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SOME HEAVY METALS CONTENT AND THEIR BINDING FORMS IN SOME SOILS OF MIDDLE EGYPT

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ABSTRACT

Content of Cu, Zn, Fe, Mn, and Pb, their mobility and their specific binding to soil constituents of sandy and alluvial soils of Egypt were measured according to a sequential extraction scheme. The results showed that, total contents of these metals were higher in alluvial soils than in sandy desert soils. In contrast, no or less differences were found in the mobile and easy mobilisable fractions of both soil types. At least the same amounts of heavy metals were available to plants. In sandy and alluvial soils most of Cu and Zn were bound to silicates. In the soils with high carbonate contents considerable part of these two elements were carbonatic bound and not easily available. In alluvial soils most of Cu, Zn and Pb were mainly organically bound, however, in sandy soils most Pb was measured in the residual fraction.

For most of the studied metals, the relative distribution of the various chemical fractions in the alluvial soils descended as follows: organically bounded > oxide occluded >bound to lime > easily mobilisable > soluble + exchangeable, while in desert sandy soils it was in the following order: oxide occluded > bound to lime > easily mobilisable > organically bounded > soluble + exchangeable.

INTRODUCTION

Copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) are micronutrients, which are in low or moderate concentrations essential for plant growth, in high concentrations however they can have toxic effects. For heavy metals like Cd and Pb no physiological significance with regard to nutrition could still be recognized but already low concentrations of these elements can reduce plant growth or cause damage to plants.

The contents and supplies of these elements in soils vary to a great extent. The geogeneic background content of heavy metals in the soil is due to the mineralogical composition of the parent rock material from which the soil derived and to the pedogene processes like weathering and redistribution of the weathering products in soil profiles (Mitchell, 1964). Different particle sizes contain different amounts of trace heavy metals (Rabie *et al*., 1996). Additional to the geogeneic caused content, atmospheric depositions raise the heavy metal levels in the soils. These depositions derive essentially from anthropogeneic sources.

The total element content in soils, however, allows only limited statements about plant availability of Cu, Zn, Mn and Fe or about potential toxicity, including lead (Pb). The ecological significance depends on the actual heavy metal concentration in the soil solution and on the amount of exchangeable forms.

Most of the metals are insoluble, but part of them are bound reversibly to soil particles. Fractionation schemes can help to study the portion of soluble, exchangeable, organic complexed or on fractions which are bound to Fe- and Mn-oxides (Shuman, 1985; Rauret *et al*., 1989; Calvet *et al*., 1990). Small shifts in the distribution to the various groups can induce deficiency or toxicity.

Different factors affect the binding forms and therefore the concentration of the microelements in the soil solution, which in turn influence availability to plants. These factors are: a) the total heavy metal content, b) the specific solution reaction of the considered element c) the soil reaction (pH), d) the content of organic matter in the soil, e) the ionic strength of the soil solution, f) the content of Mn- and Fe-oxides, g) the redox potential and h) the nature of the adsorbing soil surfaces (Salomons and Förstner, 1984; König *et al*., 1986; Buffle, 1988; King, 1988; McGrath *et al*., 1988). Moreover, calcium carbonate can play an important role, but the behaviour differs with respect to the single micronutrients. The carbonate content in the soil was found to be negatively correlated with both the total and the mobile Fe and Mn fraction (Kishk *et al*., 1980), but a positive or no correlation was found with Cu and Zn (Malewar and Randhawa, 1977).

Among all factors, the soil pH and the organic matter content seem to be most important for the control of the mobility of metals in the soil (Narwal and Singh, 1997). After long-term applications of poultry litter which was enriched with microelements, Mitchell *et al.* (1992) found increases of the concentrations of heavy metals up to toxic levels.

The availability of micronutrients in Egyptian soils is commonly low especially in calcareous sandy soils. The same will be expected for soils under high salt concentrations which characterize the arid and semi-arid climates (Abdel-Hamied *et al*., 1991). For growth and especially for the yield of agricultural plants, uptake of these elements is very important. Characterizing the metal binding forms can help to find methods to enhance the availability of the microelements.

In Egypt till now only there were few attempts to determine the amounts of micronutrients in soils and their different binding forms. Therefore, we studied the total contents of Cu, Zn, Mn, Fe and Pb as well as the heavy metal binding forms in selected soils of Middle Egypt. A method of sequential extraction of trace metals was applied (Zeien and Brümmer, 1989) and further developed.

The study was carried out on some desert and alluvial soils. In particular, the objectives of the study are:

1- to characterize heavy metal binding forms of typical agriculturally used soils in Egypt.
2- to further adapt the sequential extraction method to carbonatic soils.

MATERIALS AND METHODS

Nineteen soil profiles were sampled in Egypt. Eleven of them are desert soils and eight are alluvial soils from the Nile valley. In ten profiles A and B horizons were sampled, while in nine profiles A, B and C horizons were sampled to a maximum depth of 90 cm.

The soil samples were air-dried, and sieved through a 2 mm sieve and analyzed for some physical and chemical properties as shown in Table (2) according to the standard procedures, described by Page *et al*., (1982).

Total contents of the heavy metals were measured after aqua regia extraction by using a microwave digestion. A sequential extraction method, proposed by Zeien and Brümmer (1989), was used to assess specific binding forms and the distribution to the single binding forms (Table 1). Each procedure included shaking, centrifuging with 1500 or 2500 rpm and decanting in 100 ml flasks. For stabilizing the solutions, 1 ml HNO_3 conc. was added and the flasks were filled with deionized H_2O to 100 ml. For further information about the extraction procedure see Zeien and Brümmer (1989).

All nineteen profiles were carbonatic with $CaCO_3$ contents up to 37 % (Profile No. 15 in 60-90 cm depth). With Cu or Zn, $CaCO_3$ can form stable complexes, which cannot easily be dissolved. To assess the amount of carbonatic bound heavy metals inserted an additional step, No. 3. Carbonates were dissolved with HCl in stochiometric amounts.

Copper, Zn, Mn, Fe and Pb were measured by atomic absorption spectrometer using flame AAS and graphite tube AAS.

Table 1: Sequential heavy metal extraction procedure (according to Zeien and Brümmer, 1989, modified).

No	Fraction	Form	Extract solution	Soil: solution	Procedure
1	Soluble + exchangeable	Mobile	1M NH_4NO_3 unbuffered	1 : 2.5	Shaken for 2 h
2	Specially adsorbed and weakly bound species, easily mobilisable	Mobilis	1M NH_4Oac pH 6.0	1 : 25	Shaken for 16, 10, 0.5 h
3	Bound to carbonates	Lime	1M NH_4OAc +HCl pH 6.0, amount of HCl to dissolve carb.	1 : 25	Shaken for 10 h
4	Occluded in Mn oxides	Mn- ox	0.1 M NH_2 OH- HCl + 1M NH_4OAc pH 6.0	1 : 25	Shaken for 30, 10, 10 min
5	Bound to organic substance	Organ.	NH_4EDTA pH 4.6	1 : 25	Shaken for 45, 45, 45 min
6	Bound to amorphous Fe oxides	Am- Fe	0,2M NH_4-Oxalate pH 3.25	1 : 25	Shaken for 4 h
7	Bound to crystalline Fe oxides	Cry -Fe	0.1 M Ascorbic Acid in 0.2 M NH_4-Oxalate pH 3.25	1 : 25	30 min in boiling water
8	Residual fraction, mainly bound to silicates	Resid.	5 parts conc. HCl 3 parts conc. HNO_3	1 : 50	Digestion by microwave

RESULTS AND DISCUSSION

1. General characterization of the studied soils

The properties of the studied soils (Table 2) showed some differences between the sandy (profile numbers 1-11) and the alluvial soils (profile numbers 12-19). The alluvial soils from the Nile valley are fine textured with clay contents up to 56 % (profile 18). In contrast the soils from the desert are pure sandy soils with a low content of clay and silt. Simultaneously, cation exchange capacity of alluvial soils are higher than of the desert soils.

Table (2): Some physical and chemical characteristics of the studied soils

Profile No.	Depth, cm	Particle size %			Texture	pH value	$CaCO_3$ %	O.M. %	Exchange cations C mol kg-1			
		Sand	Silt	Clay					Ca^{++}	Mg^{++}	Na^{+}	K^{+}
1	0-40	89.78	9.78	0.44	Sand	8.27	12.66	0.23	10.11	0.31	7.70	0.064
	40-90	92.44	3.69	3.97	Sand	8.31	13.32	0.17	9.70	0.29	6.90	0.071
2	0-40	90.59	8.59	0.82	Sand	8.39	8.75	0.18	10.49	0.54	8.80	0.106
	40-90	87.93	6.26	5.80	Sand	8.28	13.43	0.12	10.11	0.45	7.30	0.115
3	0-60	94.91	2.60	2.49	Sand	8.28	9.10	0.14	9.46	0.60	8.00	0.074
	60-90	89.79	6.35	3.86	Sand	8.17	9.34	0.32	9.19	0.67	7.40	0.064
4	0-40	86.13	10.65	3.22	Sand	8.20	12.32	0.14	10.80	0.40	9.50	0.064
	40-90	87.32	2.27	10.41	Sand	8.15	11.2	0.10	10.34	0.26	13.00	0.061
5	0-30	89.09	6.93	3.98	Sand	8.77	9.94	0.39	9.53	1.04	8.80	0.115
	30-60	90.74	3.69	5.57	Sand	8.18	9.15	0.11	10.63	0.34	8.00	0.045
	60-90	92.27	1.57	6.16	Sand	8.15	8.75	0.10	10.19	0.31	4.60	0.035
6	0-60	87.05	8.54	4.41	Sand	8.16	15.10	0.10	10.69	0.51	11.00	0.141
	60-90	89.41	7.43	3.16	Sand	8.39	5.65	0.03	8.43	1.79	7.10	0.064
7	0-60	90.23	4.47	5.30	Sand	8.26	10.10	0.65	10.11	0.44	6.80	0.061
	60-90	93.82	2.79	3.39	Sand	8.27	9.10	0.49	8.31	0.33	4.10	0.054
8	0-40	91.41	1.65	6.94	Sand	8.28	10.30	0.46	11.37	0.29	15.00	0.061
	40-90	92.27	3.62	4.11	Sand	8.30	7.61	0.23	10.39	0.47	6.00	0.051
9	0-40	90.21	2.23	7.56	Sand	8.42	10.12	0.10	10.36	0.27	7.90	0.112
	40-90	90.77	1.57	7.66	Sand	8.40	9.54	0.27	10.20	0.29	6.50	0.054
10	0-40	85.87	6.71	7.43	Sand	8.27	14.11	0.10	10.26	0.45	8.30	0.131
	40-90	86.92	8.85	4.23	Sand	8.65	10.70	0.13	9.93	0.86	5.30	0.064
11	0-30	70.81	21.67	7.52	Sandy loam	10.04	69.60	0.05	11.34	0.21	42.00	0.048
	30-60	81.09	8.08	10.83	Sandy loam	8.48	62.10	0.05	10.08	0.22	33.00	0.045
	60-90	57.77	37.28	4.95	Sandy loam	8.47	60.00	0.06	9.12	0.16	0.30	0.026
12	0-30	58.10	31.85	10.05	Sandy loam	7.55	2.53	0.30	6.74	0.29	40.00	0.151
	30-60	83.14	4.67	12.19	Sandy loam	7.76	4.87	0.12	7.36	0.21	17.00	0.061
	60-90	73.89	7.24	18.87	Sandy clay loam	7.76	5.65	0.12	8.23	0.23	27.00	0.074
13	0-30	69.85	11.87	18.29	Sandy loam	8.86	17.13	0.45	9.02	3.78	15.00	0.122
	30-60	82.96	4.35	12.69	Sandy loam	8.04	23.46	0.19	9.65	0.30	8.80	0.074
	60-90	82.80	5.68	11.52	Sandy loam	8.02	24.25	0.29	7.74	0.27	8.50	0.074
14	0-30	48.06	53.29	21.66	Loam	7.84	4.97	0.41	9.47	0.48	38.00	0.196
	30-60	12.84	68.43	18.73	Silt loam	7.97	2.80	0.66	8.69	0.48	31.00	0.090
	60-90	4.72	15.71	20.84	Silt loam	7.99	2.88	0.66	8.25	0.52	30.00	0.109
15	0-30	46.88	24.88	28.24	Sandy clay loam	8.19	31.00	0.38	11.16	0.70	23.00	0.292
	30-60	32.33	52.00	15.67	Silt loam	7.90	31.60	0.31	11.35	0.67	16.00	0.147
	60-90	27.68	56.56	15.76	Silt loam	7.85	37.37	0.52	11.49	0.67	16.00	0.157
16	0-30	15.58	54.25	30.17	Silty clay loam	7.76	2.53	1.33	17.36	0.61	37.00	0.467
	30-60	10.97	51.51	37.52	Silty clay loam	7.83	2.90	1.16	17.21	0.61	32.00	0.353
	60-90	7.53	60.14	32.33	Silty clay loam	7.91	3.12	1.17	16.93	0.59	31.00	0.359
17	0-30	11.67	56.79	31.54	Silty clay loam	7.77	3.88	1.24	7.90	0.81	39.00	0.474
	30-60	21.14	52.05	37.81	Silty clay loam	7.94	3.90	0.73	8.72	0.59	36.00	0.266
	60-90	7.16	57.65	35.19	Silty clay loam	7.97	3.20	0.92	8.56	0.48	30.00	0.208
18	0-10	20.12	45.86	49.02	Clay	7.86	4.10	1.11	9.39	0.93	32.00	0.804
	10-30	5.39	38.78	55.83	Clay	7.93	4.67	1.04	9.59	0.96	27.00	0.782
	30-60	5.02	39.48	55.50	Clay	7.85	3.70	0.75	9.28	0.70	25.00	0.369
	60-90	5.09	41.57	53.34	Clay	8.00	3.31	0.80	8.64	0.67	25.00	0.327
19	0-30	10.34	38.49	51.17	Clay	7.80	2.88	0.66	6.15	0.59	37.00	0.429
	30-60	7.62	64.24	28.14	Clay	7.76	2.53	0.79	5.62	0.53	33.00	0.353
	60-90	4.93	47.60	47.47	Clay	7.76	2.50	0.70	5.16	0.58	32.00	0.199

All samples had neutral to alkaline soil reaction and pH ranged between 7 and 10, but the alluvial soils had a slightly lower pH than the sandy soils. The contents of organic substance in all sampled soil horizons were low and reached the maximum of 1.3% (profile 16). The sandy soils still contained less organic material with a maximum of 0.4 % (profile 5). Carbonate content varied from 2.5% $CaCO_3$ up to nearly 70 % (profile 11).

2. Total contents of heavy metals in the soils

The results in Table (3) show that in upper depth, mean Cu content of the sandy desert soils is 5.8 mg kg^{-1} and of the alluvial soils 61 mg kg^{-1}. In both soil types, the concentrations slightly decreased with depth in sandy soils, and highly in alluvial soils (with a mean value of 4.4 and 44 mg kg^{-1} Cu respectively,. at 60-90 cm depth).

Table (3): Concentrations of various forms of Cu by sequential fractionation procedures (mg kg-1)

Profile No.	Depth, cm	Total content mg kg-1	No. of extraction and forms of fractions							
			1	2	3	4	5	6	7	8
			Mobile	Mobilise	Lime	Mn-Ox	Organic	Am-Fe	Cry-Fe	Residual
			Desert sandy soils							
1	0-40	4.00	0	0.69	0.53	0	0.01	0.10	0.63	1.88
	40-90	3.78	0	0.36	0.46	0				1.98
2	0-40	5.25	0	1.20	0.31	0	0.03	0.20	0.58	2.10
	40-90	3.83	0	0.44	0.75	0				2.34
3	0-60	4.00	0	0.43	0.19	0	0.01	0.14	0.38	1.00
	60-90	3.30	0	1.00	0.25	0				1.18
4	0-40	4.75	0	0.55	0.24	0	0.15	0.38	1.01	1.44
	40-90	4.20	0	0.54	0.21	0				1.89
5	0-30	5.50	0	0.71	0.18	0.08	0.08	0.79	1.23	1.49
	30-60	3.50	0	0.44	0.06	0.08				2.01
	60-90	2.03	0	0.38	0	0.19				1.21
6	0-60	5.98	0	0.43	0.61	0	1.03	0.83	1.28	1.45
	60-90	4.88	0	1.18	0.20	0				3.25
7	0-60	3.50	0	0.39	0	0	0.10	0.15	1.29	0.60
	60-90	2.33	0	0.34	0.23	0				0.96
8	0-40	5.00	0	0.54	0.09	0	0.09	0.14	1.40	1.75
	40-90	3.98	0	0.33	0	0				2.95
9	0-40	9.00	0	0.48	0.13	0	0.08	0.09	1.80	6.30
	40-90	7.23	0	0.30	0.09	0				6.55
10	0-40	5.75	0	0.16	0.63	0	0.14	0.56	1.80	2.25
	40-90	3.78	0	0.63	0.24	0				2.58
11	0-30	10.58	0.03	1.21	4.86	0.19	0.18	0.15	2.11	0.23
	30-60	9.50	0	0.50	4.41	0.23				2.10
	60-90	8.98	0	0.60	4.35	0.16				3.08
Alluvial Soils										
12	0-30	27.50	0.05	0.28	0	0	5.93	3.04	3.39	6.76
	30-60	26.48	0	0.54	0	0.04				9.60
	60-90	26.48	0	0.60	0	0				10.48
13	0-30	63.00	0.18	1.60	1.48	0.08	6.21	4.11	4.73	24.71
	30-60	16.83	0	0.66	2.14	0.10				9.48
	60-90	16.40	0	0.56	0.95	0				8.88
14	0-30	64.00	0	0.58	0	0.08	7.53	5.36	5.75	36.85
	30-60	63.33	0.02	0.40	0	0.01				44.98
	60-90	62.45	0	0.28	0	0.03				45.88
15	0-30	64.50	0	0.40	2.26	0.01	8.19	5.48	5.91	35.50
	30-60	45.98	0	1.00	2.28	0				29.88
	60-90	35.73	0	1.50	2.68	0.18				30.25
16	0-30	65.50	0.07	0.84	0	0	8.80	6.53	6.75	30.00
	30-60	52.28	0	0.51	0	0				33.40
	60-90	51.98	0	0.48	0	0				31.21
17	0-30	66.00	0.02	0.60	0	0.05	11.06	6.11	6.48	29.78
	30-60	54.40	0.10	0.58	0	0.13				47.80
	60-90	51.98	0	0.51	0	0.08				49.05
18	0-10	67.25	0.02	0.79	0	0.05	10.94	7.00	6.76	2.88
	10-30	58.98	0.03	0.71	0	0.03	10.98	5.50	5.75	23.09
	30-60	52.53	0	2.46	0	0.01				45.25
	60-90	51.98	0	0.68	0	0				46.00
19	0-30	69.00	0	0.51	0	0.25	11.33	7.50	8.01	43.50
	30-60	64.03	0	0.39	0	0.25				53.75
	60-90	53.18	0	0.48	0	0				50.18

In surface samples of sandy desert soils, mean Zn content was 4.5 mg kg^{-1} and in the alluvial soils is 56.63 mg kg^{-1}. Also, Zn concentrations were decreased with soil depth (Table 4).

Data given in Table (5) show that Fe and Mn concentrations are also higher in alluvial soils. Mean Fe content at surface soil samples is 58.58 g kg^{-1} and 12.41 g kg^{-1} in alluvial and sandy soils, respectively. It is worthy to note that the total iron contents in Egyptian desert and alluvial soils (5.4 to 34 g kg^{-1}), which were measured by El-Gala and Hendawy (1972), were lower than the Fe contents of the soils of this study. Mean Mn content at this depth was 703.0 mg kg^{-1} and 123.6 mg kg^{-1}, respectively. Also, Ghanem *et al*. (1972) found that in alluvial soils, Mn concentrations were higher than in sandy desert soils. Deposits from the river Nile contain high amounts of iron minerals which are concentrated in the clay and silt fraction (Rabie *et al*., 1981). Fe and Mn may be released from clay mineral deterioration. In contrast, the mineralogical composition of the sandy soils is responsible for their low Fe and Mn concentrations (Sillanpaa, 1962); the significant positive correlations between total iron and clay, silt and organic matter supported these results.

Data presented in Table (6) show that the total Pb contents of the alluvial soils are nearly twice the amount of the sandy soils (9.2 mg kg^{-1} and 4.8 mg kg^{-1}, respectively.). From the 1st depth to 2nd depth the concentrations reduced in both groups of soils to 4.8 mg kg^{-1} and 2.4 mg kg^{-1}, respectively.

On the base of the data of all soils, included in this study, the concentrations of Cu, Zn, Fe and Mn were positively correlated with the clay content (Cu: r=0.87***) and the amount of organic matter (Cu: r = 0.65**) Nutrients i.e. Cu, Zn, Fe and Mn ions were included in clay fractions or/and in parts of the organic matter. The results correspond well with those of Mohamed (1982), where concentrations of Cu, Zn, Fe and Mn were highest in clay, silt and sand fractions of soils of Egypt. Lead contents significantly and positively correlated with the $CaCO_3$ contents in the soils.

3. Heavy metals and their binding forms

Only very small part of the total heavy metal contents in the soils was mobile (Fig. 1 - 3). This is true for all measured metals. In the sandy desert soils no mobile Cu, Zn, Pb and Mn could be found. In the alluvial soils small mobile fractions of less than 0.5% of the whole metal contents were measured. In contrast, mobile Fe contents were about 2 mg kg^{-1} in sandy soils and 8 mg kg^{-1} in alluvial soils.

The solubility of heavy metals depends mainly on the soil reaction. Decreasing pH is correlated with increasing solubility (Abou-Seeda *et al*., 1992). Soil reaction differed only slightly between the investigated soils, showing neutral to alkaline soil reactions, no dependency on pH and little amounts of mobile metals were expected.

More Cu, Zn and Pb were found in the easily mobilisable fraction (Fig1-3) than in the mobile fraction. By using this extraction, in the Egypt alkaline soils a light weathering effect was simulated, which in natural systems can be caused by plant roots which can decrease the soil pH in the rhizosphere.

Table (4): Concentrations of various forms of Zn by sequential fractionation procedures (mg kg-1)

Profile No.	Depth, cm	Total content mg kg-1	No. of extraction and forms of fractions							
			1	2	3	4	5	6	7	8
			Mobile	Mobilise	Lime	Mn-Ox	Organic	Am-Fe	Cry-Fe	Residual
			Desert sandy soils							
1	0-40	3.00	0	0.39	0.43	0.11	0.02	0.10	0.56	1.33
	40-90	2.78	0	0.16	0.35	0				1.33
2	0-40	4.22	0	0.91	0.20	0.09	0.02	0.15	0.45	2.36
	40-90	2.80	0	0.27	0.66	0				1.82
3	0-60	2.99	0	0.27	0.25	0.09	0.01	0.14	0.29	1.96
	60-90	2.27	0	0.25	0.18	0				1.79
4	0-40	3.66	0	0.37	0.20	0.08	0.11	0.26	0.92	1.73
	40-90	3.11	0	0.31	0.17	0				2.60
5	0-30	4.47	0	0.49	0.15	0.18	0.18	0.60	1.11	1.69
	30-60	2.50	0	0.27	0.05	0.16				1.98
	60-90	1.00	0	0.17	0	0.09				0.75
6	0-60	4.88	0	0.25	0.51	0.11	1.00	0.61	1.15	1.22
	60-90	3.88	0	0.25	0.20	0				3.38
7	0-60	2.44	0	0.19	0.27	0.12	0.14	0.18	1.20	0.36
	60-90	1.29	0	0.14	0.19	0				1.00
8	0-40	3.97	0	0.33	0.08	0.08	0.19	0.11	1.31	1.85
	40-90	2.91	0	0.15	0	0				2.78
9	0-40	7.87	0	0.29	0.11	0.08	0.14	0.10	1.62	5.51
	40-90	5.98	0	0.13	0.07	0.08				5.39
10	0-40	4.61	0	0.11	0.54	0.13	0.14	0.39	1.69	1.61
	40-90	2.66	0	0.11	0.21	0.08				2.23
11	0-30	7.99	0.01	0.92	3.77	0.23	0.20	0.13	1.86	0.82
	30-60	6.45	0	0.44	3.11	0.19				2.70
	60-90	6.00	0	0.30	2.97	0.16				2.53
Alluvial soils										
12	0-30	24.50	0.03	0.30	1.22	0.12	4.66	2.11	2.98	13.00
	30-60	22.58	0	0.24	1.00	0.04				19.97
	60-90	22.44	0	0.22	0.66	0				21.50
13	0-30	48.11	0.13	1.18	1.24	0.20	5.48	3.22	3.66	32.86
	30-60	13.93	0	0.49	1.11	0.10				12.00
	60-90	13.41	0	0.36	0.84	0				12.30
14	0-30	49.50	0.01	0.48	1.10	0.17	6.77	4.13	4.70	32.00
	30-60	47.88	0.01	0.29	0.94	0.11				45.39
	60-90	45.45	0	0.19	0.47	0.03				43.99
15	0-30	50.00	0.01	0.27	1.26	0.18	7.63	4.48	4.97	31.13
	30-60	31.98	0	0.26	1.15	0.11				29.78
	60-90	23.25	0	0.26	0.99	0				21.55
16	0-30	51.41	0.05	0.64	0.54	0.22	8.00	5.49	5.78	31.00
	30-60	48.00	0	0.33	0.32	0.12				46.33
	60-90	42.22	0	0.27	0.29	0				40.78
17	0-30	52.44	0.10	0.48	0.59	0.15	10.44	5.53	5.96	30.00
	30-60	43.40	0.02	0.35	0.28	0.13				42.14
	60-90	42.00	0	0.26	0.19	0.08				41.60
18	0-10	52.88	0.03	0.58	0.61	0.19	10.11	6.24	6.13	29.50
	10-30	47.44	0.02	0.47	0.48	0.11	8.88	4.59	5.23	27.91
	30-60	40.66	0	0.47	0.27	0.07				40.31
	60-90	39.88	0	0.31	0.11	0				40.19
19	0-30	54.22	0.03	0.46	0.66	0.22	11.00	6.71	7.16	28.13
	30-60	49.78	0	0.24	0.44	0.20				48.10
	60-90	42.44	0	0.19	0.15	0				42.00

Table (5): Total content and mobile of Fe and Mn in the studied soils (mg kg^{-1}) .

Profile	Depth,	Total content		Mobile		Profile	Depth,	Total content		Mobile	
No	cm	Fe	Mn	Fe	Mn	No	cm	Fe	Mn	Fe	Mn
Desert sandy soils						Alluvial soils					
1	0-40	8886	81.50	2.16	0.03	12	0-30	44836	406.5	2.96	0.20
	40-90			0.78	0.03		30-60			1.84	0.20
2	0-40	6686	95.75	1.30	0.03		60-90			0.03	0.08
	40-90			1.24	0.03	13	0-30	22361	213.5	4.94	1.78
3	0-60	11536	115.0	0.38	0.03		30-60			3.21	1.16
	60-90			0.99	0.08		60-90			4.73	0.76
4	0-40	13561	126.3	1.09	0.01	14	0-30	71911	868.5	0.01	0.26
	40-90			3.93	0.00		30-60			0.21	0.06
5	0-30	14811	148.5	0.78	0.06		60-90			0.15	0.00
	30-60			0.53	0.00	15	0-30	31411	274.3	4.49	0.26
	60-90			0.68	0.05		30-60			3.85	0.38
6	0-60	20036	213.0	1.66	0.03		60-90			11.28	0.10
	60-90			1.34	0.03	16	0-30	69336	1011	2.88	0.63
7	0-60	14211	137.8	1.60	0.00		30-60			2.81	0.04
	60-90			0.33	0.03		60-90			2.76	0.00
8	0-40	9361	84.75	1.18	0.05	17	0-30	75836	659.0	0.64	0.34
	40-90			0.91	0.01		30-60			0.14	0.30
9	0-40	9861	96.25	1.04	0.00		60-90			4.45	0.10
	40-90			2.04	0.00	18	0-10	70261	957.5	1.75	0.10
10	0-40	18936	173.3	2.54	0.03		10-30	79086	1210.0	1.08	0.15
	40-90			6.39	0.01		30-60			0.96	0.01
11	0-30	8661	86.75	6.78	0.16		60-90			0.65	0.03
	30-60			4.45	0.13	19	0-30	82686	1232.0	0.10	1.25
	60-90			0.18	0.11		30-60			0.59	0.46
							60-90			0.18	0.21

Table (6): Concentrations of various forms of Pb by sequential fractionation procedures (mg kg-1)

Profile No.	Depth, cm	Total content mg kg-1	No. of extraction and forms of fractions							
			1	2	3	4	5	6	7	8
			Mobile	Mobilise	Lime	Mn-Ox	Organic	Am-Fe	Cry-Fe	Residual
			Desert sandy soils							
1	0-40	6.95	0.00	1.74	0.00	0.00	0.66	1.89	0.00	1.18
	40-90	1.95	0.00	0.58	0.00	0.00				0.83
2	0-40	6.63	0.00	1.23	0.36	1.04	0.70	1.43	0.29	1.20
	40-90	2.30	0.00	1.16	0.18	0.00				0.83
3	0-60	4.73	0.00	0.60	0.75	0.00	0.00	0.96	0.26	1.25
	60-90	3.50	0.24	2.49	0.00	0.00				0.63
4	0-40	2.18	0.23	0.00	0.00	0.00	0.21	0.48	0.09	1.00
	40-90	1.50	0.19	0.00	0.35	0.09				0.35
5	0-30	3.90	0.10	0.03	0.81	0.86	0.39	0.58	0.00	0.65
	30-60	3.40	0.10	0.00	0.64	1.18				0.45
	60-90	0.00	0.00	0.00	0.00	0.00				0.00
6	0-60	2.90	0.00	1.23	0.00	0.14	0.20	0.39	0.00	0.75
	60-90	1.25	0.00	0.40	0.00	0.00				0.63
7	0-60	3.70	0.00	1.23	0.40	0.00	0.00	0.00	0.44	1.38
	60-90	1.50	0.00	0.34	0.00	0.00				1.08
8	0-40	3.98	0.00	0.00	0.11	0.00	0.85	1.09	0.00	1.75
	40-90	2.00	0.00	0.00	0.58	0.76				0.25
9	0-40	6.03	0.00	0.43	0.39	2.74	0.13	0.00	0.00	1.05
	40-90	2.00	0.00	0.00	0.00	1.70				0.25
10	0-40	4.80	0.00	0.29	0.40	0.91	2.20	0.00	0.00	0.75
	40-90	3.20	0.00	1.63	0.78	0.20				0.50
11	0-30	6.50	0.00	1.59	1.75	0.00	0.00	0.46	0.11	2.25
	30-60	3.48	0.00	1.35	0.56	0.29				1.03
	60-90	2.00	0.80	1.58	0.28	0.00				0.00
Alluvial soils										
12	0-30	5.63	0.00	0.00	0.48	1.96	1.36	0.11	0.00	0.98
	30-60	3.00	0.00	0.00	0.58	1.73				0.65
	60-90	2.00	0.00	0.00	0.00	1.96				0.00
13	0-30	9.88	0.00	0.84	2.28	2.58	2.15	0.88	0.00	0.83
	30-60	5.00	0.00	0.00	2.66	1.35				0.75
	60-90	1.50	0.10	0.00	0.55	0.49				0.00
14	0-30	9.43	0.18	0.41	0.10	2.45	3.04	1.99	0.03	1.05
	30-60	4.80	0.00	0.00	0.40	2.80				0.75
	60-90	2.70	0.00	0.00	0.66	1.66				0.00
15	0-30	8.90	0.00	1.38	0.89	2.51	0.48	0.05	0.00	2.50
	30-60	8.45	0.00	2.31	0.38	2.76				2.50
	60-90	4.48	0.00	1.40	0.39	0.21				2.25
16	0-30	10.00	0.40	0.75	0.49	0.18	5.16	0.44	0.00	2.75
	30-60	3.98	0.80	0.55	1.14	0.00				2.00
	60-90	2.78	0.00	0.85	0.29	0.00				1.25
17	0-30	11.08	0.00	1.94	0.00	0.71	4.65	1.63	0.00	1.80
	30-60	5.50	0.00	0.70	0.00	2.03				0.83
	60-90	1.95	0.00	0.00	0.71	0.91				0.35
18	0-10	8.23	0.00	0.00	0.00	0.81	3.90	0.00	0.13	3.00
	10-30	7.70	0.00	0.00	0.44	2.33	3.39	0.93	0.00	0.45
	30-60	5.75	0.00	0.00	0.18	2.41				0.45
	60-90	0.00	0.00	0.00	0.00	0.00				0.00
19	0-30	10.29	0.24	1.09	0.23	0.68	3.01	2.21	0.03	2.5
	30-60	4.95	0.16	0.55	0.00	1.33				2.00
	60-90	4.70	0.48	0.88	0.83	1.90				1.00

Fig. (1)

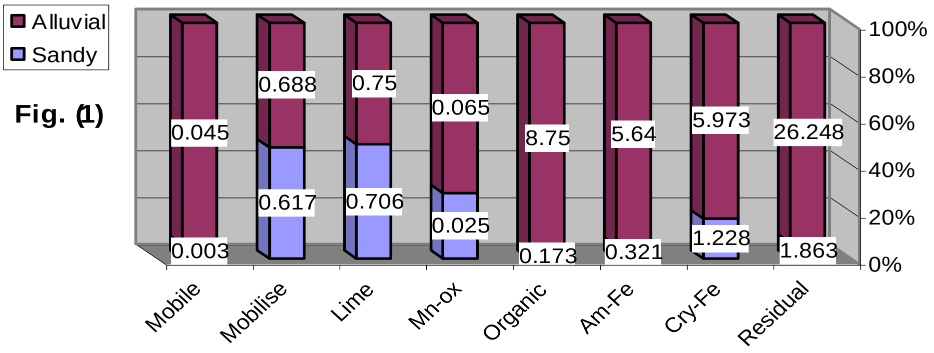

Fig. (2)

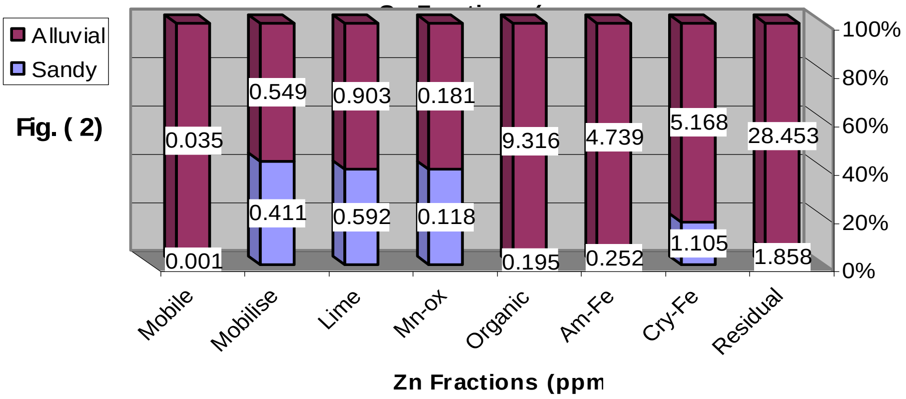

Fig.(3)

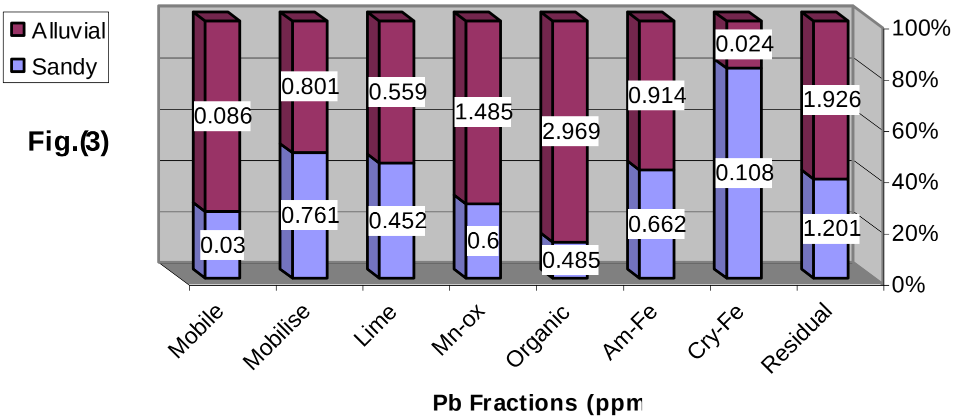

Fig. (1-3): Means of concentrations of Cu, Zn and Pb in various fractions (ppm) in the studied soils, A-horizons.

The percentage of these weakly bound metals reached a maximum of about 10% of the total Cu and Zn contents in the sandy soils. In the alluvial soils, however, a maximum of 2.5% Cu were found in the mobilisable fraction. On average, the total contents of copper in the alluvial soils were ten times higher than in the sandy soils, but nearly the same amounts of copper were assessed by the second step (0.6 mg kg^{-1} and 0.69 mg kg^{-1} in sandy and alluvial soils, resp.). It can therefore be concluded that both groups of soils deliver the same available metal pool for plant growth. The same results were found for Zn (0.4 mg kg^{-1} of easily mobilizable Zn for sandy soils and 0.5 mg kg^{-1} for alluvial soils). Comparable results were found for lead. In sandy soils 16 % of total Pb was easily mobilisable and 8.7 %.in alluvial soils.

All soil samples of this study were carbonatic (Table 2). The extraction method proposed by Zeien and Brümmer (1989), listed in Table 1, combined step 2 and 3 is supposed to lead to an overestimation of the mobilisable fraction of the tested heavy metals. Therefore we introduced a new step and seperated the easily mobilisable fraction from the metals bound to carbonates.

In sandy soils, up to 12% of Cu and Zn were lime bound and the concentrations of metals which were extracted by the third extraction step were positively correlated to the $CaCO_3$ contents in the soils (r=0.96,0.70,0.78 for Cu,Zn and Pb, respectively). However, Ca ions are strong exchangers and when carbonates are dissolved, Ca ions might cause a release of heavy metals which are bound to the exchange complex. As a consequence, the concentration of metals in the soil solution will raise. Further investigations are necessary to support these assumptions.

Small amounts of Cu, Zn and Pb were occluded in Mn-oxides in both groups of soils, but 10%and 15%were bounded in Mn-oxides in sandy and alluvial soils , respectively .

Heavy metals which were bound to the organic fraction depended on the amount of organic matter in the soils. In alluvial samples a large part of Cu, Zn (about 14%) and Pb (32%) were bound to the soil organic matter. In the desert soils only small fractions of these heavy metals were bound to the organic matter of the soils.

Significant fractions of Cu, Zn and Pb were occluded in amorphous or crystalline Fe-oxides. In sandy soils up to 24 % of total Zn and 21% of total Cu were measured in the fraction of crystalline Fe-oxides. Less metals were occluded in amorphous Fe-oxides in these soils. The contents of amorphous Fe-Oxides were low in sandy soils. This might be due to a long time period of soil development which led to Fe-oxides of high cristallinity . In alluvial soils, however, higher concentrations of amorphous Fe-Oxides were found, the metals were equally distributed between amorphous and crystalline Fe-oxides and the metal contents were approx. 10 % of the total metal contents. In contrast, the fraction of Pb which was bound to Fe-oxides was very low; higher amounts were measured in amorphous Fe-oxides than in crystalline ones.

The major parts of Cu, Zn and Pb were bound to the residual fraction of both groups of soils. In alluvial soils, however, most Pb was bound to the organic fraction.

CONCLUSION

Determination of the total contents of heavy metals in soils allow no statement about their availability for plants. Total contents of Cu and Zn were higher in the alluvial soils as compared to the reclaimed desert soils, but nearly the same amounts of mobile and easily mobilisable metals were measured in the two types of soil.

This study on selected soils in Middle Egypt characterized the heavy metal contents and their specific binding forms. On the base of this characterization, further investigations will be made to assess the impact of metal mobility on the uptake of metals in agricultural plants growing on these soils.

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محتوى بعض العناصر الثقيلة والصور الكيميائية المختلفة لها فى بعض أراضى مصر الوسطى

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- فى هذه الدراسة تم حفر 19 قطاع تمثل الأراضى الرملية والرسوبية فى منطقة مصر الوسطى لتقدير محتوى هذه الأراضى من بعض العناصر الثقيله (النحاس والزنك والحديد والمنجنيز والرصاص) ، وكذلك الصور الكيميائية المختلفة لهذه العناصر وذلك بطريقة الإستخلاص المتتابع ، حيث إستخلصت الأرض بواسطة محلول نترات أمونيوم 1 مولر (يستخلص الجزء الذائب + المتبادل) ، محلول خلات أمونيوم 1 مولر (يستخلص الجزء القابل للتيسر) ، محلول خلات أمونيوم 1 مولر + حامض هيدروكلوريك (يستخلص الجزء المرتبط بكربونات الكالسيوم) ، هيدروكسيل أمين هيدروكلوريد 0.1 مولر + خلات أمونيوم 1 مولر (يستخلص الجزء المرتبط بأكسيد المنجنيز) ، محلول NH_4 – EDTA (يستخلص الجزء المرتبط بالمركبات العضوية) ، محلول أكسالات الأمونيوم 0.2 مولر (يستخلص الجزء المرتبط بالحديد الغير متبلور) ، حامض الأسكوربيك 0.1 مولر + أكسالات الأمونيوم 0.2 مولر (يستخلص الجزء المرتبط بالحديد المتبلور) وأخيرا محلول حامض هيدروكلوريك + حامض نيتريك مركز (يستخلص الجزء الذى لم يستخلص بالمحاليل السابقة وهو المرتبط بمعادن السيليكات ويسمى بالجزء المتبقى) .
- تبين من نتائج هذه الدراسة مايلى :

□ المحتوى الكلى من عناصر النحاس والزنك والحديد والمنجنيز والرصاص فى الأراضى الرسوبية أعلى من محتواه فى الأراضى الرملية الصحراوية .

□ الإختلافات بين الأرضين فيما يتعلق بالصورة الذائبة والصورة القابلة للتيسر من هذه العناصر إختلافات قليلة وتكاد تنعدم .

□ وجد أن معظم النحاس والزنك فى الأراضى الرملية والرسوبية كان مرتبطا مع السيليكات.

□ فى الأراضى المحتوية على نسبة عالية من الكربونات إرتبط جزء من النحاس والزنك مع كربونات الكالسيوم فى صورة غير ميسره .

□ فى الأراضى الرسوبية وجد أن معظم النحاس والزنك والرصاص كان مرتبطا بالمادة العضوية ، بينما فى الأراضى الرملية وجد أن معظم الرصاص كان مرتبطا بالجزء المعدنى من مكونات التربة .

- وقد كان التوزيع النسبى للصور الكيميائية لمعظم الفلزات فى الأراضى الرسوبية كالآتى :

الجزء المرتبط عضويا > الجزء المرتبط بالأكاسيد الحره > الجزء المرتبط بكربونات الكالسيوم> الجزء القابل للتيسر > الجزء الذائب + المتبادل .

بينما فى الأراضى الرملية الصحراوية كان التوزيع النسبى للصور الكيميائية المختلفة لمعظم الفلزات كالآتى :

الجزء المرتبط بالأكاسيد الحره > الجزء المرتبط بكربونات الكالسيوم > الجزء القابل للتيسر >الجزء المرتبط عضويا > الجزء الذائب + المتبادل .