Mineralo-Chemical Study of Copper Distribution and Forms in Soils of The 10th of Ramadan Region

S. El-Demerdashe*, Tomader El- Essawi**, N.M.A. Bahnasawy* and A.M. Elwa*

*Desert Research Center, Cairo and **Faculty of Science, Benha Univ., Benha, Egypt

THE CURRENT study is performed to investigate Cu status, content, distribution and speciation in the newly reclaimed soils of the 10^{th} of Ramadan region. To achieve this objective, the physico-chemical and mineralogical soil characteristics were first identified to shed light on the major soil properties that may control Cu behavior in the concerned soils. Eight soil profiles were selected to represent the soil mapping units and the variations encountered in these soils with respect to texture, CaCO₃, OM, soil reaction, soil salinity and its components. Besides, surface area and adsorption desorption areas on the soil surface and their relations to clay minerals and accessory minerals constitution which displayed certain differences that reflected on the different Cu forms. Noteworthy that none of Cu-bearing minerals has been detected.

The obtained results reveal that total Cu, DTPA - extractable Cu and speciation (forms) of Cu vary widely within and between the examined soil profiles. For convenience, total and DTPA – extractable Cu range from 4.88 to 19.19 mg/kg and 1.56 to 4.51 mg/kg, respectively. The total and extractable Cu as well as the speciation forms of Cu were interpreted and their distribution in relation to soil variables and interrelations between Cu forms were statistically evaluated.

Sequential extraction indicates that the residual Cu which is the inert fraction is the major abundant form, while, Fe-Mn form is the second important form. Those forms constitute 44.43 to 76.50 % and 14.75 to 32.76 % of total Cu. Other labile fractions, i.e. soluble Cu, exchangeable Cu, carbonate bound Cu and organic–bound forms constitute 2.35 to 4.02 %, 1.71 to 4.09 %, 1.54 to 4.84 % and, 0.45 to 2.73 % of total Cu, respectively. Consequently, the study provides useful information about soil Cu mobility and bioavailability as essential micronutrient to plants, and food- chain of animals and human beings. The contribution of Cu to soil pollution and contamination is also considered through computation of enrichment factor and single pollution index.

Introduction

Copper (Cu^{2+}) is one of the heavy trace metals that naturally occurs in soils due to its inheritance from parent rock forming these soils and could be modified during pedogenesis. Though Cu^{2+} is an essential micronutrient for plants, yet it is one of the major toxic metals and a highly reactive one as well. Elevated levels of Cu^{2+} in agricultural soils result from the use of Cu^{2+} containing compounds to control plant diseases, applied fertilizers, amendments, pesticides, waste water irrigation, atmospheric deposition, waste materials and industrial activities. Due to the lack of information about Cu^{2+} status, distribution and speciation (forms) in the newly reclaimed soils of the 10^{th} of Ramadan region, which exhibits rapid urbanization due to population growth in the Nile valley and Delta region, this research work is conducted. Undoubtedly, total Cu^{2+} content and chemical speciation are essential to characterize Cu^{2+} behavior in the soil ecosystem(Marija et al., 2014), especially in the newly reclaimed coarse textured soils as they determine not only plant uptake, soil retention and pollution of Cu^{2+} but also the extent to which Cu^{2+} is leached out of the active zone of grown plant roots (Robson et al., 2013).

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Therefore, the current research is carried out to study Cu^{2+} content and distribution in eight soil profiles representing the study area, to identify the common Cu^{2+} forms, to assess their bioavailability and to correlate the Cu^{2+} content and forms to physicochemical properties of the studied soils.

Materials and Methods

Soils and irrigation water sampling

The study area (Fig. 1) is located between Long. $31^{\circ}16^{\circ}$ N to $31^{\circ}46^{\circ}$ E and Lat. $30^{\circ}22^{\circ}$, N to $31^{\circ}76^{\circ}$ E. Eight soil profiles representing the dominant soil mapping units identified in this area were selected for study. Soil samples were carefully collected from the subsequent layers including the top layer, the subsurface and the layer beneath in each profile, respectively. All the soil samples were air- dried, ground and passed through a 2 mm sieve to get the "fine earth". Quartering is undertaken to get homogenous subsamples for the different analyses.

Besides, seven irrigation water samples from the same sites of each profile (Nile water, drainage water, groundwater and mixed water) were collected and kept for analysis.



Fig. 1. Location of the studied soil profiles.

Soil analyses

- -The main characteristics of the studied soils were determined as follows:
- -Particle size distribution by the pipette and dry sieving methods and soil texture was recorded (James, 2007).
- -Calcium carbonate content was determined using Collin's calcimeter (Cottenie et al., 1982 and Bui et al., 1990).

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- pH in the soil extract 1: 2.5 using pH meter, 3320 Jenway, Black (1986) and Soil Testing Laboratory (2012).
- -Total soil salinity (ECe) was measured in the soil saturation extract using conductivity meter (YSI model 35) and soluble cations & anions were determined following the methods of Page et al. (1982), Klute (1986) and Black (1986).
- Organic matter content and CEC were determined as recommended by Jackson (1973) and Mehlich (1984), respectively.
- -Separation of the clay fraction (less than 2 μ) was carried out after the essential pretreatments. The separated clays were X-rayed by a Philips PW 3710 installation supplied with a horizontal goniometry and a vertical object plane, using Ni-filtered Cu radiation (40 Kv operating voltage and current of 35 m Å). Identification of the different clay and nonclay minerals was carried out following the criteria established by Brown & Brindley (1980), Moore & Reynolds, (1989) and Burhan (2011).
- Surface area was measured by BET method (Ostafiychuk et al., 2014).
- Cumulative adsorption and desorption surfaces (BJH and DH) and external surface area were determined by Quanta chrome Nova automated gas sorption system Model (Nova 2000 series, USA).

Soil copper fractionation procedure

Total soil Cu was determined by the mineralization of soil sample in the solution of aqua regia (HCl and HNO₃) in the ratio 3:1 (Sparks, 1996).

Sequential extraction procedure of Tessier et al. (1979) modified by Qiao and Ho (1997) was used on 2 g soil to partition total soil Cu into fractions or forms follows:

i) Water soluble fraction (F1): extracted with 20 ml deionized water for 2 hr.

ii) Exchangeable fraction (F2): residue from F1 extracted with 20 ml of 1 mol l^{-1} Mg Cl₂, pH 7 for 1 hr.

iii) Carbonate-bound fraction (F3): residue from F2 extracted with 20 ml of 1 mol 1^{-1} NH₄OH₂, pH5 for 5 hr.

iv) Fe-Mn oxide-bound fraction (F4): residue from F3 after cooling, 5ml of 3:2 mol l^{-1} NH₄OAc in 20 % HNO₃ was added and shaken for 30 min. before final dilution to 20 ml with deionized water. *V) Organic bound fraction (F5):* residue from Fe-Mn oxide fraction was extracted with 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ (adjusted to pH 2 with HNO₃). The mixture is heated to

of 0.02 *M* HNO₃ and 5 ml of 30% H₂O₂ (adjusted to pH 2 with HNO₃). The mixture is heated to 85°C for 2 hr, with occasional agitation. A second 3-ml aliquot of 30 % H₂O₂ (pH 2 with HNO₃) was added and the mixture was heated again to 85°C for 3 hours with intermittent agitation. After cooling, 5 ml of 3.2 *M* NH₄OAc in 20 % (v/v) HNO₃ was added and the samples diluted to 20 ml and agitated continuously for 30 min.

vi) Residual fraction (F6): residue from F5 was digested using HF-HCl-HNO₃ (hydrofluoric / aqua regia). All the solid phases from F1 to F5 were washed with 10 ml deionized water before further extraction. The washes were collected with supernatant from the previous fraction. After each extraction, the supernatant was separated by centrifugation at 10,000 ppm for 30 min. Moreover, chemically extractable Cu was extracted from all soil samples by DTPA, Lindsay and Norvell (1978). Total Cu, DTPA – extractable Cu and extracted Cu fractions were determined by Inductively Coupled Plasma (ICP).

-Irrigation water samples were also analyzed for their chemical properties (pH, EC, soluble cations and anions) (Jackson, 1973) and their Cu contents were determined by ICP.

Results and Discussion

Soil characteristics

The soils under study are mineral soils formed essentially of sand with clay and silt intercalations, mostly in the uppermost surface in some profiles (1, 3, 4 and 6) and sometimes in deeper layer (profile 5). Consequently soil texture (Table 1) is sand to sandy loam. CaCO₃ content is quite low, not exceeding 4.34 % and organic matter content is very low (0.05-0.69). Soil reaction is neutral to alkaline as indicated by pH values (6.98- 8.68) (Table 2). The soil layers are non-saline to saline as shown by EC values which range from 0.8- 8.12 dS/m. Cationic and anionic compositions of the soil extract follow two distinct patterns for cations of which Ca⁺²> Mg $^{+2}$ Na⁺> K⁺ is the dominant in about two thirds of the samples while Ca^{2+>} Na $^+>$ Mg $^{2+>}$ K⁺ is less abundant. The soluble anions are dominated with $\mathrm{SO}_{\scriptscriptstyle\!A}^{\ 2\text{-}}$ followed by Cl- in almost all profiles layers except for few cases, CO₃²⁻ is entirely absent and HCO, is the least abundant. CEC values vary from 1.42 to 7.34 me/100g with higher values for the loamy sand and sandy loam layers. In brief, the data concerning soil characteristics of the studied profiles are presented in Tables 1 and 2.

TABLE 1. Particle size distribution and texture classes of the	studied soils
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	D 01		Gravel		Soil fractions (%	6)		
Land use	Profile No.	Depth, Cm.	%	Coarse sand	Fine sand	Silt	Clay	Texture Class
		0 - 30	12.25	58.69	23.20	8.02	10.09	Loamy sand
		30- 60	5.51	33.83	40.10	8.01	18.06	Loamy sand
	1	60 - 90	0.33	16.84	80.77	0.30	2.09	Sand
		90 - 120	4.92	53.8	21.90	6.25	18.05	Loamy sand
		120 -150	41.38	61.5	37.27	0.23	1.00	Sand
		0 - 20	19.18	77.78	21.69	0.12	0.41	Sand
		20 - 35	16.67	28.90	69.28	0.70	1.12	Sand
ted	2	35 - 60	8.99	64.99	33.99	0.15	0.87	Sand
tiva		60 - 80	29.63	79.99	18.95	0.21	0.85	Sand
Cul		80 - 160	8.47	81.50	17.70	0.15	0.65	Sand
		0 - 30	27.95	33.82	49.83	2.17	14.18	Loamy sand
	2	30 - 70	11.76	60.68	12.52	12.60	14.20	Loamy sand
	3	70 -100	3.28	68.47	30.18	0.33	1.02	Sand
		100 -150	3.57	74.11	25.19	0.16	0.54	Sand
		0-20	15.63	33.34	41.60	6.24	18.82	Loamy sand
	4	20 - 70	487.57	74.70	24.15	0.13	1.02	Sand
	-	70 -100	25.93	75.96	23.09	0.16	0.79	Sand
		100 -150	0.40	67.92	31.27	0.18	0.63	Sand
	5	0-20	26.05	66.12	32.28	0.49	1.11	Sand
	5	20 - 50	0.33	58.97	38.97	0.21	1.85	Sand

pr e	Profile	Depth.	Gravel		Soil fractions (9	%)		Texture
Lar use	No.	Cm.	%	Coarse sand	Fine sand	Silt	Clay	Class
ed		50 - 80	3.17	63.78	13.94	4.17	18.11	Loamy sand
ıltivat	5	80-110	7.84	60.08	38.16	0.64	1.12	Sand
Un-cı		110-150	2.60	60.75	37.69	0.50	1.06	Sand
		0 - 30	15.38	49.47	20.18	11.10	19.25	Sandy Loam
		30 - 60	45.45	69.21	8.75	16.02	6.02	Loamy sand
	6	60 - 110	16.44	75.09	24.21	0.15	0.55	Sand
		110 -150	38.34	86.87	12.81	0.06	0.26	Sand
		0-20	80.86	65.98	32.04	0.52	1.46	Sand
ed		20 - 50	51.61	64.85	33.84	0.25	1.06	Sand
ıltivat	7	50 - 80	45.16	65.99	32.07	0.43	1.51	Sand
C		80-125	33.33	80.12	18.97	0.31	0.60	Sand
		125 -160	41.78	81.92	17.35	0.14	0.59	Sand
		0 - 50	6.06	82.25	17.29	0.12	0.34	Sand
	8	50 - 100	3.73	86.61	12.82	0.13	0.44	Sand
		100 -150	3.89	86.98	12.75	0.08	0.19	Sand

TABLE 1. Contd.

TABLE 2. Chemical properties of the studied soils.

Land	Profile	Depth,	pH	EC	CaCO ₃	O.M		Catio	ıs (me/l)			Anions	(me/l)		C.E.C
use	No.	Cm.	(1:2.5)	dS/m	%	%	Na ⁺	\mathbf{K}^{+}	Ca ²⁺	Mg ²⁺	CO ₃ ²⁻	HCO ¹	Cŀ	SO42-	me/100g
		0 -30	8.68	1.18	2.60	0.46	3.78	0.75	4.44	2.78	0.00	3.33	6.11	2.29	4.04
		30 -60	7.07	2.67	2.90	0.35	1.91	0.18	18.50	6.00	0.00	4.50	7.25	14.84	5.58
	1	60 -90	7.08	3.36	3.15	0.35	1.11	0.15	25.50	7.00	0.00	2.50	5.75	25.51	5.08
		90 -120	7.42	1.95	3.23	0.29	0.66	0.11	12.00	6.50	0.00	4.00	6.75	8.52	3.50
		120 -150	7.83	1.16	0.68	0.29	1.89	0.15	6.00	3.00	0.00	4.00	4.50	2.54	4.82
		0 - 20	7.05	2.12	1.28	0.46	4.74	0.31	11.50	4.50	0.00	1.50	6.25	11.30	3.26
		20 - 35	7.41	2.88	1.02	0.17	4.57	0.32	20.50	3.50	0.00	5.00	6.50	17.39	3.34
_	2	35 - 60	6.98	1.16	1.10	0.29	3.57	0.31	5.00	3.00	0.00	3.50	4.50	3.88	3.36
atec		60 - 80	7.07	2.99	1.19	0.28	3.63	0.43	21.50	4.00	0.00	2.00	3.75	20.81	3.86
ıltiv		80 - 160	7.18	1.69	0.85	0.35	2.57	0.31	12.50	1.50	0.00	2.50	5.00	9.38	3.04
C		0 - 30	7.03	2.59	1.28	0.69	5.01	0.81	11.00	9.00	0.00	5.00	6.50	14.32	4.74
	2	30 - 70	7.15	2.14	3.40	0.28	4.93	0.48	10.00	6.00	0.00	4.50	6.25	10.66	4.66
	3	70 -100	6.79	2.65	1.96	0.23	4.32	0.22	13.00	8.50	0.00	2.00	6.75	17.29	5.22
		100-150	8.28	1.89	2.21	0.23	6.48	0.17	8.50	3.50	0.00	5.00	6.00	7.65	4.62
		0-20	7.10	1.95	2.13	0.12	6.76	0.73	7.50	5.00	0.00	3.00	5.50	11.49	6.22
	4	20 - 70	7.02	3.26	2.13	0.41	5.62	0.72	23.00	3.50	0.00	3.50	6.50	22.84	6.16
	4	70 -100	7.08	3.57	1.02	0.29	1.94	0.19	25.00	8.50	0.00	3.50	7.00	25.13	4.70
		100 -150	7.92	3.23	0.60	0.17	2.25	0.15	22.50	7.50	0.00	1.50	4.00	26.90	4.58
		0-20	7.35	4.73	1.19	0.41	9.44	0.56	25.00	12.50	0.00	3.00	15.00	29.50	4.10
ated		20 - 50	7.43	3.42	1.79	0.35	4.97	0.61	20.00	8.50	0.00	2.50	6.75	24.83	4.52
ltiva	5	50 - 80	7.32	3.51	1.79	0.35	2.79	0.39	25.00	7.00	0.00	4.50	5.75	24.93	4.46
ncu		80-110	7.06	3.45	1.70	0.23	3.73	0.43	24.00	6.50	0.00	4.00	5.56.	24.10	4.42
D		110-150	7.20	4.35	1.70	0.05	8.52	0.17	28.50	6.50	0.00	2.00	6.00	29.69	4.82
Ξ÷		0 - 30	7.11	8.12	4.34	0.12	33.69	0.85	42.50	4.00	0.00	4.20	50.00	26.84	7.34
Cul	6	30-60	7.20	3.14	1.45	0.41	5.53	0.25	22.50	3.50	0.00	3.00	8.25	19.53	3.86
		60-110	7.14	2.06	1.70	0.35	2.66	0.23	12.00	5.50	0.00	3.00	7.00	10.39	3.96

TABLE 2	2. Contd	l.													
Land	Profile	Depth,	pН	EC	CaCO ₃	O.M		Catior	ns (me /l)			Anions	(me/l)		C.E.C
use	No.	Cm.		dS/m	%	%	Na^+	\mathbf{K}^{+}	Ca ²⁺	Mg^{2+}	CO32-	HCO3.	Cŀ	SO42-	me/100g
	6	110 -150	7.51	2.21	0.43	0.29	4.21	0.18	11.50	6.50	0.00	3.00	5.50	13.89	2.82
		0-20	6.98	1.19	1.96	0.41	1.53	0.29	6.00	4.00	0.00	3.50	6.00	2.32	4.06
		20 - 50	8.17	1.12	0.85	0.23	2.32	0.21	5.00	3.50	0.00	3.00	4.00	3.82	3.68
	7	50 - 80	7.54	1.39	2.99	0.17	3.64	0.23	6.00	4.00	0.00	3.50	5.00	5.37	4.08
Cultivated		80-125	7.40	2.21	3.40	0.05	4.93	0.38	12.00	5.00	0.00	2.00	4.00	16.31	4.86
		125-160	7.84	1.26	3.06	0.29	4.14	0.17	4.50	4.00	0.00	2.50	7.65	2.66	4.08
		0 -50	8.32	4.02	0.00	0.12	7.61	0.31	22.50	10.00	0.00	1.50	9.25	29.67	2.34
	8	50 -100	7.73	1.06	0.00	0.29	2.43	0.12	4.50	3.50	0.00	1.50	3.50	5.55	2.16
		100-150	8.35	0.81	0.17	0.12	2.41	0.11	3.50	2.00	0.00	2.00	4.00	2.02	1.42

-Mineralogy of the clay fraction.

To provide more information about the studied soils, the mineralogical composition of the clay fraction which is the most reactive portion of soils was identified. The clay fractions separated from the seven loamy sand and sandy loam layers as well as one of the sandy layers were X- rayed and their X-ray diffraction patterns are presented (Fig. 2), and identified on the basis of the guidelines provided by Dixon & Schulze (2002) and Harris & White (2007) (Table 3).

The obtained results indicated that kaolinite is present in moderate amounts in all clays except the clay fraction of 50-80 Cm. and 0-30 Cm. layers of profiles 5 and 6, respectively which exhibit few kaolinite. Montmorillonite is detected in traceable amounts (surface and subsurface layers of profile 1 and surface layer of profile 6) to few amounts (surface layer of profile 3, subsurface of profile 6 and deep layer of profile 5,) and in moderate amount in the top layer of profile 4 while being entirely absent in the uppermost surface layer of profile 7. Illite is detected in traces to few amounts in four layers while being absent in other layers. In short, the dominant clay minerals in almost all the investigated layers are kaolinite followed by montmorillonite in all the examined samples.

The identified accessory minerals are dominated with gypsum and quartz which are present in few to dominant and few amounts, respectively.

The identified carbonate group is dominated with dolomite which occurs in all samples in trace to moderate amounts while calcite is found in traceable amounts in the top layers of profiles 1 and 7 and the subsurface layer of profile 6.Aragonite is also detected in few amounts only in the top surface of profile 1 and the subsurface layer of profile 6.This means that dolomite is the main carbonate mineral.

Besides, magnetite is only identified in the surface layer of profile 4 and disappeared in other examined samples.

Fe group is dominated with hematite which is detected as traces to few amounts in 5 samples while disappeared in the surface layers of profiles 3, 4 and 7. Pyrite and goethite are only detected in the top surface of profile 1 and the deepest layer of profile 5, magnetite is detected as traces in the surface layer of the same profile. Micaceous group is detected as few amounts of biotite only in the clay fractions of the top surface of profiles 1 and 6 with few amounts of muscovite in the subsurface layer of profile 6. Likewise, K- feldspar is only detected in the surface layer of profile 6. Halite is also detected as traces in some samples representing the subsurface layers or deeper (profiles 1, 5, 6) and the top surface of profile 7.

Commenting on the aforementioned mineralogical composition of the clay fraction, it is apparent that it displays remarkable variations within and between the studied clay samples. These variations are mainly rendered to landscape toposequence, chance of variation in parent material of these soils and sedimentation regime of parent sediments according to Trudgill (1985). Noteworthy to mention that none of the Cu- bearing minerals are identified in the studied samples.

Surface area

Align with mineralogical composition, surface area of the same samples and cumulative gas adsorption and desorption on surface area are presented (Table 4). From the table it is clear that the surface area of the selected clay samples ranges from 13.26 to 20.17 m²/g. The lowest area characterizes the top surface layer of profile 7 whereas the highest area is associated with the top surface layer of profile 4. The great variations in surface area are mainly rendered to the occurrence of montmorillonite in various amounts ranging from traces to moderate. This is also reflected on gas adsorption and desorption on surface area which ranges from 1.795 to 2.728 m²/g and 1.837 to 2.789 m²/g for cumulative adsorption and 1.897 to2.866 m2/g and 1.934 to 2.917 m²/g for desorption, as measured by BJH and DH methods which provide results within the same range of magnitude according to Ostafiychuk et al. (2014).



Fig. 2. X-Ray Diffractogrames of the Clay Fraction of the Studied Soils in the 10th of Ramadan Region.

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	No.	Cm.																
		0-30	+	3+		2+	2+	+	+	2+	2^{+}	+			2+			ı
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Cultured and	4	0-20	3+	3+	ı	5+	2+	ı	ı	·			·	+	ı	ı	ı	·
Uncultivated soils	5	50-80	2+	5+	+	5+	2+	3+	ı	,	+	ı	+	ı	,	ı		+
		0-30	+	2+	ı	4+	2+	÷ +	·	ı	+	ı	ı	ı	2+	ı	+	ı
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Chemical composition of irrigation water

Data in Table 5 show pH values of irrigation water ranging from 7.59 to 8.23, indicating alkaline, mildly alkaline and moderately alkaline reactions for Nile water, mixed water and drainage water, respectively. Nile water is non saline, drainage and mixed waters are non- saline to slightly saline while ground- water is highly saline as shown by EC values. Soluble cations follow two patterns namely; $Mg^{2+>} Ca^{2+} > Na^+ >$ K $^{\scriptscriptstyle +}$ for Nile water and $~~Na^{\scriptscriptstyle +} > Mg^{2 \scriptscriptstyle +} > Ca^{2 \scriptscriptstyle +} > K^{\scriptscriptstyle +}$ in the other irrigation waters. Soluble anions also follow two patterns; $SO_4^{2-} > Cl^- > HCO_3^-$ in Nile and drainage waters (profile 2), and $HCO_3^- > Cl^-$ > SO₄²⁻ in the other irrigation waters. Soluble Cu in irrigation water was also determined to search for its contribution to soil Cu and it is found that its content ranges from < 0.01 to 0.10 mg/Kg, the lowest content is that of groundwater and mixed water while other waters contain 0.07 to 0.10 mg/ Kg soluble Cu. Soluble Al, Fe and Mn were also detected due to their possible role in Cu forms of soils. Their content ranges from 0.04 to 0.78,0.05 to 1.73 and 0.01 to 0.64 mg/Kg, respectively.

Copper (Cu) in the studied soils Total Cu

The results of total Cu contents in the 10th of Ramadan soils are tabulated, Table 6. These results indicate that the soils have a total Cu content that ranges from 4.88 to 19.19 mg/kg with a mean of 9.95 mg/kg. The lowest content is found in the deepest layer (100 - 150 cm.) of profile 8 while the highest content is detected in the top surface layer of profile 6. Log₁₀ Histogram, Figure 3 reveals the frequency distribution of total Cu which shows the mean of total Cu, range of abundance and the standard deviation.

Depthwise distribution of total Cu (Fig. 4) follows three distinct patterns where its values tend to increase with depth in profiles 2 and decreases progressively with depth (profile 8) while in the other profiles total Cu does not portray any specific pattern with depth. Nevertheless, some profiles display a considerable increase or reaches its minimum content of total Cu in their deepest layers. These results agree, to some extent, with Stevenson & Fitch (1981) and El-Demerdashe et al. (1995).

To find out the relationship between total Cu and soil variables on the one hand, and total Cu and its forms on the other, statistical analysis is carried out. The obtained results reveal that total Cu is significantly negatively correlated with coarse sand (r = -0.418*) while being significant positively correlated with silt (0.410*), Na⁺(r = 0.506^{+}), HCO₃⁻, (r = 0.413)*, Cl⁻ (r = 0.498*), and highly significant positively correlated with CaCO₃ (r = 0.668**), clay (r = 0.625**) and (C.E.C r = 0.681**). Moreover. Total Cu is highly significant positively correlated with chemically extractable Cu (r = 0.959**), soluble Cu (r = 0.692^{*}) exchangeable Cu (0.639**) carbonate bound Cu (r = 0.530*) and Fe-Mn bound Cu (r = 0.737**). The regression equations are given hereafter:

Total Cu = -15.965 + 0.216 pH + 13.294 OM + 1.408 CEC +1.579 Na⁺ + 0.094 Ca²⁺ + 0.079 Mg²⁺ -14.650 K⁺ +1.257 HCO₃⁻ 2.106 CO₃⁻²⁻ 0.946 Cl⁻ + 2.263 CaCO₃ -0.104 fine sand -0.631 Very fine sand -0.537 Silt + 0.135 Clay (r = 0.912**).

Total Cu = 0.083 + 0.067 Extractable Cu + 0.927Soluble Cu + 1.212 Exchangeable Cu + 0.47 Carbonate bound Cu + 1.052 Fe-Mn bound Cu + 0.964 Organic bound Cu + 0.989 Residual Cu (r = 1.00^{**}).

TABLE 4. Surface area and cumulative gas a	dsorption & desorption on surface area of the investigated soil samp	les
	Cumulative method	

				Cumulative	memou	
		-	BJ	Н	DI	1
Profile	Depth,	Surface _	Adsorption	Desorption	Adsorption	Desorption
No.	Cm.	area _		Surface area	(m ² /g)	-
		(m²/g)				
	0-30	16.98	2.441	2.528	2.497	2.571
1	30-60	17.26	2.43	2.329	2.490	2.370
3	0-30	17.83	2.363	2.440	2.422	2.492
4	0-20	20.17	2.728	2.866	2.789	2.917
5	50-80	19.09	2.703	2.616	2.766	2.656
-	0-30	18.97	2.636	2.549	2.696	2.598
6	30-60	18.92	2.481	2.668	2.543	2.722
7	0-20	13.26	1.795	1.897	1.837	1.934

TABLE 5. Chemical composition of irrigation water used in the studied soils

Sample	Types of		FC		Cations	5 (me/l)			Anions	(me/l)			mg	/kg	
No	water	рН	dS/m	Na ⁺	\mathbf{K}^{+}	Ca ²⁺	Mg^{2+}	CO ₃ ²⁻	HCO3-	Cl	SO4 ²⁻	Al	Cu	Fe	Mn
1	Nile water	8.23	0.81	1.5	0.2	2.0	4.5	0.0	3.6	3.2	1.1	0.8	0.10	0.4	0.1
2		7.59	1.89	12.4	0.7	3.8	2.3	0.0	8.8	7.2	3.1	0.3	0.07	1.0	0.5
3	Drainage water	7.73	3.56	26.5	1.0	2.8	6.3	0.0	5.6	9.6	21.2	0.3	0.07	0.9	0.6
4		7.85	2.75	18.5	1.0	3.8	4.2	0.0	6.2	9.9	11.4	0.5	0.07	0.8	0.5
6	Ground water	7.71	12.05	80.0	0.3	19.5	23.0	0.0	13.6	46.5	62.7	0.2	< 0.01	0.6	0.01
7	Drainage water	7.78	2.79	20.7	0.1	4.5	3.5	0.0	6.8	6.9	15.2	0.4	0.07	1.7	0.6
8	Mixed water	8.16	4.04	31.7	0.2	4.5	5.0	0.0	2.4	11.3	27.7	0.1	< 0.01	0.1	0.1

Chemically extractable Cu

The values of chemically extractable Cu in the investigated soil profiles are presented in Table 6 which reveals that the chemically extractable Cu ranges from 1.56 to 4.51 mg/kg with a mean 3.07 mg/kg. The lowest content is found in the deepest layer of profile 8 whereas the higher contents agree well with those of total content indicating a harmony between total and chemically extractable Cu.

The histogram constructed for providing a visual information on the frequency distribution of chemically extractable Cu Log_{10} data (Fig.3) displayed symmetric appearance and becomes more convenient to calculate the mean of

chemically extractable Cu (0.607 and -0.446) and the standard deviation (0.798 and 0.467).

The vertical distribution of chemically extractable Cu (Fig. 4) shows different patterns where its content decreases with depth in profiles 2, 3 and 8 while increases downwards in profile 7 and increases in the middle layer of profiles 1 and 4 or in the top surface of profile 6 or in the deeper layers of profile 7. In other words, the vertical distribution of chemically extractable Cu does not portray any specific pattern pertaining to locality.

To figure out the relationship between chemically extractable Cu and soil variables that probably control its behavior in the studied

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	Dwoflo	Depth	Total	Chemically]	Extractable	Solu	ble	Ехсһаı	ngeable	Carbona	te bound	Fe-Mn	punoq	Organic	pond	Resi	dual
Land use	No.	(Cm)	mg/kg	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
		0 -30	9.77	3.63	37.15	0.29	2.97	0.21	2.15	0.23	2.35	2.65	27.12	0.15	1.54	6.14	62.8
	-	30 - 60	11.57	3.75	32.43	0.34	2.94	0.25	2.16	0.21	1.82	2.74	23.69	0.18	1.56	7.82	67.6
	-	06-09	9.24	3.16	34.20	0.30	3.25	0.20	2.16	0.16	1.73	2.27	24.57	0.08	0.87	6.08	65.8(
		W^*	10.19	3.51	34.59	0.31	3.05	0.22	2.16	0.20	1.97	2.55	25.13	0.14	1.32	6.68	65.47
		0 - 20	5.53	3.07	55.57	0.13	2.35	0.14	2.53	0.26	4.71	1.81	32.76	0.06	1.09	2.46	44.4
	ç	20 -35	5.79	2.55	44.08	0.16	2.77	0.17	2.94	0.28	4.84	1.57	27.14	0.08	1.38	3.24	56.0
	4	35-60	6:39	2.49	39.00	0.17	2.66	0.20	3.13	0.15	2.35	1.61	25.22	0.09	1.41	3.90	61.0
Cultivated		W^*	5.95	2.70	45.79	0.15	2.59	0.17	2.88	0.22	3.76	1.67	28.21	0.08	1.30	3.26	54.20
Soils.		0 -30	13.27	3.86	29.10	0.36	2.71	0.37	2.79	0.21	1.58	2.71	20.43	0.11	0.83	9.41	70.9
	۲	30 -70	13.44	3.64	27.08	0.41	3.05	0.40	2.98	0.21	1.56	2.39	17.78	0.13	0.97	9.80	72.9
	r	70-100	9.93	2.71	27.29	0.30	3.02	0.23	2.32	0.17	1.71	1.86	18.73	0.09	0.91	7.22	72.7
		W*	12.33	3.43	27.75	0.36	2.94	0.34	2.72	0.20	1.61	2.33	18.86	0.11	0.91	8.91	72.2
		0 - 20	10.03	3.34	33.32	0.36	3.59	0.41	4.09	0.18	1.80	2.11	21.05	0.19	1.90	69.9	66.7.
	~	20 -70	10.48	3.65	34.83	0.38	3.63	0.34	3.24	0.22	2.10	2.43	23.19	0.23	2.19	6.83	65.1
	t	70 -100	12.25	3.17	25.88	0.42	3.43	0.39	3.18	0.20	1.63	2.06	16.82	0.07	0.57	9.08	74.13
		W*	9.87	3.08	28.36	0.35	3.20	0.34	3.07	0.18	1.69	2.01	18.53	0.15	1.43	6.79	61.6
		0 - 20	6.47	2.39	36.94	0.26	4.02	0.18	2.78	0.18	2.78	1.64	25.35	0.09	1.39	4.08	63.00
Uncultivated	v	20 -50	5.77	2.07	35.88	0.21	3.64	0.15	2.60	0.14	2.43	1.37	23.74	0.11	1.91	3.70	64.13
Soils.	2	50 - 80	15.23	4.09	26.85	0.46	3.02	0.48	3.15	0.27	1.77	2.77	18.19	0.07	0.46	11.14	73.1:
		*M	9.49	2.91	32.76	0.32	3.50	0.28	2.85	0.20	2.27	1.96	22.06	0.09	1.24	6.59	67.2
		0-30	19.19	4.51	23.50	0.57	2.97	0.44	2.29	0.43	2.24	2.83	14.75	0.18	0.94	14.68	76.5
	9	30 - 60	7.33	2.22	30.31	0.29	3.96	0.16	2.18	0.18	2.46	1.37	18.70	0.20	2.73	5.11	69.7
	>	60 -110	11.67	2.82	24.16	0.37	3.17	0.23	1.97	0.18	1.54	1.89	16.20	0.09	0.77	8.85	75.8
		M	12.54	3.12	25.66	0.40	3.33	0.27	2.12	0.25	1.98	2.00	16.48	0.14	1.35	9.42	74.3
		0 - 20	8.76	2.73	31.18	0.28	3.20	0.15	1.71	0.16	1.83	1.96	22.39	0.16	1.83	6.03	68.8
Cultivated	L	20 -50	8.53	2.86	33.55	0.29	3.40	0.18	2.11	0.19	2.23	2.02	23.70	0.19	2.23	5.67	66.5
Soils.	-	50 - 80	15.48	4.08	26.37	0.45	2.91	0.32	2.07	0.28	1.81	2.94	19.00	0.07	0.45	11.42	73.8
		W*	11.19	3.29	30.26	0.35	3.17	0.23	2.00	0.22	1.97	2.35	21.61	0.14	1.46	7.92	69.8
		0 -50	10.90	3.18	29.17	0.38	3.49	0.22	2.02	0.26	2.39	2.09	19.17	0.20	1.83	7.72	70.8
	×	50 - 100	8.21	2.90	35.34	0.31	3.78	0.20	2.44	0.22	2.68	1.85	22.55	0.22	2.68	5.31	64.7
	þ	100-150	4.88	1.56	31.97	0.16	3.28	0.11	2.25	0.13	2.66	1.03	21.11	0.07	1.43	3.32	68.0
		*M	8.00	2.55	32.16	0.28	3.51	0.18	2.24	0.20	2.58	1.66	20.94	0.16	1.98	5.45	67.8
		**M	9.95	9.94	3 07	32 17	0.37	316	30.0	3 50	111			11 10	c • •		202



Fig. 3. Frequency distribution of Cu forms in the studied soils



Fig. 4. Depthwise distribution of Cu forms in the studied soils.

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soils, simple correlation and regression analysis are computed and presented in Table 6. These statistical data reveal that chemically extractable Cu is highly significant positively correlated with clay % (r =0.615**), soluble Na⁺ (r = 0.587**), Cl⁻ (r =0.578**), CaCO₃% (r = 0.671**) and CEC (r = 0.631**), while being significant positively correlated with EC (r = 0.408*).

With regard to the relationship between chemically extractable Cu and other forms of Cu, the correlation coefficients dictate that chemically extractable Cu is highly significant positively correlated with total Cu ($r = 0.959^{**}$), soluble Cu ($r = 0.595^{**}$), exchangeable Cu ($r = 0.556^{**}$), carbonate - bound Cu ($r = 0.634^{**}$) and Fe - Mn bound Cu ($r = 0.668^{**}$) and significant positively correlated with residual Cu ($r = 0.480^{*}$). The regression equations read:

Extractable Cu =3.591-0.465 pH -0.155 OM -0.076 CEC -0.081 Na⁺ -0.033 Ca ²⁺ -0.022 Mg²⁺ +1.133 K⁺ -0.009 HCO₃ -0.070 CO₃ - + 0.147 Cl⁻ -0.256 CaCO₃ + 0.007 fine sand +0.236 Very fine sand +0.014 Silt + 0.042 Clay (r= 0.979**).

Extractable Cu = 0.761 - 9.682 Total Cu + 5.073 Soluble Cu + 12.633 Exchangeable Cu + 5.593 Carbonate bound Cu + 9.959 Fe-Mn bound Cu+11.781Organic bound Cu + 9.736 Residual Cu (r = 0.911**).

Soluble Cu

Data in Table 6 show clearly that soluble Cu ranges from 0.13 to 0.57 mg/kg in the whole soil layers of the investigated profiles with a mean 0.32 mg/kg. The lowest content of soluble Cu is found in the top (0 - 20 cm) layer of profile 2 whereas the highest content is associated with the uppermost surface layer of profile 6.

When the frequency distribution of soluble Cu is expressed in Log $_{10}$ histogram, Fig. 3 it is quite clear that data have more systematic appearance and allowed the easy calculation of soluble Cu mean (-0.523) and standard deviation (0.161).

The relationship between soluble Cu and soil variables is guided by the statistical data of correlation coefficients and regression analysis which indicate that some factors are involved in controlling soluble Cu content and distribution in the studied soils. The correlation coefficients dictate that soluble Cu is highly significant positively correlated with clay % (r = 0.542**), CaCO₃ % (r = 0.525**), CEC (r = 0.584**) and significant positively correlated with soluble Na⁺

 $(r = 0.468^*)$, soluble Ca²⁺ $(r = 0.443^*)$ and Cl⁻ $(r = .496^*)$.

With regard to the relationship between soluble Cu and other forms of Cu, the correlation coefficients reveal that soluble Cu is highly significant positively correlated with total Cu ($r = 0.692^{**}$), extractable Cu($r = 0.595^{**}$,), exchangeable .Cu ($r = 0.832^{**}$) carbonate bound Cu ($r = 0.563^{**}$) and Fe-Mn bound Cu ($r = 0.757^{**}$)

The regression equations are figured out as follows:

Soluble Cu = $-0.392+0.063 \text{ pH} + 0.357 \text{ OM} + 0.048 \text{ CEC} + .040 \text{ Na}^+ + 0.003 \text{ Ca}^{2+} + 0.003 \text{ Mg}^{2+} -.416 \text{ K}^+ + 018 \text{ HCO}_3 -.089 \text{ CO}_3^{-2-} -.024 \text{ Cl}^- + 0.039 \text{ CaCO}_3 -0.004 \text{ fine} + 012 \text{ very fine sand} -0.009 \text{ Silt} +0.005 \text{ Clay} (r = 0.884**)$

Soluble Cu =.041-.016 Extractable Cu + 0 .169 Exchangeable Cu -.059 Carbonate bound Cu -.017 Fe-Mn bound Cu + 0.445 Organic bound Cu + 0.034 Residual Cu ($r = 0.980^{**}$).

Exchangeable Cu

Data in Table 6 show that exchangeable Cu content in the studied soils ranges from 0.11 to 0.48 mg/kg with a mean 0.25 mg/kg. The lowest content characterizes the deepest layer (100 - 150 cm.) of profile 8 whereas the highest content is associated with the deepest layer (60 - 80 cm.) of profile 5.

When exchangeable Cu is considered as percent of total Cu, it is found that this form of Cu constitutes 1.71 to 4.09 %.

Regarding the frequency distribution of exchangeable Cu, the constructed histogram for Log_{10} data (Fig. 3) reveals more informative since the histogram provides the range of exchangeable Cu values, the range of greatest abundance, and more symmetrical appearance, the mean of exchangeable Cu is (-0.629) and the standard deviation is (0.18).

Depthwise distribution of exchangeable Cu reveals a tendency of decrease with depth in profiles 2 and 7, a tendency of increase (profile 8) and an irregular patterns in the rest of the investigated profiles.

To substantiate the relationship between exchangeable Cu and soil variables, correlation, coefficients are worked out. These correlations indicate highly significant positive correlations between exchangeable Cu and clay % ($r=0.695^{**}$), CaCO₃% ($r=0.470^{*}$), HCO₃⁻($r=0.543^{**}$), and

CEC (r = 0.637^{**}) and significant positively correlated with soluble K⁺. With regard to Cu forms, exchangeable Cu is shown to be highly significant positively correlated with total Cu (r = 0.639^{**}) and soluble Cu (r = 0.832^{**}). The obtained regression equations are presented as follows:

Exchangeable Cu = 0.170-0.012 pH + 0.055OM + $0.039 \text{ CEC} + 0.033 \text{ Na}^+ + 0.005 \text{ Ca}^{2+} -0.002$ Mg ²⁺- $0.099 \text{ K}^+ + 0.036 \text{ HCO}_3 -0.054 \text{ CO}_3 -0.026$ Cl⁻+ $0.028 \text{ CaCO}_3 -0.003 \text{ fine} -0.022$ Very fine sand - $0.014 \text{ Silt} + 0.005 \text{ Clay} (r = 0.921^{**}).$

Exchangeable Cu = -.062 + 0.703 Total Cu + 0.050 Extractable Cu -0.490 Soluble Cu -.327 Carbonate bound Cu -.731 Fe_Mn bound Cu -.753Organic bound Cu -0.697 Residual Cu (r = 0.981^{**}).

Carbonate bound Cu

Data in Table 6 show that the carbonate bound Cu ranges from 0.13 to 0.43 mg/kg in the whole layers of the studied profiles with a mean of 0.21 mg/kg. In general, the lowest carbonate bound Cu is found in the deep sandy layer of profile 8 whereas the highest content is associated with the top surface sandy loam layer profile 6. If the carbonate bound Cu is computed as percent of total Cu, it constitutes 1.54- 4.84 %.

Regarding the frequency distribution of carbonate bound Cu, Fig. 3 shows Log_{10} histogram displaying the range of values of this form, the range of greatest abundance, the mean and the standard deviation.

Depthwise distribution of carbonate bound Cu Fig. 4 reveals that the values of this form displayed three patterns; a tendency of decrease downwards (profiles 1, 3, 6 and 8); a tendency of increase downwards (profile 7) and irregular distribution in the rest of profiles.

To figure out the relationship between carbonate bound Cu and soil variables that control its behavior in the studied soils and also its relationship, with other Cu forms, correlation coefficients and regression equations are used. The obtained results reveal that carbonate bound Cu is highly significant positively correlated with soluble Na⁺ (r = 0.725**), soil EC (r = 0.602**), Cl⁻ (r = 0.710**), total Cu (r = 0.530**) and soluble Cu (r = 0.563**) while being significant positively correlated with Ca²⁺ (r = 0.513*) and exchangeable Cu (r = 0.488*).

The obtained regression equations are presented as follows:

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Carbonate bound Cu = -0.381+0.060 pH + 0.141OM + 0.004 CEC+ 0.028 Na⁺ +0.003 Ca²⁺ -0.002 Mg²⁺-0.200 K⁺+ 0.030 HCO₃+ 0.046 CO₃²⁻ -0.014 Cl⁻ +0.026 CaCO₃-0.001 fine sand+0.008 Very fine sand-0.010 Silt+0.003 Clay (r = 0.917**).

Carbonate bound Cu = 0.099 + 0.031 Fe_ Mn bound Cu+0.113 Organic bound Cu +0.16 Residual Cu+0.023 Extractable Cu -.253 Soluble Cu -.058 Exchangeable Cu (r = 0.722^{**}).

Fe-Mn bound Cu

Data presented in Table 6 show that this Cu form constitutes 1.03 to 2.94 mg/kg in the whole layers of the investigated soil profiles with a mean of 2.07 mg/kg. The lowest content characterizes the deepest layer of profile 8 whereas the highest content is that of the top surface of profile 6. When these values of Fe - Mn bound Cu are considered as percent of total Cu it is evident that this form constitutes 14.54 to 32.76. %. In other words, Fe-Mn bound Cu is among the major components of total Cu.

With respect to the frequency distribution of Fe-Mn bound Cu, the Log $_{10}$ histogram illustrated in Fig. 3 shows the Fe-Mn bound range of 1.03 - 2.94 mg/kg as the range of abundance & mean of 2.08 mg/kg and a standard deviation of 0.05.

Regarding the vertical distribution of Fe - Mnbound Cu, it is quite clear that the values of this form tend to decrease with depth in profiles 3 and 8 while tend to increase downwards in profile 7 and displayed an irregular pattern of distribution in the rest of profiles.

To figure out the relationship between Fe-Mn bound Cu and soil variables and also between this form and other forms of Cu, correlation coefficient and regression equations are computed. The obtained results dictate that Fe-Mn bound Cu is highly significant positively correlated with clay % (r =0.609**), CaCO₃% (r =0.631**), CEC (r = 0.569**), total Cu (r = 0.737**), soluble Cu (r =0.757**), exchangeable Cu (r =0.716**) and carbonate bound Cu (r = 0.577**), while being significant positively correlated with soluble HCO_3^- (r = 0.504*). The regression equations are given hereafter:

Fe-Mn bound Cu = -4.123 + 0.598 pH + 465 OM + 0.151 CEC + 199 Na⁺ + 0.003 Ca²⁺ + 0.032 Mg²⁺ + 2.288 K⁺ + 0.141 HCO₃ + 0.002 CO₃²⁻-0.118 Cl⁺ +0.389 CaCO₃ + 0.006 fine sand +014 Very fine sand -0.088 Silt+0.050 Clay (r = 0.911**). Fe-Mn bound Cu = -.071-.890 Organic bound Cu -.931Residual Cu +0.943Total Cu +0.062 Extractable Cu -0.900 Soluble Cu -1.131Exchangeable Cu -.411 Carbonate bound Cu (r = 0.999**).

Organic - bound Cu

Data in Table 6 dictate that the values of organic bound Cu ranges from 0.06 to 0.23 mg/kg with a mean of 0.13 mg/kg. The lowest content characterizes the top surface layer of profile 2 whereas the highest content is that of the subsurface layer of profile 4.

Depthwise distribution of this Cu form indicates an irregular pattern except in profile 2 where the values of this form tend to increase downwards. Furthermore, it is remarkable that the values of this form are considerably at its higher level in the subsurface layers of almost all profiles. This is rendered to the presence of decomposed organic matter, though of lower content yet it plays an active role.

To find out the relationship between organic bound Cu and soil variables and other forms of Cu, statistical analysis indicates that organic bound Cu is insignificantly correlated with any soil variable. Nevertheless, the obtained regression equations clarifying the combined interrelationships are given hereafters:

Organic bound Cu = -0.104+ 0.031 pH +0.178OM+0 .017 CEC +0.011 Na⁺-0.002Ca²⁺-0.001Mg²⁺-0.186 K+ -0.028 HCO3 -0.041CO3²⁻-0.03Cl⁻-0.039CaCO₃+ 0.001 fine sand + 0.034 Very fine sand + 0.009 Silt+0.005Clay(r= 0.881**).

Organic bound Cu = -0.057 + 0.638 Total Cu+ 0.054 Extractable Cu -0.107 Soluble Cu-0.859 Exchangeable Cu-0.256 Carbonate bound Cu -0.657 Fe-Mn bound Cu-0.648 Residual Cu (r = 0.919^{**}).

Based on the foregoing results, one can work out the following discussion:

i) Most, if not all, Cu forms are of relatively higher content in the loamy sand to sandy loam layers relative to the sandy ones.

ii) The sequence of partitioned Cu forms follows the order:

Residual >> Fe-Mn bound >> Soluble > Exchangeable > Carbonate-bound > Organic-bound.

Total and chemically extractable Cu (DTPAextractable) vary considerably within and between the soil profiles representing the soils of the 10^{th} . of Ramadan region. To suffices, the total Cu varies from 5.53 to 19.19 mg/Kg with an average of 10.00 mg/Kg. Though the average total Cu varies, some profiles have nearly similar average such as profiles 1, 4 and 7 on the one hand and profiles 3 and 6 on the other. The variations encountered in total Cu are mainly rendered to soil origin and weathering, *i.e.*, parent material from which the soils are derived (sandstone with shales intercalations); weathering sequence as well as sedimentation regime. This does not exclude the slight contribution of irrigation water and amendments since these soils are newly reclaimed and cultivated for a short period.

With regard to DTPA-extractable Cu, it is evident that its values in the studied profiles averaged at 25.97 to 46.52 % with a total average of 32.25 % of total Cu. The variations in DTPAextractable Cu depend on chemical speciation which can be defined as the process of identifying and quantifying different speciation, forms or phases present in soil material. These species can be defined functionally (assimilated by plants), operationally according to the procedure or reagents used for extraction, and specifically as particular components or oxidation state (Fuentes et al., 2004).

To figure out Cu speciation and distribution in different forms or fractions, the total soil Cu content is particular through sequential extraction. The obtained results indicate the following:

i) The order of abundance of sequentially– extracted Cu speciation (forms) as presented is :

Residual >> Fe-Mn bound >> Soluble > Exchangeable > Carbonate-bound > Organic- bound.

The first form is according to Yobouet et al. (2010) is the inert fraction whereas the other forms are supposed to be the labile fraction which is potentially bioavailable and toxic following the diagrammatic sketch of Singh and Kalamdhad (2013 a & b).

ii) The labile fractions already identified in the present study agree very well with the DTPAextractable Cu as it constitutes 92 to 100 % with a mean of 98 % of the DTPA extractable Cu.

iii) The residual form of Cu is by far the most dominant form of soil Cu. Its values range from 44.48 to 76.50 % of total Cu content with an average of 67.55 %. This residual form

represents the Cu ions combined or incorporated in aluminosilicates lattice, it is considered to have no bioavailability owing to strong stability and therefore the lowest toxicity (Wang et al., 2008 and Liu et al., 2010).

iv) The second important form of Cu is the Fe-Mn bound form. This form is the part of soil Cu wrapped by Fe/Mn oxides or hydroxides precipitation which is difficult to release due to strong ionic bonding. However if the Eh and oxygen decreased they deoxidize and cause secondary pollution, Lin et al., (2011). In this study, the presence of Fe minerals (hematite, pyrite, goethite and magnetite) as well as amorphous inorganic materials supports the higher contents of Fe-Mn bound Cu especially under the oxidation condition of coarse – textured soil matrix.

v) The contents of residual and Fe- Mn bound forms of Cu in the studied soil profiles averaged at 86.83 - 91.35 %. of total soil Cu with little variations between profiles and a total average of 89.59 % of total Cu. These results confirm the major dominance of residual Cu and Fe-Mn bound Cu which is consistent with previous findings of Lin et al. (2011) who showed that Cu was mainly composed of residual and Fe- Mn bound fractions. Though Cu- bearing minerals are entirely absent as declared from X-ray diffraction patterns of soil clays of the examined profiles, yet the relative dominance of Fe- Mn bound Cu form suggests that formation of chalcopyrite (Cu FeS₂), bornite (Cu, FeSO₄) or tetrahedrite [(Cu, Fe)₁₂ Sb₄ S_{12} in soils could be at their initial state due to the short period of land use.

vi) The soluble form of Cu also varies within, indicating that readily water soluble Cu is markedly low. This form includes Cu with low bonding strength or free ionic form of Cu that is mobile and bioavailable. In soil solution, Cu exists as Cu^{2+} or one of the stable complexes of the ion. The solubility of various Cu minerals has been reported, Lindsay (1979) since the hydrolysis constant of Cu is $10^{-7.6}$, the hydrolysed species, Cu OH⁺, will be present in significant concentrations at pH values above 7 and may enter into soil adsorption reactions, Ellis and Knezek (1972). The hydrolysed species, Cu (OH)²⁺ and Cu (OH)⁻₃ also exist in very small quantities but do not significantly influence Cu reactions in soils.

vii) The exchangeable form of Cu varies considerably within and between profiles. This Cu form is essentially absorbed or adsorbed on clay

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minerals and organic matter which are sensitive to environmental change, easy to transform and have high bioavailability and toxicity. In this regard, Menzel and Jackson (1951) reported that montmorillonite is capable to adsorb Cu above the CEC at neutral and alkaline soil pH values and Cu (OH) was the form adsorbed even when only 1 % of the soluble Cu was in the hydrolysed form. Other authors have attributed the excess retention of Cu by montmorillonite to precipitation of hydroxides (Bingham et al., 1964) and hydroxyl carbonates (Misra and Tiwari, 1966). Murray and McBride (1994) found that Cu can be adsorbed by amorphous alumina. Kinniburgh (1983) added that Cu specific adsorption which is not significant for most metal ions, seems to play a more important role than non-specific adsorption. Amorphous and crystalline oxides of Fe and Al easy adsorb Cu 3+ regardless of the excess alkali metals in solution. The presence of montmorillonite, kaolinite and hydrous mica in the clay fraction of the studied profiles in different proportions, Fig. 2 and Table (3), together with the low amount of organic matter explains the variations in the exchangeable form of Cu. Therefore, identified clay minerals contribute to this form and also organic matter, though low, but it is one of the most efficient mechanisms of Cu²⁺ retention in soil, Murray and McBride (1994).

viii) Carbonate bound Cu^{2+} varies widely within and between soil profiles and represents the Cu^{2+} coprecipitated with carbonate minerals and easily released under acidic condition, therefore its low value is attributed to the low content of $CaCO_3$ % and carbonate minerals which are identified (dolomite, aragonite and calcite) in the X-ray diffraction patterns, Fig. 2 and Table 3 as well as high soil pH values (alkaline).

ix) Organic bound Cu is the least among Cu forms in the studied soil profiles. This form also exhibits wide variability within and between soil profiles. The form is one of the important sink of Cu in soil and organically complex Cu²⁺ is bound more tightly than any other divalent transition metal and of low labiality, Murray (1994). Align with this, Uzaira et al. (2011) reported that more than 98 % of Cu in soil solution was in an organic complexed forms, Ellis and Knezek (1972) demonstrated the existence of stable Cu complexes with organic matter. In this respect, carboxyl and phenolic groups bind Cu to organic matter and complexation involves fulvic acid Cu compounds as soluble forms and humic acid binding Cu in largely insoluble forms with stability constant (Log k) of 8.7 for Cu), Stevenson (1982). In short, Cu forms very stable complexes with organic ligands, Qiao and Ho (1997), however, organic matter may not necessarily represent the main binding site for Cu in soil which may depend to an extent on the soil type (Smith 2009).

x) The relation between total Cu, chemically extractable Cu and sequentially – extracted forms of Cu with soil variables controlling their behaviours and also between Cu forms are already presented.

Undoubtedly, Cu is an essential micronutrient for plant growth at low concentration, but excess amounts are phytotoxic and can bring potential threat to human health. To assess the Cu mobility and bioavailability, degree of enrichment factor, Cu contamination and pollution of the studied soil environment (soil ecosystem), some measures are computed as follows: Quantification of Cu mobility, enrichment and single pollution

Mobility factor (MF)
Mobility Factor (MF) of Cu =
[Soluble(Cu) + exchangeable(Cu) + carbonatebound(Cu)]x100

Total forms of Cu

(Cezary and Bal, 2001).

The mobility factor (MF) of Cu in all layers of the studied profiles is presented in Table 7. Mobility factor ranges from 6.72 to 11.1 with an average of 8.20, the lowest MF is found in the deepest layer of profile 6 while the highest is associated with the subsurface layer of profile 2. Moreover, the highest average MF is that of profile 2 whereas the lowest average MF is that of profile 7. In general, higher MF is either associated with the top layer or subsurface layer, or both. Moreover, MF tends to decrease progressively with depth in profiles 4 (cultivated soil) and 5 (uncultivated soil). In general, Cu has higher MF vales, indicating higher reactivity, high lability and high bioavailability in the studied soils.

Land use	Profile No.	Depth, - (Cm.) -	*MF	**EF	***SEPI
			For		
			Cu		
Cultivated Soils		0 - 30	7.55	3.67	18.15
	1	30 - 60	6.94	2.14	18.75
		60 - 90	7.26	3.82	15.80
		0 - 20	10.92	2.07	15.20
	2	20 - 35	11.10	4.23	12.75
		35 - 60	8.50	9.97	12.45
		0 - 30	7.14	4.61	19.30
	3	30 - 70	7.65	6.73	18.20
		70 -100	7.09	8.29	13.55
		0 - 20	9.56	1.54	16.70
	4	20 - 70	9.01	1.43	18.25
Un cultivated Soils		70 - 100	8.27	4.90	15.85
		0 - 20	9.64	2.46	11.95
	5	20 - 50	8.80	1.84	10.35
		50 - 80	7.97	1.89	20.45
		0 - 30	7.53	2.28	22.55
Cultivated Soils	6	30 - 60	8.62	0.97	11.10
		60 - 110	6.72	1.57	14.10
		0 - 20	6.75	5.44	13.65
	7	20 - 50	7.73	3.40	14.30
		50 - 80	6.79	1.21	20.40
		0 - 50	7.91	6.67	15.90
	0	50 -100	9.01	3.48	14.50
	8	100 - 150	8.30	4.86	7.80

 TABLE 7. Mobility factor (MF) ,Enrichment factor (EF) and Single element pollution index (SPI) of Cu in the studied soils.

Enrichment factor (EF)

The enrichment factor is calculated (Table 7) to derive the degree of soil Cu contamination and Cu accumulation in soil, Kisku et al. (2000).

Cu/Fe (sample) Enrichment Factor (EF) =Cu/Fe (Earths crust) Casas et al., (2003).

Indication, EF< 2 Deficiency to minimal enrichment, 2-5: moderate enrichment, 5-20: significant enrichment, 20-40: very high enrichment and >40: extremely high enrichment (Abrahim and Parker, 2008).

where; EF is the enrichment factor, is the ratio of Cu /Fe concentration in the sample and Cu/Fe concentrations in the earth's crust.

The obtained values for EF ranged widely from 0.97 to 9.97, indicating relative enrichment. Cu accumulation is either in the top surface layer (profiles 5, 6, 7 and 8) or in the deepest layers of other profiles. Moreover, the values of EF increase with depth in profiles 2 and 3 while decrease in profile 7 and follow an irregular pattern in the rest of profiles. The values of EF especially those displaying relative accumulation in the deepest layers indicate that total Cu is mostly inherited from the parent rock from which these soils are derived (sandstone sedimentary rock) and the variations encountered are mainly rendered to depositional regime with possible aereal deposition or anthropogenic inputs. In general, EF factor dictates minimal enrichment to significant enrichment irrespective of profile location or depth.

Single element pollution index (SEPI) Cu Single Pollution Index (SEPI) = Cu content in soils

Permissible level of Cu

(Kabata-Pendias, 2004).

Data presented in Table 7 reveal that SEPI values range from 7.80 to 22.55. The lowest value characterizes the deepest layer of profile 8 while the highest value is associated with the uppermost surface layer of profile 6. Referring to the suggested limits by Shao-Wen and Ji-Yun (2007), all the studied profiles are highly polluted as they exhibit SEPI values more than 3.

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دراسه منر الوكيميائيه لتوزيع النحاس وصوره في أراضي منطقة العاشر من رمضان

سعد الدمرداش ، تماضر العيسوي ** ، نبيل محمد عبداللطيف بهنساوى * و عبدالسلام علوه

*مركز بحوث الصحراء- القاهرة و**كلية العلوم - جامعة بنها - بنها- مصر

أجريت هذه الدراسه لفحص حالة النحاس وكميته وتوزيعه وتحديد صوره في الأراضي المستصلحه حديثاً بمنطقة العاشر من رمضان. ولتحقيق هذا الهدف تم التعرف أولاً على صفات التربه الطبيعيه –الكيميائيه والمنر الوجيه بغرض إلقاء الضوء على أهم صفات التربه التي قد تتحكم في مسلك النحاس بالأراضي تحت الدراسه. تم إختيار ثمانية قطاعات أرضيه لتمثل الوحدات الخرائطيه للتربه والإختلافات التي تواجهها هذه الأراضى وأهمها القوام ومحتوى التربه من كربونات الكالسيوم والماده العضويه ورقم الحموضه (pH) وملوحة التربه ومكوناتها بالإضافه للتركيب المنر الوجى والسطح النوعى ومساحة الإدمصاص والإنطلاق على سطح التربه وعلاقة ذلك بالإضافه للتركيب المنر الوجى والسطح النوعى ومساحة الإدمصاص والإنطلاق على سطح التربه وعلاقة ذلك بالتركيب المنر الوجى للطين والذى أظهر إختلافاً واضحاً في معادن الطين والمعادن المصاحبه ، حيث تؤثر المعادن ومساحة السطوح بدرجه واضحه على صور النحاس . وجدير بالذكر أن الدراسه المراطوجيه لم تظهر أى من المعادن الحامله للنحاس.

وقد أظهرت النتائج المتحصل عليها أن المحتوى الكلى للنحاس والمستخلص كيميائياً (DTPA) وصور النحاس تختلف إختلافاً بيناً داخل كل قطاع وبين القطاعات المدروسه. بالمناسبه فقد تراوح النحاس الكلى والمستخلص كيميائياً بين ٨٨,٤- ١٩,١٩ مجم /كجم و ٢٥,٦- ٢٥,٤ مجم /كجم على التوالى.

وأظهر الإستخلاص المتتابع أن النحاس المتبقى والذى يعتبر الجزء الخامل هو الصوره السائده الأساسيه. بجانب ذلك فإن الصوره المرتبطه بالحديد والمنجنيز هى الصوره الهامه الثانيه فى السياده. ويكون كلا الصورتين 44,43 – 76,50 % و 14,75- 32,76 من محتوى النحاس الكلى. وتشكل الصور دائمة التغير أى النحاس الذائب والمتبادل والمرتبط بالكربونات والمرتبط بالماده العضويه ٢,٣٥ – ٤,٢ ٪ و ١,٧١ - ٤,٠٩ ٪ و ٤،٢ - ٤,٨٤ ٪ و ٤٠,٥-٢,٣٣ ٪ من محتوى النحاس الكلى على التوالى.

وقد نوقشت نتائج النحاس الكلى والمستخلص كيميائياً بالإضافه للصور المختلفه للنحاس وتوزيعها وعلاقتها بمتغيرات التربه وعلاقة صور النحاس ببعضها مع تقييم إحصائي لها.

وتبعاً لذلك فإن الدراسه تعطى معلومات ذات أهميه عن حركة النحاس ومدى تيسره بيولوجياً كمغذى نادر ضرورى للنبات ولسلسلة غذاء للحيوان والإنسان . وقد أخذ في الإعتبار مدى مشاركة النحاس في التلوث البيئي للتربه من خلال عامل إثراء التربه ومعامل التلوث بالنحاس.