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Trace elements fractionation in calcareous soils of Peshawar-Pakistan

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Abstract

Trace elements mobility in uncontaminated soils even present at typical soil concentrations remains a problem once their availability to plants is assessed. The objective of this study was to develop a relationship between total Cu, Pb and Zn concentrations and their availability to plants. For that purpose, three soil profiles (Entisols, Inceptisols and Alfisols) were selected from model agricultural fields within Peshawar-Pakistan. Soil samples were collected from each horizon of a soil profile and were sequentially extracted for Cu, Pb and Zn into six operationally defined forms: water soluble (F1= deionized water soluble), exchangeable (F2 = $MgCl_2$), carbonate (F3 = Sodium acetate), Fe+Mn oxide (F4= NH_2OH), organic (F5 = Ammonium accetate), residual (F6 = $HCl/HF/HNO_3$). The result shows that the total content of Cu, Pb and Zn in Entisols, Inceptisols and Alfisols ranged from 6.33-22.17, 4.20-12.6, 27.51-52.23; 1.65-21.57, 3-13.5, 36.93-54.12 and 11.28-16.59, 3.09-16.8, 52.71-73.38 mg kg^{-1} with average value of 11.48, 7.72, 43.2; 14.6, 8.85, 47.5; 13.87, 9.46, 59.65 mg kg^{-1}. Copper, Pb and Zn were found to be at typical soil concentrations. The sequential extraction of Cu, Pb and Zn showed that Cu was strongly associated as carbonate, Pb was as residual and Zn was as oxide fractions. All metals were weakly associated with exchangeable and organic fractions in all soils. Copper was found to be more mobile and available to plants in all soils than Zn and Pb.

Keywords: Total heavy metals, Sequential extraction, Trace elements, Cu, Pb, Zn

Introduction

Copper, Pb and Zn occur naturally in the soil in minute quantity. Trace elements occurrence in the earth crust is not more than 0.1% (Alloway, 1995). Among trace elements, the average value of Cu, Pb and Zn in the lithosphere is 55, 14, 80 mg kg^{-1} (Lindsay, 1972; Baker, 1990). In contrast to that, their medain in the typical normal world surface soil is 20, 10, 50 mg kg^{-1} and ranged from 2-100, 2-100 and 10-300 mg kg^{-1} (Bowen, 1966). According to Baseer (1979), the range of Cu, Pb and Zn in calcareous soils of Peshawar-Pakistan varies from 2-250, 2-200 and 10-300 mg kg^{-1} and average values are 30, 19 and 80 mg kg^{-1}. Khattak and Hussain (2007) and Kashif *et al.* (2009) reported that the mean value of available Cu and Zn in the soils ranged from 4.44 to 6.20 and 3.35 to 18.43 mg kg^{-1}.

Total concentrations of trace elements in any soil can provide background information about the fertility and metals status of the soil (Dornia & Micheal, 2005; Albanese, 2008). However, this does not provide knowledge about metals speciation with various fractions of the soil namely carbonates, oxides, exchangeable, organic and mineral fractions (Gilbert, 1952; Nale *et al*., 2007; Ajiboye and Ogunwale, 2008). Moreover, from total content of metals it is difficult to predict their mobility, bio-availability and toxicity to plants (Sillanpää, 1972; Hussain *et al*., 2006). The only reason for this could be that metals do not occur in soils in a single chemical form (Bruns, 1945; Iyer and Satyanarayana, 1958; Huang, 2008) and are found to be strongly associated with organic and inorganic ligands of soils (Ramesh and DeLaune, 2008). However, the extents to which these metals are bound with other soil fractions differ widely for elements more likely because of the difference in their origin, geochemical and physical characteristics (Marantos *et al*., 2008). Therefore it is necessary to evaluate this difference once their bioavailability is assessed.

The technique which is successfully used to extract trace elements from various fractions of soils is as described by Tessier *et al.* (1979). This technique is well known in the literature as sequential extraction technique. Through this technique, elements are fractionated into water soluble (F1), exchangeable (F2), carbonate (F3), Fe+Mn oxides (F4), organic (F5) and residual fractions (F6) of the soil (Harrison, 1981). The water soluble, exchangeable, carbonate, oxide, organic fractions are also known as non-residual fraction and high percentage of recovery of elements from any of this fraction shows their high mobility in soils and availability to plants (Stephen *et al*., 2008) whereas other fraction such as residual is considered to be

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highly immobile and high percentage of recovery of elements in this fraction represents low mobility and unavailable to plants (Singh and Singh., 1966; Clevenger and Mullins., 1982). Burt *et al.* (2003) reported that around 93% of Cu and 41% of Zn was recovered as residual fraction from spoils and very low percentage of Cu was recovered as water soluble and exchangeable fractions of spoils. They concluded that in spoils residual fraction is the dominant sink for trace elements.

Elements mobility in a soil is determined from mobility factor which is calculated from the following equation as described by Kabala and Singh (2001) and Oluwatson (2008).

Mobility Factor (MF) =

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

The value of MF for elements provides information about their potential mobility in soils and availability to plants (Yusuf, 2007). The value of MF up to 10% for any element indicates that this element is highly immobile and unavailable for plants (Torri and Lavado, 2008). In addition to that, the value of MF up to 50% or greater than 50 % for a particular element suggests that this element is highly mobile and available for plants (Ahumada *et al*., 1999). Oluwatson *et al.* (2008) reported while studying the availability and mobility of Cd, Pb and Zn in the urban soils of North-West Nigeria, that the percentage of mobility factor (MF) for Cd, Pb and Zn varied from 13 to 30, 5 to 6, and 15 to 25% in all soils. They concluded that Pb was highly stable in soils hence unavailable to plants.

Total trace element concentrations in the calcareous surface soil of semi-arid zone of Peshawar-Pakistan are studied by several researchers. However, no attempt has been made to understand trace elements distribution and speciation within a calcareous soil profile of Peshawar district. There is no information available in the previous literature on trace elements mobility, availability and toxicity in Peshawar soils. The main objective of this study was to provide information about trace elements distribution and speciation within calcareous soil profiles and then to evaluate their mobility and bioavailability in soils. For that purpose Cu, Pb and Zn were sequentially extracted into their six operationally defined chemical forms i.e., water soluble, exchangeable, carbonate, oxide, organic and residual fractions in soils using a technique as described by Tessier *et al.* (1979). Trace elements mobility in soils and availability to plants was assessed from mobility factor using equation as described by Yusuf (2007).

Materials and Methods

Sample collection and processing

Three representative soil profiles were selected from model agricultural fields in Peshawar-Pakistan. According to U.S soil taxonomical classification, the selected soil profiles are classified into Entisols, Inceptisols and Alfisols. The soils are used for growing sugar cane (Entisols and Inceptisols), and maize crops (Alfisols) over the last several years. The soils are not under the influence of anthropogenic activities (Gul, 1998).

Surface litter was removed with a spade and a pit was excavated up to 100-170 cm. Soil samples were collected from A, B and C horizons of three soil profiles namely Entisols, Inceptisols and Alfisols. The variation in the depths of A, B and C horizons among three soil profiles was most probably because of the differences in the soil formation.

The exposed soil was derived from Paleozoic Sedimentary rocks. Bulk sample of 2 kg was collected from each horizon of a soil profile. Representative soil samples were brought to the laboratory and composite samples were broken down and mixed thoroughly by hand. The soils were partially dried just to allow sieving through 2 mm mesh size. The sieved soils were divided into three equal portions of 500 g and were kept in plastic bottles in the refrigerator at 2^{o} C until one week prior to incubation.

The soil samples were analyzed for organic matter content, texture, pH, EC_e and calcium carbonates. Total soil organic matter was determined by wet digestion method as described by Jackson (1968). Soil texture was determined by pipette method as described by Avery and Bascomb (1974). Soil pH was estimated in all soils as explained by McLean (1982) and calcium carbonate was determined by gravimetric method as described by Black (1965).

Trace elements extraction

Soil samples were extracted for total content of Pb, Cu, and Zn following the procedure of Buckley and Cranston (1971). Triplicate subsamples of one gram oven dry soil was transferred to a 120 mL Teflon pressure digestion vessel followed by adding 4 mL of HF and were allowed to react overnight in order to ensure dissolution of silicate matrix. The vessels were placed on a hot plate until the white paste was obtained. Thereafter, the vessels were removed from the hot plate and allowed to cool at room temperature. The white paste in the vessel was treated with 10 mL of aqua regia (1:3 HNO_3: HCl) and was placed on the hot plate for 30-min to ensure dryness. After dryness, yellowish brown residue was obtained and was dissolved in 20 mL of 2 N HCl. It was placed on a hot plate for an additional 5-10 min to ensure re-digestion but avoid complete dryness. Boric acid (1 g) was added after digestion in order to prevent the volatilization losses of the SiF4 gas (Sridhar and Jackson, 1974; Jackson, 1974). After cooling, yellowish brown dry residue was diluted with 30 mL of distilled water and was mixed thoroughly by continuous manual shaking for 5 min and was filtered through Whatmann No. 2. The filtered aliquots of each residue was pipetted into 50 mL plastic bottles and was airtight with caps and analyzed for trace metals using Atomic Absorption Spectrophotomer.

Sequential extraction techniques

Metals distribution and speciation in soil was determined by the sequential extraction as described by Tessier *et al.* (1979) and presented in Table 1.

Table 1: Sequential extraction steps as described by Tessier *et al* (1979)

Steps	Fractionation	Reagents	Time
1	F1 = water soluble	20 mL deionized water	1 h 20 °C
2	F2 = exchangeable	20 mL 1-M NH_4oAC (pH 7)	2 h 20 °C
3	F3 = carbonates	20 mL 1-M NaOAc (pH adjusted to 5 by adding HOAc)	2 h 20 °C
4	F4 = Fe+Mn oxide	20 mL 0.04 M NH_2OH. HCl in 25% (v/v) at HOAc	6 h 80 °C
5	F5 = organic matter	15 mL of 30% H_2O_2	5.5h 80 °C, 0.5h 20 °C
6	F6 = residual	7M HNO_3^-	6 h 80 °C

Samples of finely grounded air-dry soil, usually 2 g, were transferred to a shaking bottle followed by 20 mL of deionized water and samples were shaken on a reciprocating shaker for 1 hour. The soil suspension was centrifuged for 30 minutes and then the suspension was filtered through Whatman (# 42) filter papers. An aliquot of each extract was pipetted into a plastic bottle and was diluted with 40 ml of distilled water and the concentration of trace elements were measured on Atomic Absorption Spectrophotometry (AAS). The residue was used for further extraction. All reagents were of analytical grade and all glassware was rinsed with deionized water prior to use. The results were evaluated statistically using Microsoft Excel package.

Statistical analysis

All data were analyzed by multifactor analysis of variance (ANOVAs) using the software package “Excel” where correlation between total metals concentrations and total metals concentrations in individual fractions were studied.

Results and Discussion

Physicochemical characteristics of soils

The soils are calcareous in nature and are characterized by silty loam (Inceptisols), sandy (Entisols) and silty clay (Alfisols) texture. The pH of soils ranged from 7.9 to 8.8, whereas EC_e (dS m^{-1}) was from 41.9-140.7 dS m^{-1}. All soils were found to be deficient in organic matter (>1%). Soils were found to be high in $CaCO_3^{-2}$ (Table 2).

Metals (Cu, Zn and Pb) content in the calcareous soil profiles (Entisols, Inceptisols, Alfisols) of Peshawar

The total concentrations of Cu, Pb and Zn in Entisols, Iinceptisols and Alfisols ranged from 6.33-22.17, 4.20-12.6, 27.51-52.23, 1.65-21.57, 3-13.5, 36.93-54.12 and 11.28-16.59, 3.09-16.8, 52.71-73.38, mg $kg^{-1}$with an average value of 11.48, 7.72, 43.2; 14.6, 8.85, 47.5; 13.87, 9.46, 59.65 mg kg^{-1} (Table 3a). The average value of metals in this study is within the reported average value of these metals for world soils by Bowen (1979).

There was no correlation between metals concentrations and soil organic matter in any of the soil. No significant difference in the concentration of metals was noted in relation to depth in soils except for Inceptisols.

Copper in soils

When Cu distribution and speciation in all soils was determined by the sequential extracted method of Tessier *et al* (1979), it was noted that the sum of all fractions in Entisols was not more than 50% to the total content of Cu and none was detected at depth greater than 61 cm (Table 3). This is more likely because of sandy nature of this soil. Sandy soils usually have more leaching capacity and low adsorption capacity for metals (Alloway, 1995).

Although greater concentration of Cu was recovered from carbonate fraction than other fractions in any of the soil (Table 3), but the percentage recovery of Cu as carbonate was not more than 30% in Entisols and increased to 56% in Alfisols and Inceptisols. The greater recovery of Cu as carbonate in this study is positively correlated (*r* = 85 at $p < 0.05$) with the greater percentage of $CO3^{-2}$ in soils (Table 2). This also suggests that in calcareous soils CO_3^{-2} can be the dominant Cu^{+2} sink. It might be possible that carbonates in soils can provide large surface area for Cu^{+2}

ions to be adsorbed or occluded in the structure, hence become unavailable under alkaline condition.

Table 2: General and Physicochemical characteristics of three soil orders of Peshawar district

Soil series	Soil order	horizon	depth	pH	EC dS m^{-1}	$CaCO_3$ (%)	OM (%)	Particle size distribution (%)		
								clay	silt	sand
warsak	Inceptisols	Ap	0-13	8.3	120	10.3	0.49	17	66	17
		Bt1	13-26	7.9	52.5	11.3	0.47	16	70	14
		Bt2	26-57	8.2	87.1	8.5	0.47	16	65	20
		Bt3	57-97	7.9	80.6	7.8	0.372	14	54	32
		2C1	97-122	7.9	68.6	10.3	0.141	14	30	66
		2C2	122-134	8.6	41.9	11.25	0.071	6	56	38
		2C3	134-153	8.8	89.6	11.23	0.19	9	77	13
		3Btb	153-170+	8.8	54.7	11.0	0.001	11	85	4
Khazana	Entisols	Ap	0-9	7.8	276	4.0	0.79	4	10	86
		C1	9-23	8.3	106.2	3.5	0.68	4	6	90
		C2	23-3	8.7	57	3.3	0.65	3	11	85
		C3	30-42	8.9	85.9	3.1	0.56	5	15	80
		C4	42-49	8.7	59.9	2.6	0.46	5	12	83
		C5	49-61	8.7	71.2	2.2	0.36	6	10	84
		C6	61-83	8.6	96.5	2.0	0.32	4	6	90
		C7	83-93	8.7	95.0	2.0	0.23	4	4	92
		C8	93-104	8.6	140.7	2.0	0.22	3	2	95
		C9	104-123	8.6	71.6	2.0	0.20	2	3	95
		C10	123-127	8.4	111.3	2.0	0.18	2	2	96
		C11	127-140+	2.8	1206	2.0	0.16	2	2	96
Peshawar	Alfisols	Ap	0-11	8.3	107.3	13.5	1.02	28	69	3
		Btb1	11-43	8.8	65.6	12.6	0.86	28	70	2
		2Btb1	43-66	8.7	117.2	11.8	0.56	26	71	3
		2Btb	66-98	8.8	80.6	13.6	0.44	29	65	6
		2Btkb	98-138	8.8	82.9	14.6	0.34	31	64	5
		2Btb1	138-150	8.6	110.1	13.8	0.33	30	62	3

Moreover, low percentage of Cu (3-6%) was removed from exchangeable and organic fractions in all soils. The percentage of recovery of Cu as residual fraction varies from 7-25% in the soil (Figure 1). The result of this study is in agreement with the findings of Mengel and Kirkby (2001) who revealed that Cu was strongly associated in carbonate fraction of calcareous soils. Similar result was reported by Adamo *et al.* (1996). They found that 75% of Cu was associated with carbonate fractions of spoils whereas 25% of Ni was recovered from exchangeable fractions of spoils. Graf *et al* (2007) studied the fractionation of Cu in young and old alluvial soils and found that greater percentage of Cu was associated with carbonate and Fe+Mn oxide fractions. The results of this study contradict with the findings of Li *et al.* (2009) who reported that around 90% of Cu was associated with the residual fraction of contaminated soils.

The distribution and speciation of Cu in all soils followed the following pattern;

Cu = carbonate > residual > oxide = organic = exchangeable fractions

Copper distribution in various fractions depends on the total Cu content in each horizon of a soil profile (Xu *et al.*, 2009). The result of this study shows that as the concentration of total Cu increases with increase in depth in case of Inceptisols (Table 3a), the percentage of total Cu in carbonate and residual fractions also increases whereas no change in the total concentrations of Cu was noted in oxide, organic and exchangeable fractions (Figure1). There is a positive correlation (*r* =0.99; P<0.01) between total Cu content in soils and total Cu in carbonate + residual fractions whereas no correlation was observed between total Cu content in soils and other soil fractions. The result of this study is in agreement with the findings of He *et al.* (2006) who reported that Cu positively correlated (*r* =

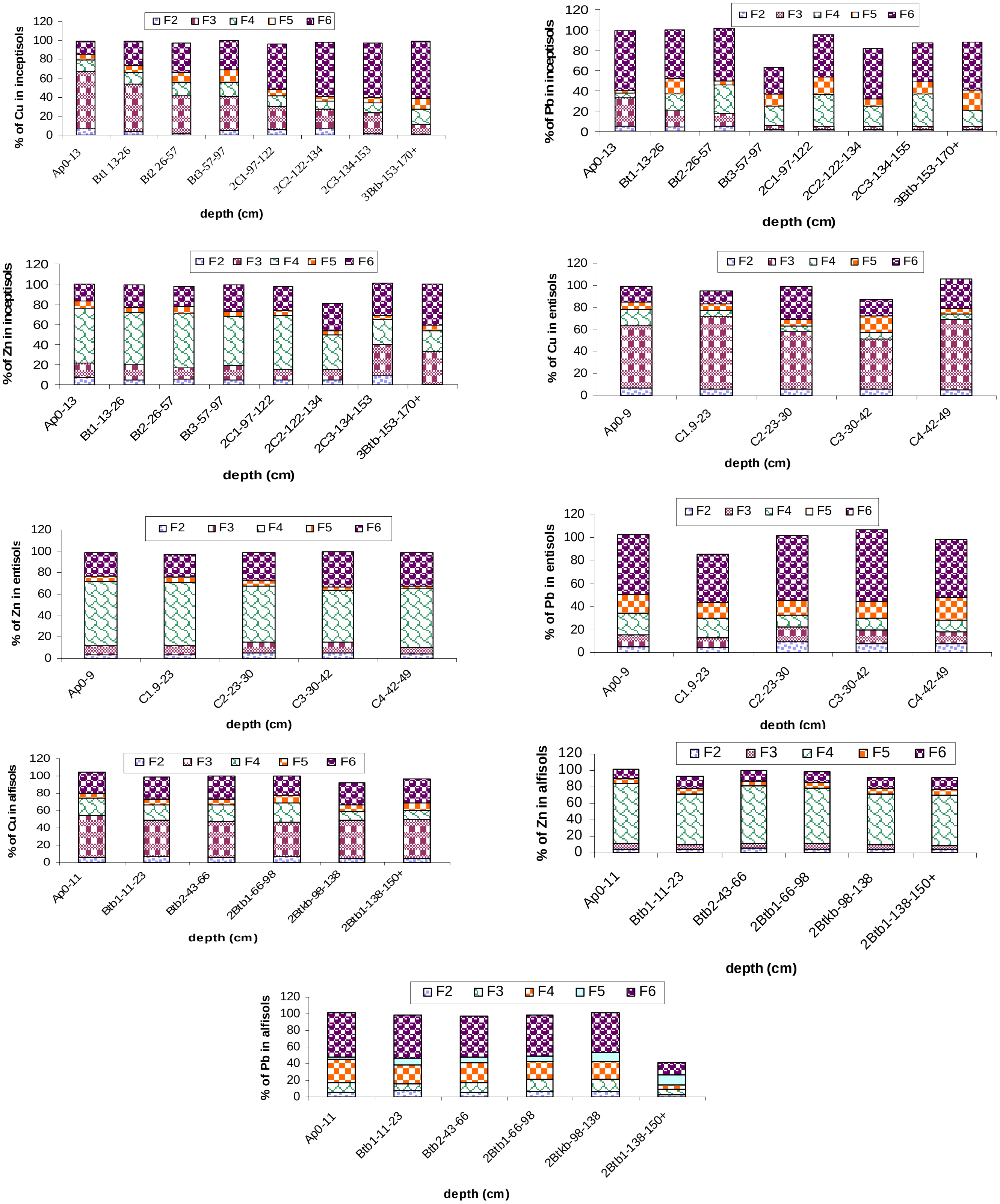

Figure 1: Percentage of Cu, Pb and Zn in exchangeable (F2), carbonates (F3), Fe+Mn oxides (F4), organic matter (F5) and residual (F6) fractions in inceptisols, entisols and alfisols of Peshawar valley

0.66 and 0.81, respectively; $P < 0.01$) with carbonate fraction of the soil.

Table 3: Sequential extraction as described by Tessier *et al.* (1979) of Cu in Inceptisols, Entisols and Alfisols of Peshawar

Soil order	Horizon	Depth (cm)	Cu content in mg kg^{-1}					
			F2-exch	F3-carb	F4-Fe+Mn	F5-org	F6-resid	Total
Inceptisols	Ap	0-13	0.12	0.8	0.2	0.1	0.23	1.65
	Bt1	13-26	0.1	1.5	0.3	0.2	0.3	2.4
	Bt2	26-57	0.4	12	0.2	0.3	6	18.99
	Bt3	57-97	0.2	12	0.8	0.3	8	21.9
	2C1	97-122	1	9	0.2	0.2	6	16.35
	2C2	122-134	0.2	9	0.2	0.1	6	15.99
	2C3	134-153	0.3	11	0.2	0.2	7.3	18.3
	3Btb	153-170+	0.2	12	0.5	0.6	8	21.57
Entisols	Ap	0-9	0.5	4	1	0.5	1	14.01
	C1	19-23	1	6	1	1	3	17.01
	C2	23-30	0.5	1.3	0.4	0.5	0.3	7.71
	C3	30-42	0.4	1	0.4	0.6	0.6	6.63
	C4	42-49	1	6	1	1	3	22.17
	C5	49-61	nd	nd	nd	nd	nd	10.86
	C6	61-83	nd	nd	nd	nd	nd	16.14
	C7	83-93	nd	nd	nd	nd	nd	9.33
	C8	93-104	nd	nd	nd	nd	nd	9.75
	C9	104-123	nd	nd	nd	nd	nd	7.53
	C10	123-127	nd	nd	nd	nd	nd	8.58
	C11	127-140	nd	nd	nd	nd	nd	8.4
Alfisols	Ap	0-11	1	7.72	3	1	4	15.72
	Btb1	11-43	0.75	4.9	2.1	0.8	2.9	11.73
	Btb1	43-66	0.8	6.66	3	1	4	15.66
	2Btb	66-98	1.2	6.7	3.6	1.5	3.6	16.59
	2Btkb	98-138	0.6	5.4	1.2	1	3	12.24
	2Btb1	138-150	0.5	5.2	1.1	1	3	11.28

nd: not determined

In contrast to inceptisols, total Cu concentration does not increase with depth in entisols+alfisols (Table 3a). The result of this study suggests that Cu content was less than 2 mg kg^{-1} in the surface and subsurface horizons of inceptisols than the recommended value of Cu for world surface soils (30 mg kg^{-1}) (Bowen, 1979). This low content of Cu is most probably because of its high availability to plants. In contrast to that the other horizons ranged Cu within its typical concentration for normal soil (up to 30 mg kg^{-1}) (Alloway, 1995). Copper was found to be within its typical concentrations for normal soils i.e. 20-30 mg kg^{-1} irrespective of depth in entisols and alfisols except for a few exceptions. Copper was strongly associated with carbonate fraction of soils and is more mobile and available to plants.

Lead in soils

Unlike Cu, Pb was strongly associated with the residual fraction of inceptisols, alfisols and entisols (Table 4). The percentage recovery of Pb as residual fraction in three soils ranged from 25 to 75% of Pb (Figure 1). The result of this study agrees with the findings of Oluwatosin *et al.* (2008) who reported that around 65% of Pb was associated with residual fraction of soils. The results of this study contradicts with the findings of Pulford *et al* (2009) who revealed that more than 70% of Pb was associated as carbonate fraction of the lead contaminated sediments.

The sum of percentage recovery of Pb in exchangeable, organic and oxide fractions was not more than 5%, however, carbonate fraction showed 28% of extracted Pb in any of the soils (Figure 1).

No difference in the recovery pattern of Pb was noted between Entisols and Inceptisols + Alfisols (Table 2). The main differences between the soils in the percentage recovery of Pb were that Entisols showed a very small percentage of Pb extracted as residual fraction. This difference in the percentage recovery of Pb between Entisols and Inceptisols + Alfisols is more likely because only 50% of Pb was recovered from all other fractions to the total Pb content in soils (Table 4).

Table 4: Sequential extraction (as described by Tessier *et al*. (1979)) of Pb in Inceptisols, Entisols and Alfisols of Peshawar

Soil order	Horizon	Depth (cm)	Pb content in mg kg^{-1}					
			F2-exch	**F3-carb**	**F4-Fe+Mn**	**F5-org**	**F6-resid**	**Total**
Inceptisols	Ap	0-13	0.2	0.2	0.2	0.1	3.5	4.2
	Bt1	13-26	0.5	0.2	2.3	2.1	8.5	13.5
	Bt2	26-57	0.4	0.5	2.2	0.3	4.6	7.8
	Bt3	57-97	0.25	0.5	0.5	1.5	8.3	12.9
	2C1	97-122	0.2	0.25	0.8	1.5	5.0	8.1
	2C2	122-134	0.05	0.1	0.1	0.2	2.0	3
	2C3	134-153	0.2	0.3	0.5	0.2	6.2	8.4
	3Btb	153-170+	0.3	0.5	0.2	0.6	10	12.9
Entisols	Ap	0-9	0.4	0.6	1	0.6	3.4	12.6
	C1	19-23	0.3	0.7	0.6	0.4	2.2	7.8
	C2	23-30	0.2	0.8	0.65	0.4	3	10.5
	C3	30-42	0.2	0.3	0.3	0.3	2.2	5.7
	C4	42-49	0.1	0.2	0.3	0.4	1.2	4.2
	C5	49-61	nd	nd	nd	nd	nd	7.5
	C6	61-83	nd	nd	nd	nd	nd	7.8
	C7	83-93	nd	nd	nd	nd	nd	4.5
	C8	93-104	nd	nd	nd	nd	nd	4.8
	C9	104-123	nd	nd	nd	nd	nd	12.3
	C10	123-127	nd	nd	nd	nd	nd	5.4
	C11	127-140	nd	nd	nd	nd	nd	9.6
Alfisols	Ap	0-11	1	1	4.5	0.5	9.8	16.8
	Btb1	11-43	0.5	0.2	1.5	0.5	3.7	6.6
	Btb1	43-66	0.5	0.3	2.0	0.5	4.9	8.4
	2Btb	66-98	0.5	1	3	0.8	8.5	14.1
	2Btkb	98-138	0.2	0.4	1.6	0.8	4.2	7.8
	2Btb1	138-150	0.2	0.1	0.41	0.9	1.09	3.09

nd: not determined

The pattern of distribution and speciation of Pb in all soils is as below:

Entisols, Inceptisols and Alfisols: Pb: residual > carbonates = organic > Fe+Mn oxides = exchangeable

The total concentration of Pb in relation to depth in all soils showed no clear trend (Table 4). There was a positive correlation ($r = 0.99$, $P < 0.01$) between concentrations of Pb recovered as residual fraction in all soils and total concentrations of Pb. No correlation was found between total Pb content and depth in any of the soils. This suggests that in order to evaluate Pb distribution in the soil, total Pb content is not the only factor to be considered but there are other soil physical and chemical characteristics which must be considered when their distribution and speciation is assessed.

The result of this study shows that low percentage of metals was removed from exchangeable and organic fractions of the soil (Figure 1). This is more likely because metals are non-specifically adsorbed in the exchangeable fraction and can easily be replaced by other competing cations (Kenneth *et al*., 2000). Whereas low percentage recovery of all metals from organic fraction of the soil is more likely because of the low percentage of organic matter in these soils (> 1%) (Table 2). In contrast to exchangeable+organic fractions, high percentage of metals was extracted from residual, carbonate and oxide fractions of the soil.

Zinc in soils

In contrast to Cu, Zn showed greater affinity with Fe+Mn oxides in all soils (Table 5). The percentage of Zn recovery as oxide fraction varies from 30 to 70% in all soils (Figure 1). The greater percentage of Zn in oxide fraction suggests that sesquioxides provide large surface area for Zn adsorption or may be occluded in the structure in soils.

Low percentage recovery of Zn as oxides fraction in Entisols than Inceptisols + Alfisols is most probably because only 50% of Zn was removed from all fractions to the total Zn content in Entisols (Figure 1). The results of this study are in agreement with the findings of Ramos *et al* (1994) who reported that around 90% of Zn was recovered from Fe+Mn oxide fraction in natural soil. The result of this study does not agree with the findings of Tapan and Rattan (2007) who revealed that more than 90% of the total Zn content occurred in the residual fraction of natural soils.

However, the percentage recovery of Zn from exchangeable, organic matter and residual fractions was as low as 6% in all of the soils (Figure 1).

The distribution and speciation of Zn in all soils followed the following pattern;

Entisols, Inceptisols and Alfisols: Zn: Fe + Mn oxides > residuals > carbonates = organic = exchangeable

Zinc distribution in various fractions of a soil profile primarily depends on the total Zn content in each horizon of a soil profile (Wang *et al*., 2007). The result of this study show that the concentration of total Zn does not increase with increase in depth in all soils (Table 5). There is no correlation between total Zn concentration and Zn percentage recovered from any of the soil fraction.

The result of this study suggests that Zn was found to be its typical concentration for normal soils (50 mg kg^{-1}) (Bowen, 1979) in Entisols and Alfisols except for Inceptisols. The average value of Zn in Inceptisols was 59 mg kg^{-1} and slightly greater than the recommended value for world surface soils (50 mg kg^{-1}) (Alloway, 1995) (Table 3c). Zinc was associated with Fe+Mn oxides fraction (non-residual fractions) of soils and is more mobile in soils and available to plants.

Table 5: Sequential extraction (as described by Tessier *et al*. (1979)) of Zn in Inceptisols, Entisols and Alfisols of Peshawar

Soil order	Horizon	Depth (cm)	Zn content in mg kg^{-1}					
			F2-exch	F3-carb	F4-Fe+Mn	F5-org	F6-resid	Total
Inceptisols	Ap	0-13	2.8	5.55	18.5	2.6	8.4	37.98
	Bt1	13-26	3	8	28	2.8	12	54.12
	Bt2	26-57	2.4	4.5	21.4	2.6	8	39.75
	Bt3	57-97	2.5	7.6	26	2.8	13.8	53.16
	2C1	97-122	2	3.5	20	2	9	36.78
	2C2	122-134	2	10	13	1.5	10	36.93
	2C3	134-153	4	12	10	1.5	13	40.05
	3Btb	153-170+	0.5	15	10	2.5	19	46.83
Entisols	Ap	0-9	2	5	20	3	5	57.9
	C1	19-23	2	5	18	3	7	56.1
	C2	23-30	2	5	10	2	3	38.4
	C3	30-42	1.8	4.5	9.5	1.5	2.5	38.4
	C4	42-49	2	3	10	2	3	48.6
	C5	49-61	nd	nd	nd	nd	nd	43.5
	C6	61-83	nd	nd	nd	nd	nd	59.4
	C7	83-93	nd	nd	nd	nd	nd	64.2
	C8	93-104	nd	nd	nd	nd	nd	44.7
	C9	104-123	nd	nd	nd	nd	nd	36.9
	C10	123-127	nd	nd	nd	nd	nd	39.9
	C11	127-140	nd	nd	nd	nd	nd	42
Alfisols	Ap	0-11	3	5	53.38	4	8	73.38
	Btb1	11-43	2	3.2	32.8	3.5	7.5	52.8
	Btb1	43-66	4	4	43.57	4	8	63.57
	2Btb	66-98	3	4	41	4	7	61.77
	2Btkb	98-138	2	3.2	32.8	3.5	7.5	53.64
	2Btb1	138-150	2	3.2	32.8	3.5	7.5	52.71

nd: not determined

Mobility Factor of metals (Cu, Zn and Pb) in soils

Trace elements mobility in soils is estimated by using an equation as described by Kabata-Pendias (2001).

Mobility Factor = [(F1+F2/(F1+F2+F3+F4+F5) × 100]

The mobility factor of Cu was 60% in Inceptisols and Alfisols whereas the MF was reduced to 29% in Entisols in the surface soils. This suggests that Cu is highly mobile and available to plants in all soils. The MF for Zn and Pb was not more than 10% at depth up to 130 cm in any of the soil profiles. In addition to that the percentage of MF reduced to 6% at depth greater than 150-170 cm in all soil profiles. This suggests that Zn and Pb are least mobile and are stable in the soils hence become unavailable to plants. There was no significant difference between the MF of Cu, Zn and Pb and soil depth The results of this study agrees with the findings of Oluwatosin *et al.* (2008) who concluded that Pb is highly stable and unavailable to plants in the soil.

Conclusion

The concentrations of Cu, Pb and Zn remained similar irrespective of the soils and depth except for a few exceptions. Soils were under their typical concentrations for Cu, Pb and Zn as for normal soils. There was no correlation between soil physicochemical characteristics and total metals concentrations. The results of sequential extraction techniques revealed that Cu, Pb and Zn were strongly associated with carbonates, Fe+Mn oxide and residual fractions and weakly associated with exchangeable and organic fractions of the soils. Among three metals, Cu was considered to be highly mobile and available for plants in the surface horizon of all soils whereas Zn and Pb were considered to be stable and immobile for plants at any depth in all soils.

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