soil.

Step	Species	Reagent	Shaking time out temp.
F1	Exchangeable	10 ml of 1 m NH <sub>4</sub> NO <sub>3</sub> (pH7)	4 h at 25°C
F2	Carbonate bound	25 ml of 1 m CH <sub>3</sub> COO Na	6 h at 25°C
F3	Metal-organic complex bound	20 ml of 0.1 m NH <sub>2</sub> OH Hcl in 0.1m HNO <sub>3</sub>	30 min at 25°C
F4	Organic bound	(i) 5 ml of 30% H <sub>2</sub> O <sub>2</sub> (pH <sub>2</sub> ) 3 ml of 0.02 m HNO <sub>3</sub> (ii) 3ml of 30% H <sub>2</sub> O <sub>2</sub> (pH <sub>2</sub> ), 1ml of 0.02m NHO <sub>3</sub> (iii) Cool, add 10 ml 2 m NH <sub>4</sub> NO <sub>3</sub> in 20% HNO <sub>3</sub>	2 h at 25°C 2 h at 25°C 30 min at 25°C
F5	Amorphous Fe-Mn oxide-bound	20 ml of 0.2 m (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> / 2 m H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (pH <sub>3</sub> )	25°C (dark)
F6	Crystalline Fe-Mn oxide-bound	25 ml of 0.2 m (NH <sub>4</sub> ) C <sub>2</sub> O <sub>4</sub> (pH <sub>3</sub> ) in 0.1 m ascorbic acid	30 min at 95°C
F7	Detrital (residual)	Digestion with HNO <sub>3</sub> : HClO <sub>4</sub> (2:1)	-

the methods used in this study was checked by carrying out triplicate analysis. Triplicate results did not differ by more than 11% of the mean.

## RESULTS AND DISCUSSION

Total metal concentrations of the soils reflect natural difference in soil genesis as well as differences in the degree of contamination (Table 2). Zn was highest (714.3 - 942.9 mg kg<sup>-1</sup>) in all the locations followed by Pb (513.5 - 942.9 mgkg<sup>-1</sup>) and Cd (38.2 - 49.4 mgkg<sup>-1</sup>). In general the highest level of Zn was recorded in the city of Ibadan, while the highest level of Pb was found in the city of Akure. The highest level of Cd was found in the city of Okitipupa. The concentration of Pb, Cd and Zn found in these cities were significantly higher than typical value in garden soils (Bunzl et al., 1999). The high levels of Pb, Cd and Zn recorded might have resulted from wash of solid and liquid waste from the cities and effluent from industries which were released to the major drainage channels of the cities (streams and rivers) (Oluwatosin et al., 2005). These wastes and effluents found their way to these valley bottom soils through flooding during the raining season. Comparison of these data with uncontaminated reference rural valley bottom land showed that the valley bottom soils of the cities investigated were contaminated with heavy metals.

### Metal speciation

The total metal contents in the soil can be used as indicator of contamination intensity (Oluwatosin et al., 2005). However, the speciation of heavy metals with selective extractants gives additional information about the fundamental reactions governing the behaviour of the

metals in soils (Olajire et al., 2003). The sequential extraction procedure chosen for this study was the best because it defines a wide variety of geochemical fractions and tends to avoid overemphasis on any given fraction (Table 3). It is also useful to indirectly assess the potential mobility of heavy metals in the soils.

The distribution of metal among specific forms varied widely based on the metal chemical properties and characteristics (Soon and Bates, 1981). It is therefore necessary to evaluate the bio-availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behaviour of heavy metal contaminations in soils (Davies, 1980). Assuming that bioavailability decreases in the order: exchangeable>carbonate>reducible>organic>morphous Fe-Mn Oxide> crystalline Fe-Mn Oxide> detrital (residual). Based on this information, we can further assume that metals in non-residual fractions are more likely to be bioavailability than metals associated with residual (detrital) fraction.

### Cadmium

Cadmium was mostly concentrated in non-residual fractions (Figure 2). The percentage Cd in non-residual ranges from 50% in Owode (Ow) in the city of Lagos and 92% in Okitipupa (Ok). Among the non-residual, however, organic bound fraction was the highest while the oxide fraction was the lowest. The residual fractions ranged from 8% in Okitipupa (Ok) and 49% in Owode (Ow).

The sequence of extraction follows the order of decreasing solubility of the geochemical forms of the metals, thus exchangeable fraction may indicate the forms most available for plant uptake (Christian, 1989).

**Table 2.** Characteristics of the soils and the concentration of total metals.

Location	Soil types	Water table depth (cm)	Textual class	Land use	pH	SOM g kg <sup>-1</sup>	CEC Cmol kg <sup>-1</sup>	Cd	Pb mg kg <sup>-1</sup>	Zn
Ojoo-Lagos (OJ)	Oxyaquic Udipsamment	35	Sandy	Arable-vegetable	5.4	3.0	2.94	48.5	504.3	778.2
Owode Onirin (OW)	Aquic Udifluent	28	Sandy Clay Loam	Arable-vegetable	5.5	17.0	10.98	46.2	523.1	792.0
Wire & Cable (WC)	Oxyaquic Ustifluent	22	Sandy loam	Arable-vegetable	6.6	9.4	13.88	41.4	519.3	827.6
Mile 110 (M110)	Oxyaquic Ustifluent	28	Sandy loam	Arable-vegetable	6.5	6.1	16.20	38.2	513.5	820.0
Kudeti (KD)	Oxyaquic Ustifluent	31	Sandy loam	Arable-vegetable	6.3	10.7	13.70	40.4	525.4	825.3
Bako (Bk)	Oxyaquic Ustifluent	32	Sandy loam	Arable-vegetable	6.1	10.3	18.60	45.6	524.5	942.9
Sango (SG)	Oxyaquic Ustifluent	26	Sandy loam	Arable-vegetable	6.4	10.2	14.45	39.6	526.3	937.1
Akure (Ak)	Oxyaquic Ustifluent	22	Sandy loam	Arable-vegetable	6.2	15.1	19.78	39.6	537.4	714.3
Ikare (IK)	Oxyaquic Ustifluent	31	Sandy loam	Arable-vegetable	6.0	10.1	18.06	43.8	523.2	819.2
Ondo (OND)	Typic Fluvaquent	29	Sandy loam	Arable-vegetable	5.9	15.9	14.33	43.2	525.2	769.4
Okitipupa (OK)	Udifluent	27	Sandy Clay Loam	Arable-vegetable	5.3	16.6	9.89	59.4	518.9	887.5
Alabata	Oxyaquic Ustifluent	22	Sandy loam	Arable-vegetable	6.5	10.2	10.98	12.3	98.4	46.2

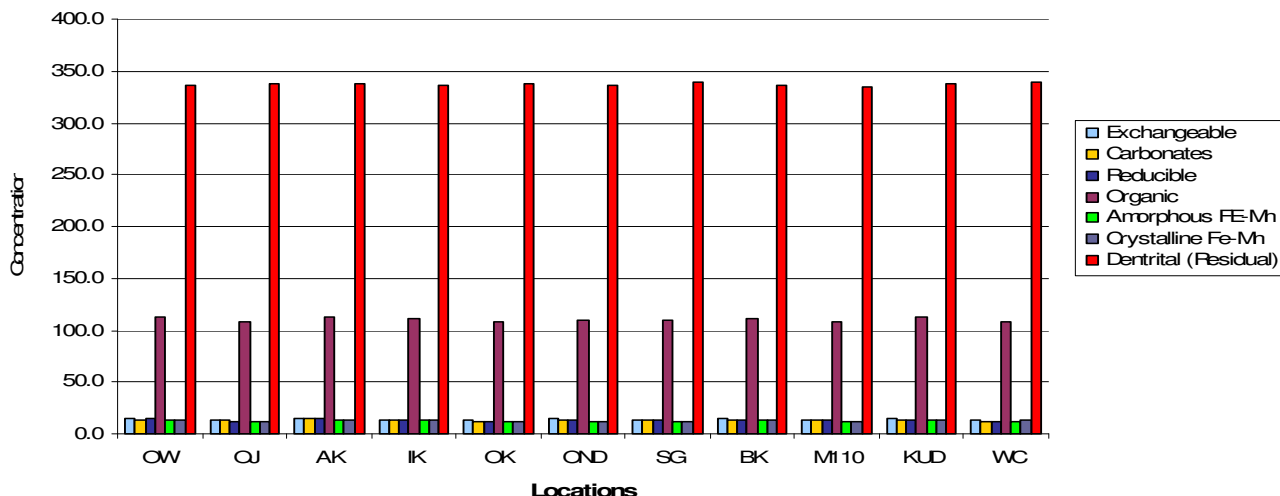
**Table 3.** Detection limits for Cd, Pb and Zn in the solutions of the geochemical fractions.

	Cd	Pb mg kg <sup>-1</sup>	Zn
Exchangeable	2.79	6.98	5.55
Carbonate	1.89	2.64	2.82
Reducable	1.46	2.54	2.84
Organic	0.54	1.10	8.05
Amorphous Fe-Mn Oxide	0.25	1.00	2.25
Crytalline Fe-Mn Oxide	0.25	1.00	2.25
Detrital	1.70	5.21	7.00

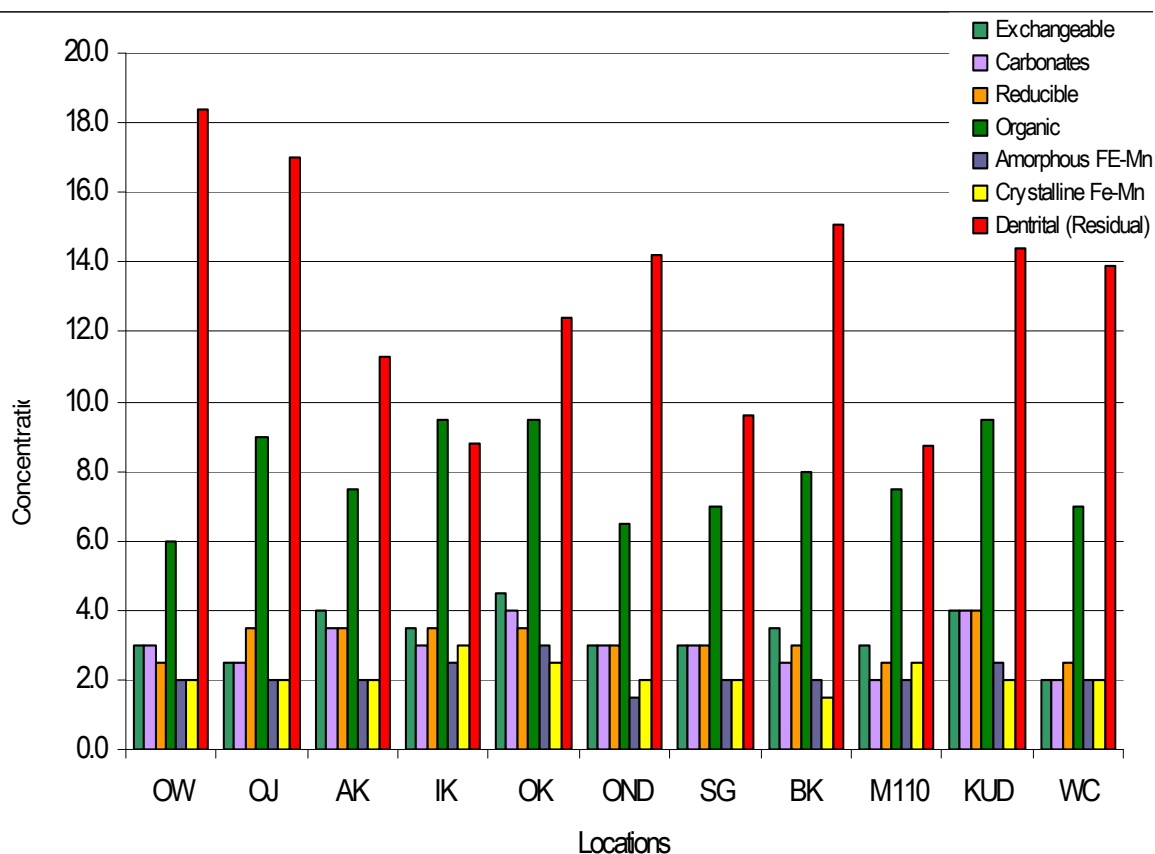
By these criteria, 6 – 15% Cd in all the soils was presently available for plant uptake. The low value of exchangeable fraction is at variance with the value reported for upland soils in south western Nigeria (Olajire et al., 2003) and elsewhere (Elsorkkary and Lag, 1978). Cadmium levels in these soils, as determined by the sum of the exchangeable and carbonate (because the soil is acidic; soil carbonates decrease the availability of metals more for their effect on soil pH than for

their absorption capacity) on average of the total and represent the bioavailability of Cd. On the other hand, Cd does appear to form a stable organic complex which is contrary to what was reported by Sposito et al. (1982) and Keefer et al. (1994). These results could be explained by the high solubility of Cd due to low pH and high absorption constant of the complexes formed with organic matter. However, organic matter being considered labile (Baron et al., 1990), Cd asso-

ciated with non-residual may easily be taken up by plants growing in the soil which agrees with the submission of Anderson, (1977). These features, plus the hazard of Cd to human health, suggest that more frequent examination of the levels of Cd in these soils may be necessary to determine potential health hazards to consumers of vegetables grown on them. The Cd association with different geochemical fractions follows the order: Residual > Organic > exchangeable = carbonate



**Figure 2.** Lead concentration in each operationally defined geochemical fraction of the soil.



**Figure 3.** Cadmium concentration in each operationally fraction of the soils.

= easily reducible > amorphous Fe-Mn Oxides = crystalline Fe – Mn oxides.

The Cd associated with Fe – Mn oxides are very low in these soils. It ranged from 1.5 to 3.0 mgkg<sup>-1</sup>. It was

observed that the distribution of Cd among the geochemical fractions is independent of the total Cd content in these soils (Table 5). Cd was present in all geochemical fractions.

**Table 4.** Lead Concentrations (Mean  $\pm$  SD, n = 5) in each operationally defined geochemical fraction of the soils.

Geochemical fractions	OW	OJ	AK	IK	OK	OND	SG	BK	M110	KUD	WC
Exchangeable	14.5 $\pm$ 2.4	13.5 $\pm$ 2.1	14.5 $\pm$ 2.1	13.5 $\pm$ 2.2	13.5 $\pm$ 2.1	14.5 $\pm$ 2.8	14.0 $\pm$ 2.3	14.5 $\pm$ 2.8	14.0 $\pm$ 2.3	14.5 $\pm$ 2.4	13.0 $\pm$ 2.1
Carbonate	14.0 $\pm$ 2.0	13.5 $\pm$ 2.0	14.5 $\pm$ 2.3	13.5 $\pm$ 2.1	13.0 $\pm$ 1.9	13.5 $\pm$ 2.1	12.5 $\pm$ 1.8	14.0 $\pm$ 2.4	14.0 $\pm$ 2.3	14.0 $\pm$ 2.5	13.0 $\pm$ 1.9
Reducible	14.5 $\pm$ 2.3	12.0 $\pm$ 1.5	14.5 $\pm$ 2.3	14.0 $\pm$ 2.1	12.5 $\pm$ 1.4	14.0 $\pm$ 2.0	13.5 $\pm$ 1.9	14.0 $\pm$ 2.3	13.5 $\pm$ 1.4	13.0 $\pm$ 1.3	11.5 $\pm$ 1.1
Organic	112 $\pm$ 6.8	107.5 $\pm$ 7.6	112 $\pm$ 7.2	110.5 $\pm$ 8.1	107.5 $\pm$ 6.2	109.5 $\pm$ 6.3	109.0 $\pm$ 6.5	110.5 $\pm$ 7.3	108.5 $\pm$ 7.2	112.0 $\pm$ 7.6	108.5 $\pm$ 6.4
Amorphous Fe-Mn	14.0 $\pm$ 1.2	12.0 $\pm$ 1.1	14.0 $\pm$ 1.2	13.5 $\pm$ 1.2	12.0 $\pm$ 1.1	12.5 $\pm$ 1.4	12.5 $\pm$ 1.3	13.5 $\pm$ 1.6	12.5 $\pm$ 1.7	13.5 $\pm$ 1.3	12.5 $\pm$ 1.1
Crystalline Fe-Mn	14.0 $\pm$ 1.2	12.0 $\pm$ 1.1	14.0 $\pm$ 1.2	13.5 $\pm$ 1.2	12.0 $\pm$ 1.1	12.5 $\pm$ 1.4	12.5 $\pm$ 1.3	13.0 $\pm$ 1.6	12.5 $\pm$ 1.7	13.0 $\pm$ 1.1	13.0 $\pm$ 1.6
Detrital (Residual)	336.4 $\pm$ 34	337.4 $\pm$ 32	338.3 $\pm$ 33	336.6 $\pm$ 34	337.4 $\pm$ 35	336.6 $\pm$ 38	339.4 $\pm$ 37	336.2 $\pm$ 32	334.6 $\pm$ 34	337.7 $\pm$ 31	339.3 $\pm$ 32
Sum of all fraction	519.4 $\pm$ 41	507.4 $\pm$ 39	521.8 $\pm$ 42	514.6 $\pm$ 40	507.9 $\pm$ 38	513.1 $\pm$ 41	513.4 $\pm$ 40	515.9 $\pm$ 43	509.6 $\pm$ 41	518.2 $\pm$ 42	511.3 $\pm$ 42
Non-residual %	35.2	33.6	35.2	34.7	33.5	34.4	33.9	34.8	34.3	34.8	33.5
Residual %	64.8	66.5	64.8	65.3	66.5	65.6	66.1	65.2	65.7	65.2	66.5
MF %	5	5	5	5	5	5	5	6	5	6	5

MF = Mobility factor: proportion of mobile (F1 + F2) to total sum of fraction

**Table 5.** Cadmium concentrations (mean  $\pm$  SD, n = 5) in each operationally defined geochemical fractions samples.

Geochemical fractions	OW	OJ	AK	IK	OK	OND	SG	BK	Km 110	KUD	WC
Exchangeable	3.0 $\pm$ 0.2	2.5 $\pm$ 0.1	4.0 $\pm$ 0.3	3.5 $\pm$ 0.2	4.5 $\pm$ 0.3	3.0 $\pm$ 0.2	3.0 $\pm$ 0.2	3.5 $\pm$ 0.2	3.0 $\pm$ 0.2	4.0 $\pm$ 0.3	2.0 $\pm$ 0.2
Carbonate	3.0 $\pm$ 0.2	2.5 $\pm$ 0.1	3.5 $\pm$ 0.2	3.0 $\pm$ 0.2	4.0 $\pm$ 0.3	3.0 $\pm$ 0.2	3.0 $\pm$ 0.2	2.5 $\pm$ 0.1	2.0 $\pm$ 0.1	4.0 $\pm$ 0.3	2.0 $\pm$ 0.1
Easily reducible	2.5 $\pm$ 0.1	3.5 $\pm$ 0.2	3.5 $\pm$ 0.2	3.5 $\pm$ 0.2	3.5 $\pm$ 0.2	3.0 $\pm$ 0.2	3.0 $\pm$ 0.2	3.0 $\pm$ 0.2	2.5 $\pm$ 0.1	4.0 $\pm$ 0.3	2.5 $\pm$ 0.1
Organic	6.0 $\pm$ 0.5	9.0 $\pm$ 0.8	7.5 $\pm$ 0.6	9.5 $\pm$ 0.8	9.5 $\pm$ 0.8	6.5 $\pm$ 0.5	7.0 $\pm$ 0.6	8.0 $\pm$ 0.7	7.5 $\pm$ 0.6	9.5 $\pm$ 0.8	7.0 $\pm$ 0.6
Amorphous Fe-Mn Oxide	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	2.5 $\pm$ 0.1	3.0 $\pm$ 0.2	1.5 $\pm$ 0.1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	2.5 $\pm$ 0.1	2.0 $\pm$ 0.1
Crystalline Fe-Mn Oxide	2.0 $\pm$ 1.6	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	3.0 $\pm$ 0.2	2.5 $\pm$ 0.1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1	1.5 $\pm$ 0.1	2.5 $\pm$ 0.1	2.0 $\pm$ 0.1	2.0 $\pm$ 0.1
Detrital (residual)	18.4 $\pm$ 2.2	17.0 $\pm$ 1.3	11.3 $\pm$ 0.9	8.8 $\pm$ 0.7	12.4 $\pm$ 1.0	12.4 $\pm$ 1.1	14.2 $\pm$ 0.8	9.6 $\pm$ 1.1	15.1 $\pm$ 0.7	14.4 $\pm$ 1.0	13.9 $\pm$ 1.0
Sum of all fractions	36.9 $\pm$ 2.2	38.5 $\pm$ 2.4	33.8 $\pm$ 2.1	33.8 $\pm$ 2.1	29.4 $\pm$ 1.7	33.2 $\pm$ 2.0	29.6 $\pm$ 1.6	35.6 $\pm$ 2.5	28.2 $\pm$ 1.7	40.4 $\pm$ 3.0	31.4 $\pm$ 2.4
Non-residual %	50.1	55.8	67.2	73.9	91.8	57.2	67.5	54.8	69.1	64.5	55.7
Residual %	49.9	44.2	32.8	26.1	8.2	42.8	32.5	45.2	30.9	35.5	49.3
MF %	16	13	22	19	30	18	20	17	18	20	13

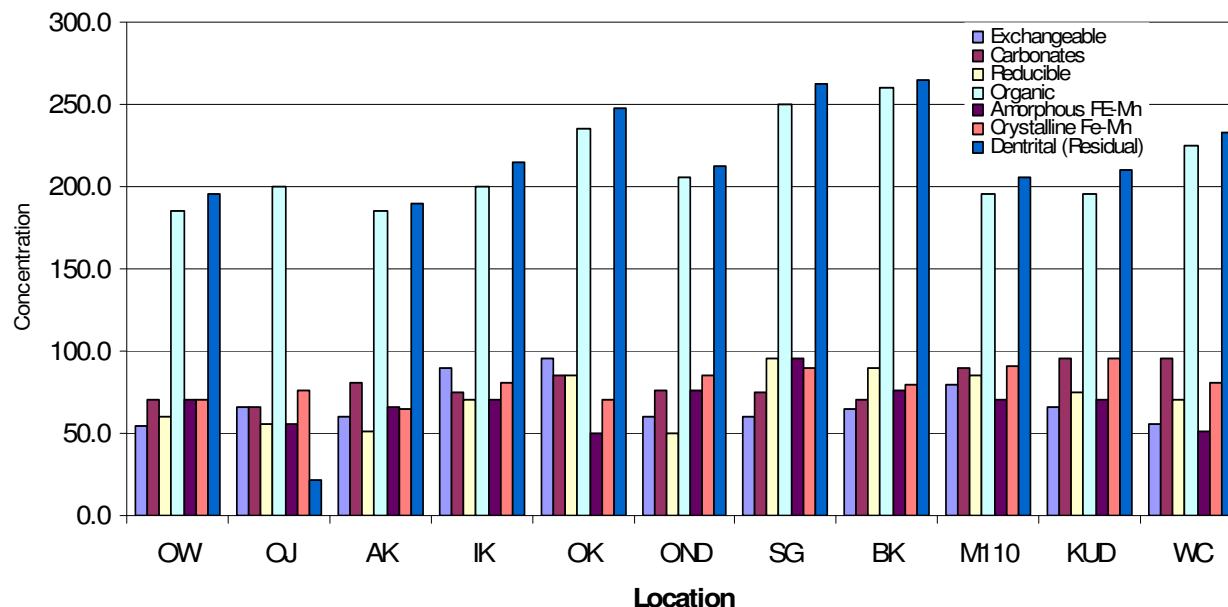
MF = Mobility factor: proportion of mobile (F1 + F2) to total sum of fractions.

## Lead

Lead was mostly concentrated in the residual fractions. The percentage of Pb in non-residual fractions ranged from 33 to 35% on the average. There was no significant difference in available Pb

content between all locations (values range from 13.0 to 14.5 mg/kg) (Table 4). All the soils have larger particle size (lower clay content), high exchange capacity and moderate organic matter resulting in moderate adsorption capacity for Pb. The sum of Pb in the exchangeable and carbo-

nate fractions in all the sites ranged from 5 to 6% on average, which indicates that the Pb in these soils may not be highly available for plant. However, organic bound fraction of these soils ranged from 21 to 22% which agreed with the reported affinity of Pb to organic matter (Kabata-Pendias



**Figure 4.** Zinc concentrations in each operationally defined geochemical fractions of the soils.

and Pendias, 1992). Among the non-residual, organic fractions contain the highest amount of Pb in the samples and the oxide fraction contains the lowest (Table 2). Approximately the same amounts are associated with carbonate and exchangeable forms. Mean percentage contributions from the different fractions are almost identical in all locations, in which Pb concentrations in most of the various forms are low except for organic that was high. Soil characteristics appear not to influence strongly the behaviour of Pb in the various fractions.

The findings are not consistent with other studies. Ramos et al. (1994) found that most Pb was associated with the oxide fraction in their study of polluted Spanish soils, with only very low amount in exchangeable fraction. Similar findings were reported by Sposito et al. (1982). It seems organic matter plays a significant role in this soil. In these soils therefore, Pb should not be phytoavailable.

## Zinc

Zinc was mostly concentrated in the non-residual fractions. The majority of the Zn was associated with the organic matter (54%) and residual (57%). There was no difference in the order of importance between other fractions as well as between locations. In general the associations of Zn in these soils are: residual > organic > exchangeable = carbonate = amorphous Fe – Mn oxide = crystalline Fe – Mn oxide = reducible. The high percentage of Zn in the organic fraction can be related to the tendency of the metal to be readily adsorbed by organic molecules (Pardo et al., 1990; Spevackova and Kucera, 1989). The pH (Zn –

organic complex is pH dependent) appear to determine the Zn distribution found in these soils. Zn was present in all geochemical fractions, irrespective of total Zn fractions (Table 6) No clear trend was observed in Zn concentration in all the geochemical fractions (Figure 4).

## Mobility of Cd, Pb and Zn in soil

The mobility of metals in soil samples may be measured on the basis of absolute and relative content of fractions weakly bound to soil component. The relative index of metal mobility was calculated as a mobility factor (MF) (Salbu et al., 1988) using equation:

$$MF = [(F1 + F2)/(F1 + F2 + F3 + F4 + F5 + F6 + F7)] \times 100$$

The above index describes the potential mobility and it is the ratio of proportion of mobile (F1 + F2) to the total sum of all fractions. The MF gave the values in the range of 13 - 30% for Cd, 5 - 6% for Pb and 15 - 25% for Zn. The indices of mobility were lowest in Pb. The low MF values in these soils are an indicator of high stability of heavy metals in these soils. Low MF has been interpreted as indicators of relatively low liability and biological availability of heavy metals in soils (Karczewka et al., 1998; Ma and Rao, 1997; Ahumada et al., 1999). The dissolution and consequently the mobility and bioavailability of metals are controlled by organic matter and oxides that act as principal adsorbents and can prevent excessive mobilization of heavy metals (McBride, 1995). The fact that organic bound fractions are highest among



**Table 6.** Zn Concentrations (mean  $\pm$  SD, n = 5) in each operationally defined geochemical fractions of the soil.

Geochemical fractions	OW	OJ	AK	IK	OK	OND	SG	BK	Km 110	KUD	WC
Exchangeable	55.1 $\pm$ 4.2	65.5 $\pm$ 5.3	60.6 $\pm$ 5.1	90.3 $\pm$ 6.8	95.3 $\pm$ 7.4	60.7 $\pm$ 5.4	60.6 $\pm$ 5.6	65.3 $\pm$ 5.8	80.1 $\pm$ 6.9	65.7 $\pm$ 6.1	55.4 $\pm$ 4.2
Carbonate	70.2 $\pm$ 6.8	65.3 $\pm$ 5.3	80.7 $\pm$ 6.9	75.2 $\pm$ 6.6	85.4 $\pm$ 6.8	75.6 $\pm$ 6.6	75.4 $\pm$ 6.7	70.2 $\pm$ 6.4	90.3 $\pm$ 7.2	95.6 $\pm$ 7.8	95.4 $\pm$ 7.7
Reducible	60.4 $\pm$ 5.1	55.3 $\pm$ 4.1	50.8 $\pm$ 4.0	70.4 $\pm$ 6.2	85.6 $\pm$ 6.9	49.5 $\pm$ 3.6	95.9 $\pm$ 7.8	90.1 $\pm$ 7.3	85.6 $\pm$ 6.4	75.2 $\pm$ 6.1	70.6 $\pm$ 6.3
Organic	185.3 $\pm$ 12	200.3 $\pm$ 15	185.4 $\pm$ 12	200.3 $\pm$ 14	235.2 $\pm$ 16	205.5 $\pm$ 15	250.3 $\pm$ 17	260.6 $\pm$ 18	195.4 $\pm$ 13	195.3 $\pm$ 13	225.2 $\pm$ 16
Amorphous Fe-Mn Oxide	70.4 $\pm$ 6.7	55.6 $\pm$ 4.3	65.6 $\pm$ 5.2	70.3 $\pm$ 6.3	50.5 $\pm$ 4.1	75.9 $\pm$ 6.5	95.2 $\pm$ 7.2	75.6 $\pm$ 6.8	70.4 $\pm$ 6.4	70.7 $\pm$ 6.4	50.6 $\pm$ 3.9
Crystalline Fe-Mn Oxide	70.3 $\pm$ 6.4	75.7 $\pm$ 6.5	65.3 $\pm$ 6.5	80.5 $\pm$ 7.0	70.6 $\pm$ 6.3	85.5 $\pm$ 6.9	90.3 $\pm$ 7.3	80.1 $\pm$ 6.9	90.6 $\pm$ 7.0	95.3 $\pm$ 7.2	80.8 $\pm$ 6.9
Detrital (residual)	195.5 $\pm$ 13	215.5 $\pm$ 16	189.8 $\pm$ 12	214.7 $\pm$ 15	247.8 $\pm$ 17	212.4 $\pm$ 16	262.5 $\pm$ 18	265.3 $\pm$ 18	205.8 $\pm$ 14	210.9 $\pm$ 15	232.9 $\pm$ 16
Sum of all fractions	707.2 $\pm$ 70	733.3 $\pm$ 71	698.2 $\pm$ 64	801.7 $\pm$ 80	870.4 $\pm$ 83	765.1 $\pm$ 73	930.2 $\pm$ 91	907.2 $\pm$ 90	818.2 $\pm$ 80	808.2 $\pm$ 80	810.9 $\pm$ 80
Non-residual %	72	72	73	73	72	72	72	71	75	74	71
Residual %	28	28	27	27	28	28	28	29	25	26	29
MF %	18	18	20	21	21	18	25	15	21	20	19

MF = Mobility factor: proportion of mobile (F1 + F2) to total sum of fractions.

the non-residual of the metal studies attest to this assertion.

The correlation coefficient between soil properties and geochemical fractions and between species of the fractions was investigated to further understand their mobility. Table 7 shows that mobility indexes of Pb and Zn significantly correlated with Fe, pH and CEC. Also, mobility indexes of Cd and Pb were significantly ( $p \geq 0.01$ ) correlated with soil organic matter (SOM). There were no significant correlations with total metals. None significant correlation with total metals indicates that anthropogenically added metals are strongly bound to soil consistent (Rasmus et al., 1994). Lack of significant correlation between mobility indexes of Pb and Cd and their total contents suggest low Pb and Cd contamination with these metals and strong relationship to soil properties.

Table 7 shows that there were significant ( $P \geq 0.05$ ) correlation between Zn<sub>2</sub> (carbonate) and Zn<sub>3</sub> (metal organic complex) and the pH. This

could be due to low pH of these soils. The extent to which fixation of Zn occur has been linked with higher pH (Niel et al., 2006). However, exchangeable Pb and Cd were found to be negative but not significantly correlated with pH. The result of other fractions showed no trend with pH, suggesting control by the sources of background metals rather than soil condition (Niel et al., 2006).

There were significant correlations ( $P \geq 0.05$ ) between fractions of each metal (Cd<sub>1</sub> with Cd<sub>2</sub>, Cd<sub>3</sub>, Pb<sub>1</sub> with Pb<sub>2</sub>, Pb<sub>3</sub> and Zn<sub>1</sub> with Zn<sub>2</sub>, Zn<sub>3</sub>). These results indicate a dynamic mobility of metals from one species to another. The result seems to suggest equilibrium between metal species. It has been revealed that the extent to which metal approaches equilibrium is independent of pH, although the equilibrium distribution between labile and non-labile is pH dependent (Niel et al., 2006). Furthermore, exchange between labile and non-labile pools has been found to appear rapidly, although not over a period that would affect the assay of labile at any one sampl-

ing time.

## Conclusion

All the metals investigated were significantly associated with non-residual fractions of the valley bottom soils studied. This indicates that the metals were potentially more bio-available. All the three metals were found in organic bound fractions in all the soils. Overall, the order of contamination was Cd > Zn > Pb. Among the soils of the cities studied, Okitipupa (Ok) recorded the highest Cd, Ibadan, Zn and Akure, Pb. The distributions of the metals in different fractions were independent of the respective total metal concentrations in the soils. The distribution of the metals in the various fractions confirms their difference in mobility and bioavailability.

The mobility indexes of the metals were negatively correlated with their total content, indication that the anthropogenically added metals

**Table 7.** Correlation between the parameters.

	pH	OC	Pb1	Cd1	Zn1	PB2	Cd2	Zn2	Pb3	Cd3	Zn3	Pb4	Cd4	Zn4	Pb5	Cd5	Zn5	Pb6	CD6	Zn6
OC	-0.441																			
Pb1	-0.163	0.223																		
Cd1	-0.118	0.333	0.309																	
Zn1	0.098	-0.006	-0.326	0.567																
Pb2	0.120	-0.215	0.533	0.063	-0.174															
Cd2	-0.205	0.413	0.356	0.769	0.250	0.000														
Zn2	0.454	0.107	0.049	0.119	0.69	0.197	0.469													
Pb3	-0.047	-0.024	0.704	0.211	-0.081	0.338	0.065	-0.242												
Cd3	-0.218	0.413	-0.080	0.713	0.646	-0.404	0.492	-0.079	-0.088											
Zn3	0.551	-0.432	-0.105	0.136	0.567	-0.234	-0.060	0.172	-0.104	0.245										
Pb4	0.092	-0.304	0.225	-0.014	-0.401	0.668	0.107	0.100	0.722	-0.386	-0.196									
Cd4	-0.133	-0.029	-0.029	0.461	0.527	-0.008	0.527	0.379	-0.467	0.514	0.191	-0.258								
Zn4	0.571	-0.106	-0.213	-0.031	0.013	-0.361	-0.140	0.187	-0.218	0.084	0.680	-0.301	-0.018							
Pb5	0.063	0.365	-0.593	0.040	-0.314	0.701	0.118	0.120	0.669	-0.319	-0.132	0.976	-0.115	-0.330						
Cd5	-0.067	-0.410	-0.414	0.239	0.555	-0.022	0.208	-0.032	-0.439	0.188	0.185	-0.284	0.653	-0.046	-0.206					
Zn5	0.166	-0.138	0.531	0.003	-0.147	-0.0190	-0.098	-0.258	0.611	0.067	0.370	0.331	-0.390	0.137	0.264	-0.391				
Pb6	0.102	-0.395	0.413	-0.113	-0.359	0.624	0.002	0.109	0.557	-0.400	-0.232	0.926	-0.206	-0.442	0.949	-0.258	0.150			
Cd6	0.173	-0.349	-0.366	0.136	0.692	-0.017	0.214	0.355	-0.084	-0.193	0.221	-0.016	0.536	-0.205	0.088	0.498	-0.176	0.164		
Zn6	0.147	0.354	0.012	-0.012	0.012	-0.245	0.002	0.249	-0.176	0.265	0.331	-0.310	0.043	0.555	-0.346	-0.254	0.364	-0.454	-0.168	
Pb7	0.431	-0.124	0.234	-0.112	-0.238	0.012	0.112	-0.110	-0.132	-0.112	-0.121	-0.133	0.062	0.133	-0.089	0.067	-0.012	0.242	-0.082	-0.041
Cd7	0.234	-0.221	-0.362	0.146	0.247	-0.012	0.016	0.217	0.023	0.253	0.062	0.106	-0.116	-0.096	-0.182	-0.242	-0.042	-0.032	0.212	-0.063
Zn7	0.223	-0.127	0.014	-0.023	0.013	-0.341	-0.231	0.212	0.214	0.232	-0.047	-0.241	0.221	0.024	0.667	-0.021	0.234	0.096	-0.044	0.246

**Table 8.** Correlation coefficient between total metal content and mobility factors, and selected physiochemical properties of the soils.

Factors	Clay	pH	Fe	CEC <sup>++</sup>	SOM <sup>+</sup>	TM <sup>*</sup>
Cd <sup>+</sup>	-0.34	0.41	0.26	0.38	-0.42	-
Pb <sup>+</sup>	0.86	0.79	-0.43	-0.82	-0.56	-
Zn <sup>+</sup>	0.76	0.94	-0.06	-0.88	0.82	-
MFCd	0.33	0.42	-0.19	-0.38	0.62	-0.98
MFPb	-0.48	-0.69	-0.58	0.69	-0.91	-0.34
MFZn	0.04	-0.57	0.66	0.60	-0.26	-0.54

\* = Total content of metal  
+ = Soil organic matter  
++ = Cation exchange capacity  
MF = Mobility factors.

were in strongly bound forms. However the strongly and positively correlation among the metal fractions indicate a dynamic equilibrium between their labile and non-labile species, suggesting a potentially bioavailability metals in these soils.

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