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Distribution and Forms of Cobalt and Its Relationship to Mineralogical Composition in Soils of the 10th of Ramadan City, Egypt

N.M.A. Bahnasawy*, A.M. Elwa*, Laila E. Sedky* and Tomader El- Essawi**

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

THE CURRENT study aimsatcomprehending the distribution of the different forms of cobalt and its relationship to the mineralogical composition of soils of the 10th of Ramadan City, Egypt.Eight representative soil profiles were selected from the study area. Results showed that soil texture ranged from sand to sandy loam. Soil pH ranged from 6.98 to 8.68. EC values ranged from 8 to 8. 12 dSm^{-1} at 25°C whereas the predominant cations followed the descending order: $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$, while the anions followed the sequence:$SO_4^{2-}>Cl^{-}>HCO_3^{-}$. The predominant clay minerals were kaolinite, montmorillonite and illite, accompanied with accessory minerals in the descending order; quartz>gypsum >dolomite >calcite>aragonite>hematite >muscovite>potassium feldspar. The total cobalt (Co)content ranged from 1.42 to 6.51 mgkg^{-1} and the DTPA-extractable Co content ranged from 0.65 to 1.75 mgkg^{-1}. The successive extraction (fractionation of Co) exhibited that the residual form was the most dominant one where its percentage ranged from 34.01 to 82.90%. The soluble, exchangeable, carbonate bound, Fe-Mn bound andorganic boundforms ranged from: 1.38 to 4.23, 5.26 to 45.58, 1.79 to 7.34, 2.63 to 7.75, and 2.29 to 9.52%, respectively.Thus, it can be said that the following sequence characterized the distribution of Co forms among the different fractions:Residual >>exchangeable >organic-bound >Fe-Mn-bound > carbonate-bound >soluble. Accordingly,theobtained results evidently showed that there were relation between cobalt forms and mineralogical composition of soils.

Keywords:Cobalt forms, Clay and accessory minerals

Introduction

Cobalt (Co) is an important trace element for animals, but not for plants except legumes, where it is required by rhizobia for N fixation in legumes modules (Howieson and Dilworth, 2016). Its importance insavingabout 25 % of nitrogen fertilizer, on one hand, and hence reducingthe environmental pollution with nitrogen, on the other hand,and., at the same time, minimizing the N fertilizer cost (Gad, 2012). Cobalt is not critical for all plants but may improve plant growth and yield (Minz etal., 2018). However, relatively lower concentration of cobalt helps in better nodulation and consequently a better growth and yield whereas at a higher level of cobalt, it reduces the bacterial population in the rhizosphere;leadingto a lower crop growth and yield (Minz et al., 2018).

Cobalt is one of the potentially toxic elements that naturally occurs in soilsdue to its inheritance from parent rock materials (Srinivasarao et al., 2013). Higher concentration levels of Co in agricultural soils result due to the use of Co-containing compounds to control plant diseases, applied fertilizers, amendments, pesticides, irrigation with waste water, atmospheric deposition, waste materials and industrial activities (Atafar et al., 2013). Nasef et al. (2008) added that Co increased both fresh and dry weights of shoots and roots, pods yield quantity and quality, chemical constituents such as total solids (TSS),

Corresponding author: nabilmohamed597@gmail.com

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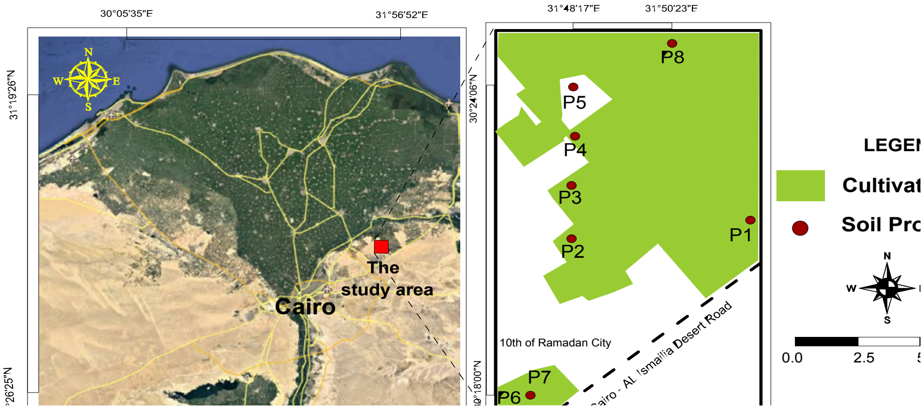
protein percentage as well as macronutrients (N,P and K) and micronutrients (Mn, Zn and Cu) in seed. Undoubtedly, total Co content and chemical speciation are essential to characterize Co behavior in the soil ecosystem (Pourret et al., 2016) especially in the newly reclaimed coarse textured soils as they determine not only the plant uptake, soil retention and pollution of Co, but also the extent to which Co is leached out of the active zone of grown plant roots (Chibuike and Obior, 2014). Due to the lack of information about Co status, its distribution and speciation (forms) in the newly reclaimed soils of the 10th of Ramadan city, the current study aimsat identifying the common Co forms, assessing their bioavailability and investigatingcorrelation of Co content and forms to the mineralogical composition of the studied soils, using some previous studies (El-Demerdashe et al., 2017).

Materials And Methods

Soils sampling and analyses

Eight soil profiles representing the dominant soil land uses in 10th of Ramadan city were identified and selected for this study (Fig. 1). The main characteristics of the studied soils were determined as follows:Particle size distribution by the pipette and dry sieving methods (James, 2007); $CaCO_3$ content volumetrically using the Collin's calcimeter according to Şenlikçi et al. (2015); pH in soil suspension 1: 2.5 using pH-meter, 3320 Jenway, (Soil Testing Laboratory, 2012); electrical conductivity (ECe) in the soil saturation extract using electrical conductivity meter (YSI model 35); soluble cations and anions according to the standard methods outlined (Haluschak, 2006); organic matter content and CEC by De Vos et al. (2007) and Dawid and Dorota (2014), respectively.



Land use	Profile No.	Location	
		Longitude (N)	Latitude (E)
Cultivated soils	1	30º21\24\\	31º52\02\\
	2	30º21\03\\	31º48\18\\
	3	30º21\06\\	31º48\18\\
	4	30º21\06 \\	31º48\20\\
Uncultivated soils	5	30º21\06\\	31º48\17\\
Cultivated soils	6	30º17\42\\	31º47\18\\
	7	30º18\00\\	31º47\33\\
	8	30º25\01\\	31º5023\\

Fig. 1. Location map of the soil profilesunder study in the 10thof Ramadan city, Egypt

Separation of the clay fraction (less than 2 µm) from eight soil samples, (loamy sand and sandy loam layers as well as one sample from sandy layers)wascarried out after the essential pretreatments.The separated clay size particles were X-rayed by a Philips PW 3710 installation supplied with a horizontal goniometry and a vertical objectplane, using Ni-filtered Cu radiation (40 Kv operating voltage and current of 35 m Å).The different clay and accessory minerals were identified following the criteria established by Dixon and Schulze (2002), Harris and White (2007) and Burhan (2011).

Total soil Co content was determined after being digested o.5 g of soil by a mixture of concentrated HNO_3(4.0 mL) + concentrated H_2SO_4(7.0 mL) + 60 % $HClO_4$(1.0 mL) as recommended by Thakur et al. (2014). Co was extracted according to Tran (2010) using diethelenetriamine pentaacetic acid DTPA-extractable Co and then was measured by Inductively Coupled Plasma (ICP). Sequential extraction of Co was performed following the procedure of (Zimmerman and Weindorf, 2010).

Results And Discussion

Characterization of the studied soils

Some morphological soil characteristics of the studied soils are shown in Table 1 according to FAO (2006). Table 2 shows that soil texture of most soil layers of the studied profiles was sand, while a few soil layers were of loamy sand or sandy loam texture. Data presented in Table 3 reveal that the soil pH values ranged from 6.98 to 8.68, indicating neutral to alkaline soil reaction. Salinity of the different soil layers of the studied profiles varied from non-saline to saline, as ECevalues ranged between 0.81 to 8.12 dS/m at 25 ^{O}C. The lowest EC_e value characterized the deepest layer of profile No.8 whereas the highest value was associated with the surface layer of profile No. 6.Calcium carbonate $CaCO_3$content in the studied soils ranged between 1.1 and 43.4 gkg^{-1}. The least content wasfound in thesurface layer of profile 8, while the highest content characterized the surface layer of profile No.6.

The organic carbon (OC) content ranged from 0.30 to 4.01 gkg^{-1}. The lowest content was recorded in the deepest layers of profile No.5 (uncultivated soils) and in the 80.0–125.0 cm. layer of profile No.7 (cultivated soils), whereas the highest organic carbon content was associated with the surface layer (0-30 cm.) of profile No.3. In most cases, the highest content in each profile occurred in the uppermost surface layer. The soil contents of the organic matter were very lowdue to the low vegetative cover on one hand and high rate of organic matter decomposition under the prevailing semi - arid climatic conditions on the other hand. Its content ranged from 0.5 to 6.9 g kg^{-1}. The lowest content was recorded in the deepest layer of profile No.5 (uncultivated soils) and in the 80.0–125.0 cm. layer of profile No.7 (cultivated soils), whereas the highest organic matter content was associated with the surface layer (0-30 cm.) of profile No.3. In most cases, the highest content in each profile occurred in the uppermost surface layer.

Calcium cation (Ca^{++}) was the predominant cation in the soil extract while K^+ is the least in abundance, whereas Na^+ and Mg^{++} same in between, the two extremes. Considering the anionic composition of the soil saturation extract, data reveal the most dominant anion was either SO_4^{-2} or $Cl^–$ and on the other hand $CO_3^{–2}$ anions were entirely absent $HCO_3^–$ was the least abundant anion.

The CEC of the soils under study varied within a narrow range from 1.42 to 7.34 $cmol_c kg^{-1}$ soil. The lowest value was recorded in the deepest layer of profile No.8, while the highest one was associated with the surface layer of profile No.6.The variations encountered in CEC values might be attributed to their different clay contents, different types and percentages of the dominant clay minerals andthe content of amorphous inorganic materials in each soil layer of the studied profiles.

Mineralogy of the clay fraction

To provide more information about the studied soils, the mineralogical composition of the clay fraction which is considered the most reactive portion of soils,was X-rayedand the diffraction patterns are illustrated by Fig. 2.The identification of the clay mineral types was carried out on the basis of the guidelines provided by Dixon and Schulze (2002), Harris and White (2007) and Burhan (2011) (Table 4).

The obtained results indicated that montmorillonite (smectite group) was detected in traceable amounts (in the surface and subsurface layers of profile No. 1 and the surface layer of profile No.6. A few amounts of montmorillonite were detected in the surface layer of profile No.3, subsurface layer of profile No.6 and deepest layer of profile No.5. It was found in moderate amount

TABLE 1. Some morphological soil characteristics of the 10th of Ramadan studied soils

LU[1]	T[2] And S[3]	Profile No.	Depth (cm.)	Color	T[4]	S[5]	C[6]			C[7]	B[8]
							Dry	Wet			
Cultivated soils	Flat and nearly level	1	0-30	10YR 6/4	LS	SG	LO	SST	NPL	MO	AW
			30-60	10YR 6/8	LS	MA	SO	SST	NPL	MO	AW
			60-90	10YR 6/8	S	MA	SHA	NST	NPL	MO	AW
			90-120	7.5YR 6/6	LS	MA	FR	SST	NPL	MO	AW
			120-150	10YR 7/4	S	MA	HA	NST	NPL	SL	-
	Gently undulating, gently sloping	2	0-20	10YR7/8	S	MA	SO	NST	NPL	SL	AW
			20-35	10YR6/4	S	MA	SHA	NST	NPL	SL	CW
			35-60	7.5YR6/6	S	MA	HA	NST	NPL	SL	AW
			60-80	10YR6/8	S	MA	FI	NST	NPL	SL	AS
			80-150	10YR6/6	S	MA	FR	NST	NPL	SL	-
		3	0-30	10YR6/4	LS	MA	SO	SST	NPL	SL	AW
			30-70	7.5YR6/6	LS	MA	SHA	SST	NPL	MO	CW
			70-100	5YR5/8	S	MA	HA	NST	NPL	SL	AS
			100-150	7.5YR6/6	S	MA	HA	NST	NPL	MO	-
	Undulating, gently sloping	4	0-20	10YR6/6	LS	MA	SHA	NST	NPL	MO	AS
			20-70	7.5YR6/6	S	MA	HA	NST	NPL	MO	AW
			70-100	7.5YR6/6	S	MA	EHA	NST	NPL	SL	CW
			100-150	7.5YR6/6	S	MA	SHA	NST	NPL	MO	-
Uncultivated soils		5	0-20	7.5YR6/8	S	SG	LO	NST	NPL	SL	AW
			20-50	7.5YR6/6	S	MA	SHA	NST	NPL	SL	AW
			50-80	7.5YR6/6	LS	MA	HA	SST	NPL	SL	AS
			80-110	10YR6/8	S	MA	HA	NST	NPL	SL	AW
			110-150	10YR7/8	S	MA	SHA	NST	NPL	SL	-
Cultivated soils	Flat and nearly level	6	0-30	10YR7/2	SL	MA	SO	SST	NPL	MO	CS
			30-60	10YR7/6	LS	MA	SHA	SST	NPL	SL	AS
			60-110	7.5YR6/6	S	MA	HA	NST	NPL	SL	AW
			110-150	7.5YR6/6	S	MA	FR	NST	NPL	SL	-
		7	0-20	10YR6/8	S	MA	SHA	NST	NPL	SL	AW
			20-50	7.5YR6/6	S	MA	HA	NST	NPL	SL	AW
			50-80	7.5YR6/6	S	MA	HA	NST	NPL	MO	AW
			80-125	7.5YR6/6	S	MA	EHA	NST	NPL	MO	AW
			125-150	7.5YR6/6	S	MA	HA	NST	NPL	MO	-
		8	0-50	10YR7/6	S	SG	LO	NST	NPL	N	GW
			50-100	10YR7/6	S	SG	SO	NST	NPL	N	AW
			100-150	10YR7/4	S	SG	LO	NST	NPL	N	-

Abbreviation:[1]Land use;[2]Topography[3]Slope.[4] Soil texture: S; Sand, LS: Loamy Sand and SL: Sandy Loam

[5] Soil Structure: MA; Massive and SG: Single Grain,[6]Consistency: LO; Loose, HA: Hard, SO: Soft, SHA: Slightly Hard, EHA: Extremely Hard, SST: Slightly Sticky, NST: Non Sticky and NPI: Non Plastic

[7]Carbonates: SL: Slightly, MO: Moderately and N: None,[8]Boundary: AW: Abrupt Wavy, CW: Clear Wavy, AS: Abrupt Smooth, CS: Clear Smooth and GW: Gradual Way

Some morphological soil characteristics of the studied soils are shown in the table(According to FAO 2006).

TABLE 2. Particle size distribution and textural classes of the 10th of Ramadan studied soils

Land use	Profile No.	Depth, cm.	Soil particle size(%)				Textural Classes
			Coarse sand	Fine sand	Silt	Clay	
Cultivated soils	1	0-30	58.69	23.20	8.02	10.09	Loamy sand
		30-60	33.83	39.56	8.01	18.60	Loamy sand
		60-90	16.84	80.77	0.30	2.09	Sand
		90-120	53.80	21.90	6.25	18.05	Loamy sand
		120-150	61.50	37.27	0.23	1.00	Sand
	2	0-20	77.78	21.69	0.12	0.41	Sand
		20-35	28.90	69.28	0.70	1.12	Sand
		35-60	64.99	33.99	0.15	0.87	Sand
		60-80	79.99	18.95	0.21	0.85	Sand
		80-150	81.50	17.70	0.15	0.65	Sand
	3	0-30	33.80	49.83	2.17	14.20	Loamy sand
		30-70	60.68	12.54	12.60	14.18	Loamy sand
		70-100	68.47	30.18	0.33	1.02	Sand
		100-150	74.11	25.19	0.16	0.54	Sand
	4	0-20	33.34	41.60	6.24	18.82	Loamy sand
		20-70	74.70	24.15	0.13	1.02	Sand
		70-100	75.96	23.09	0.16	0.79	Sand
		100-150	67.92	31.27	0.18	0.63	Sand
Uncultivated soils	5	0-20	66.12	32.28	0.49	1.11	Sand
		20-50	58.97	39.31	0.21	1.51	Sand
		50-80	63.78	13.94	4.17	18.11	Loamy sand
		80-110	60.08	38.16	0.64	1.12	Sand
		110-150	60.75	37.69	0.50	1.06	Sand
Cultivated soils	6	0-30	49.47	20.18	11.10	19.25	Sandy loam
		30-60	69.21	8.75	16.02	6.02	Loamy sand
		60-110	75.09	24.21	0.15	0.55	Sand
		110-150	86.87	12.81	0.06	0.26	Sand
	7	0-20	65.98	31.65	0.52	1.85	Sand
		20-50	64.85	33.84	0.25	1.06	Sand
		50-80	65.99	32.12	0.43	1.46	Sand
		80-125	80.12	18.97	0.31	0.60	Sand
		125-150	81.92	17.35	0.14	0.59	Sand
	8	0-50	82.25	17.29	0.12	0.34	Sand
		50-100	86.61	12.82	0.13	0.44	Sand
		100-150	86.98	12.75	0.08	0.19	Sand

TABLE 3. Chemical properties of the 10th of Ramadan studied soils

Land use	Profile No.	Depth, cm.	pH	EC dS/m at 25ºC	$CaCO_3$ gkg^{-1}	O.C gkg^{-1}	OM gkg^{-1}	Cations ($mmol_cL^{-1}$)				Anions ($mmol_cL^{-1}$)				CEC $cmol_ckg^{-1}$ soil
								Na^+	K^+	Ca^{++}	Mg^{++}	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$	
Cultivated soils	1	0-30	8.68	1.18	26.0	2.67	4.6	3.78	0.80	4.44	2.78	0.00	3.33	6.18	2.29	4.04
		30-60	7.07	2.67	29.0	2.04	3.5	1.91	0.29	18.50	6.00	0.00	4.50	7.25	14.95	5.58
		60-90	7.08	3.36	31.5	2.04	3.5	1.11	0.15	25.34	7.00	0.00	2.50	5.75	25.35	5.08
		90-120	7.42	1.95	32.3	1.69	2.9	0.89	0.11	12.00	6.50	0.00	4.00	6.75	8.75	3.50
		120-150	7.83	1.16	6.8	1.69	2.9	1.89	0.71	6.00	3.00	0.00	4.00	5.06	2.54	4.82
	2	0-20	7.05	2.12	12.8	2.67	4.6	4.74	0.46	11.50	4.50	0.00	3.65	6.25	11.30	3.26
		20-35	7.41	2.88	10.2	0.99	1.7	4.57	0.23	20.50	3.50	0.00	5.00	6.50	17.30	3.34
		35-60	6.98	1.16	11.0	1.68	2.9	3.57	0.31	4.72	3.00	0.00	3.50	4.22	3.88	3.36
		60-80	7.07	2.99	11.9	1.63	2.8	3.63	0.43	21.84	4.00	0.00	2.00	3.75	24.15	3.86
		80-150	7.18	1.69	8.5	2.04	3.5	2.57	0.31	12.52	1.50	0.00	2.50	5.02	9.38	3.04
	3	0-30	7.03	2.59	12.8	4.01	6.9	5.09	0.81	11.00	9.00	0.00	5.00	6.50	14.40	4.74
		30-70	7.15	2.14	34.0	1.63	2.8	4.92	0.48	10.00	6.00	0.00	4.50	6.25	10.65	4.66
		70-100	6.79	2.65	19.6	1.34	2.3	4.32	0.68	13.00	8.50	0.00	2.00	6.75	17.75	5.22
		100-150	8.28	1.89	22.1	1.34	2.3	6.48	0.42	8.50	3.50	0.00	5.25	6.00	7.65	4.62
	4	0-20	7.10	1.95	21.3	0.70	1.2	6.76	0.73	7.01	5.00	0.00	3.00	5.50	11.00	6.22
		20-70	7.02	3.26	21.3	2.38	4.1	5.62	0.72	22.76	3.50	0.00	3.50	6.50	22.60	6.16
		70-100	7.08	3.57	10.2	1.69	2.9	1.94	0.19	25.07	8.50	0.00	3.50	7.07	25.13	4.70
		100-150	7.92	3.23	6.0	0.99	1.7	2.25	0.16	22.39	7.50	0.00	1.50	4.00	26.80	4.58
Uncultivated soils	5	0-20	7.35	4.73	11.9	2.38	4.1	9.44	0.76	24.60	12.50	0.00	3.00	15.00	29.30	4.10
		20-50	7.43	3.42	17.9	2.04	3.5	4.97	0.61	20.12	8.50	0.00	2.62	6.75	24.83	4.52
		50-80	7.32	3.51	17.9	2.04	3.5	2.71	0.39	25.00	7.00	0.00	4.50	5.75	24.85	4.46
		80-110	7.06	3.45	17.0	1.34	2.3	3.73	0.43	23.84	6.50	0.00	4.00	6.40	24.10	4.42
		110-150	7.20	4.35	17.0	0.30	0.5	8.52	0.17	28.31	6.50	0.00	2.00	11.81	29.69	4.82
Cultivated soils	6	0-30	7.11	8.12	43.4	0.70	1.2	33.69	0.85	42.50	4.16	0.00	4.20	50.16	26.84	7.34
		30-60	7.20	3.14	14.5	2.38	4.1	5.53	0.25	22.12	3.50	0.00	3.62	8.25	19.53	3.86
		60-110	7.14	2.06	17.0	2.03	3.5	2.66	0.23	12.21	5.50	0.00	3.00	7.21	10.39	3.96
		110-150	7.15	2.21	4.3	1.69	2.9	4.21	0.18	11.21	6.50	0.00	3.21	5.00	13.89	2.82
	7	0-20	6.98	1.19	19.6	2.38	4.1	1.53	0.29	6.08	4.00	0.00	3.50	6.08	2.32	4.06
		20-50	8.17	1.12	29.9	1.34	2.3	2.32	0.21	5.17	3.50	0.00	3.38	4.00	3.82	3.68
		50-80	7.54	1.39	29.9	1.00	1.7	3.64	0.23	6.00	4.03	0.00	3.50	5.03	5.37	4.08
		80-125	7.40	2.21	34.0	0.30	0.5	4.93	0.38	11.79	5.00	0.00	2.00	4.00	16.10	4.86
		125-150	7.84	1.26	30.6	1.69	2.9	4.14	0.17	4.29	4.00	0.00	2.50	7.44	2.66	4.08
	8	0-50	8.32	4.02	1.1	0.70	1.2	7.61	0.31	22.28	10.00	0.00	1.50	9.25	29.45	2.34
		50-100	7.73	1.06	1.4	1.69	2.9	2.43	0.12	4.50	3.55	0.00	1.50	3.55	5.55	2.16
		100-150	8.35	0.81	1.7	0.70	1.2	2.41	0.11	3.50	2.08	0.00	2.00	4.08	2.02	1.42

in the surface layer of profile No.4 while,it was entirely absent in the uppermost surface layer of profile 7. Kaolinite (Kandite group) was present in moderate amounts in all layers except the clay fractions of 50-80cm. and 0-30 cm. layers of profiles No.5 and 6, respectively, which exhibited few amounts of kaolinites. Illite (hydrous mica group) was detected in trace to few amounts in only four layers of the investigated soils whileit was almost absent in the other soil layers. In short, the dominant clay minerals in almost all the investigated layers were kaolinite followed by montmorillonite. The identified dominant accessory mineralswere gypsum (sulfate group) and quartz (oxides & hydroxides), which were present in few to dominant and few amounts, respectively.

The identified carbonate group was dominated by dolomite, whichoccurred in all samples in trace to moderate amounts, while calcite was found in traceable amounts in the surface layers of profiles No.1 and 7 and the subsurface layer of profile No.6. Aragonite was also detected in few amounts onlyin the surface layer of profile No.1 and the subsurface layer of profile No.6. This means that dolomite was the main carbonate mineral.

Iron group was dominated by hematite mineral which was detected as traces to few amounts in 5 samples, while it disappeared in the surface layers of profiles No.3, 4 and . 7. Pyrite and goethite minerals were only detected in the surface of profile No. 1 and the deepest layer of profile No.5, respectively; magnetite was only identified in the surface layer of profile No.4 and disappeared in the other examined samples. Micaceous group was detected as few amounts of biotite only in the clay fractions of the surface layer of profiles No.1 and 6 with few amounts of muscovite in the subsurface layer of profile No.6. Likewise, K- feldspar was only detected in the surface layer of profile No.6. Halite was also detected as traces in some samples representing the surface layer of profile No.7 and the subsurface layers of profiles 1 and 6 and deepest layer of profile 5.

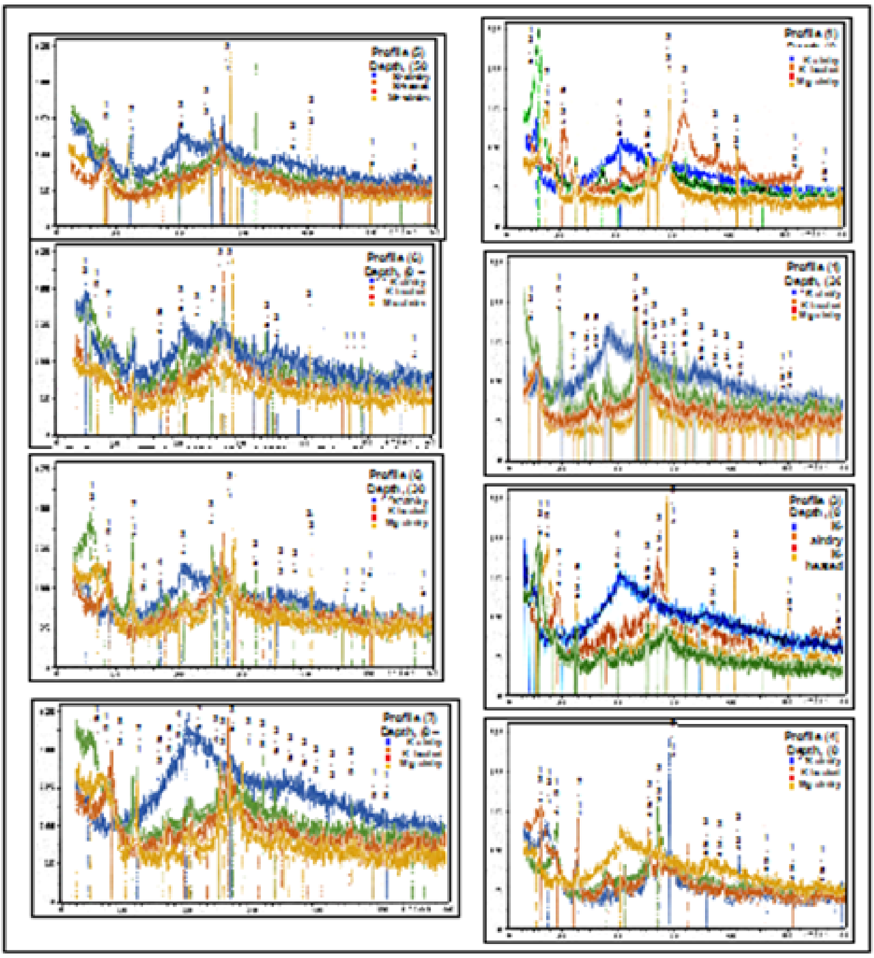


Fig. 2. X-Ray diffractograms of the clay fraction of some soils in the 10th of Ramadan City

TABLE 4. Mineralogy of the clay fraction separated from of the 10thof Ramadan studied soils

Land use	Profile No.	Depth, cm.	Clay minerals groups			Accessory minerals groups												
			Smectite	Kandite	Hyd. mica	Sulfate	Oxi. &Hyd.	Carbonate			Fe				Micaceous			Halides
			Mont.	Kao.	Illite	Gypsum	Quartz	Dol.	Calcite	Arag.	Hem.	Pyrite	Goe.	Mag.	Bio.	Musc.	K-fel.	Halite
Cultivated soils	1	0-30	*	***	-	**	**	*	*	**	**	*	-	-	**	-	-	-
		30-60	*	***	*	****	**	***	-	-	*	-	-	-	-	-	-	*
	3	0-30	**	***	**	****	**	*	-	-	-	-	-	-	-	-	-	-
	4	0-20	***	***	-	****	**	-	-	-	-	-	-	*	-	-	-	-
Uncultivated soils	5	50-80	**	**	*	****	**	***	-	-	*	-	*	-	-	-	-	*
Cultivated soils	6	0-30	*	**	-	****	**	***	-	-	*	-	-	-	**	-	*	-
		30-60	**	***	-	**	***	**	*	**	**	-	-	-	-	**	-	*
	7	0-20	-	***	*	****	**	**	*	-	-	-	-	-	-	-	-	*

Not. -: none, *< 5 %: Trace, **: Few 5-15 %, ***: Moderate 15-25 %, ****: Common 25-40 %, *****: dominant > 40 %, Mont.: Montmorillonite, Kao. : Kaolinite,.Hyd.: hydrous: Oxi&Hyd.: Oxides &Hydroxides, Dol.: Dolomite, Arag.: Aragonite, Hem.: Hematite, Goe.: Goethite, Mag.: Magnetite, Bio.: Biotite, Musc.: Muscovite and K-feld.: K-feldspar.

Forms of cobalt in the studied soils

Total cobalt

Table 5 shows that for the three layers selected from each of the studied soilprofiles,total cobalt (Co) content ranged from 1.42 to 6.51 mg/kg with a mean of 3.46 mg/kg. The lowest Co content was found in the subsurface layer of profile No.8, whereas the highest one characterizedthe surface layer of profile No.6.When the soil textural variations were taken into account, it seemed that total Co content was somewhat lower in the sandy soil layers than in the loamy sand ones, where total Co varied from 1.42 to 6.01 mg/kg and 2.58 to 6.51 mg/kg in the sandy and loamy sand or sandy loam textured layers, respectively.

Chemically DTPA extractable cobalt

Data presented in Table 5 exhibit that chemically (DTPA) extractable Co in the investigated soils varied from 0.65 to 1.75 mg/kg with a mean of 1.15 mg/kg. The lowest content occurred in the deepest layer of profile No.4,while the highest onewas found in the subsurface layer of profile No.1. When the chemically extractable Co wasexpressed as a percentage of total Co, it constituted a wide range between 18.95 and74.65 % of thetotal Co. The lowest Co percentage characterized the uppermost surface layer of profile No.4 (loamy sand), while the highest onewas associated with the subsurface layer of profile No.8 (sand). These results are expected since most of total Co can easily be extracted by DTPA from the sandy surface, while it isoften physically adsorbed in the loamy sand layers (Hamza 2008). Co is chemically or physiochemically adsorbed on clay minerals and sometimes on silt and, to a less extent, physically adsorbed, therefore, Co could not easily desorbedor partially desorbed by DTPA(Żaneta et al. 2010). When textural variations are taken into account, it has been evident that the values of chemically extractable Co ranged from 0.65 to 1.65 mg/kg and o.91 to 1.75 mg/kg in the sandy and loamy sand or sandy loam textured soil layers, respectively.

Soluble cobalt

Table 5 reveals that the values of soluble Co varied from 0.03 to 0.14 mg/kg with a mean of 0.08 mg/kg. The lowest content was found in the deepest layer of profile No.2, while the highest onewas associated with the surface layer of profile No.4.In other words; soluble Co form constitutes 1.49 to 4.23 % of total Co.

When textural variations among soil layers in the studied profiles wereconsidered, it was evident that soluble Co ranged from 0.03 to 0.13 mg/kg and from 0.06 to 0.14 mg/kg in the sandy and loamy sand to sandy loam-texturedlayers, respectively. As a general trend, soluble Co was considerably higher in the loamy sand and sandy loam layers then in to the sandy ones. When soluble Co was related to the total Co form, soluble Co constituted 1.49 to 4.23 % and 1.38 to 2.47 % of total Co in the sandy and loamy sand to sandy loam textured soil layers, respectively.

Exchangeable cobalt

Values of exchangeable Co varied from 0.08 to 1.04 mg/kg with a mean of 0.56mg/kg (Table 5). The lowest content was recorded in the deepest layer of profile No.8, whereas the highest onewas found in the surface layer of profile No.3. When soil textural variation within the layers of each profile was put into consideration, it had become evident that the values of exchangeable Co ranged from 0.08 to 0.88 mg/kg and 0.35 to 1.04 mg/kg in the sandy and loamy sand to sandy loam textured layers, respectively. This behavior has been anticipated due to the presence of clay fraction with relatively high surface area (exchange material) together with silt fraction which shared to a less extent, in the exchange capacity of loamy sand to sandy loam textured layers. Exchangeable Coas percentages of total Co constituted 5.26 to 45.58 %and 5.72 to 25.31% in the sandy and loamy sand to sandy loam textured layers, respectively.This means that exchangeable Co form is quite higher in loamy sand to sandy loam textured layers than the sandy ones due to the higher surface area and CEC of clay and silt fractions (El-Demerdashe et al. (2017).

Carbonate bound cobalt

Table 5 shows that carbonate bound Co values in the studied soil profiles varied from 0.04 to 0.26 mg/kg with a mean of 0.14 mg/kg. The lowest content occurred in the deepest layer of profile No.8 whilethe highest onewasfound in the uppermost surface layer of profile No.4. Carbonate bound Co represented 1.79 to 7.34 % of total Co.

When soil textural variations were considered, apparently carbonate bound Co values were somewhat higher in the loamy sand to sandy loam layers than in the sandy ones, being in the ranges of 0.04 to 0.21 mg/kg and 0.08 to 0.26 mg/kg in the sandy and loamy sand to sandy loam textured layers, respectively.

TABLE 5. Chemical forms of cobalt and their corresponding percentages of total Co in soils of the 10th of Ramadan studied soils

Land use	Profile No.	Depth (cm.)	Total Co	DTPA-extractable Co		Forms of Co											
					Soluble		Exchangeable		Carbonate bound		Fe-Mn bound		Organic bound		Residual		
			mg/kg	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cultivated Soils.	1	0-30	2.58	1.01	39.15	0.06	2.33	0.56	21.71	0.15	5.81	0.11	4.26	0.18	6.98	1.52	58.91
		30-60	5.22	1.75	33.52	0.11	2.11	0.94	18.01	0.24	4.60	0.23	4.41	0.26	4.98	3.44	65.90
		60-90	3.63	1.05	28.93	0.08	2.20	0.44	12.12	0.09	2.48	0.12	3.31	0.28	7.71	2.62	72.18
		W*	3.81	1.27	33.87	0.08	2.21	0.65	17.28	0.16	4.30	0.15	3.99	0.24	6.39	2.53	65.66
	2	0-20	2.52	1.08	42.89	0.05	1.98	0.63	25.00	0.17	6.75	0.11	4.37	0.16	6.35	1.40	55.60
		20-35	2.71	1.06	39.11	0.08	2.95	0.54	19.93	0.14	5.17	0.14	5.17	0.22	8.12	1.59	58.67
		35-60	1.47	0.98	66.67	0.03	2.04	0.67	45.58	0.06	4.08	0.07	4.76	0.14	9.52	0.50	34.01
		W*	2.23	1.04	49.56	0.05	2.32	0.61	30.17	0.12	5.33	0.11	4.77	0.17	7.10	1.16	49.43
	3	0-30	4.45	1.35	30.34	0.11	2.47	1.04	23.37	0.16	3.60	0.20	4.49	0.20	4.49	2.74	61.60
		30-70	3.24	1.51	46.60	0.07	2.16	0.82	25.31	0.21	6.48	0.14	4.32	0.22	6.79	1.78	54.94
		70-100	1.77	1.05	59.32	0.05	2.82	0.63	35.59	0.13	7.34	0.09	5.08	0.14	7.91	0.73	41.24
		W*	3.15	1.30	45.42	0.08	2.48	0.83	28.09	0.17	5.81	0.14	4.63	0.19	6.40	1.75	52.60
	4	0-20	6.12	1.16	18.95	0.14	2.29	0.35	5.72	0.26	4.25	0.23	3.76	0.14	2.29	5.00	81.70
		20-70	4.89	1.05	21.47	0.09	1.84	0.41	8.38	0.12	2.45	0.20	4.09	0.19	3.89	3.88	79.35
		70-100	2.84	0.65	22.89	0.06	2.11	0.27	9.51	0.07	2.46	0.12	4.23	0.14	4.93	2.18	76.76
		W*	4.62	0.95	21.10	0.10	2.08	0.34	7.87	0.15	3.10	0.18	4.03	0.16	3.70	3.69	79.27
Uncultivated Soils.	5	0-20	2.26	0.84	37.17	0.07	3.10	0.41	18.14	0.11	4.87	0.11	4.87	0.16	7.10	1.40	61.95
		20-50	4.76	1.31	27.52	0.09	1.89	0.61	12.82	0.17	3.57	0.20	4.20	0.28	5.88	3.41	71.64
		50-80	4.56	1.29	28.29	0.08	1.75	0.70	15.35	0.16	3.51	0.18	3.95	0.19	4.17	3.25	71.27
		W*	3.86	1.15	30.99	0.08	2.25	0.57	15.44	0.15	3.98	0.16	4.34	0.21	5.72	2.69	68.29
Cultivated Soils.	6	0-30	6.51	1.61	24.73	0.09	1.38	0.95	14.59	0.19	2.92	0.25	3.84	0.18	2.76	4.85	74.51
		30-60	3.22	0.91	28.26	0.06	1.86	0.52	16.15	0.08	2.48	0.17	5.28	0.13	4.04	2.26	70.19
		60-110	3.36	0.81	24.11	0.05	1.49	0.44	13.10	0.06	1.79	0.18	5.36	0.12	3.57	2.51	74.70
		W*	4.36	1.11	25.70	0.07	1.58	0.64	14.61	0.11	2.40	0.20	4.83	0.14	3.46	3.21	73.13
	7	0-20	3.66	0.77	21.04	0.11	3.01	0.88	24.04	0.20	5.46	0.21	5.74	0.14	3.83	2.12	57.92
		20-50	2.51	1.49	59.36	0.10	3.98	0.39	15.54	0.10	3.98	0.09	3.59	0.17	6.77	1.66	66.14
		50-80	6.01	1.65	27.45	0.13	2.16	0.72	11.98	0.21	3.49	0.22	3.66	0.23	3.83	4.50	74.88
		W*	4.06	1.30	35.95	0.11	3.05	0.66	17.19	0.17	4.31	0.17	4.33	0.18	4.81	2.76	66.31
	8	0-50	1.92	1.07	55.73	0.04	2.08	0.25	13.02	0.07	3.65	0.11	5.73	0.09	4.69	1.36	70.83
		50-100	1.42	1.06	74.65	0.06	4.23	0.27	19.01	0.06	4.23	0.11	7.75	0.08	5.63	0.84	59.15
		100-150	1.52	1.03	67.76	0.04	2.63	0.08	5.26	0.04	2.63	0.04	2.63	0.06	3.95	1.26	82.90
W*:weighted mean of profile		W*	1.62	1.10	66.05	0.05	2.98	0.20	12.43	0.06	3.50	0.09	5.37	0.08	4.76	1.15	70.96

Fe-Mn bound cobalt

Table 5 shows that the values of Fe-Mn bound Co ranged from 0.04 to 0.25 mg/kg with a mean value of 0.15 mg/kg. The lowest content existed in the deepest layer of profile No.8, while the highest content was associated with the surface layer of profile No.6. When the soil textural variations were taken into account, it is apparent that the content of this Co fraction ranged from 0.04 to 0.22 mg/kg and 0.11 to 0.25 mg/kg in the sandy and loamy sand textured layers, respectively. In other words, Fe-Mn bound Co was relatively high in the loamy sand to sandy loam layers than in the sandy ones. The values of this fraction expressed as a percentage of their corresponding total Co, constituted from 2.63 to7.75 % and 3.6.76 to 5.28 % of total Co of the sandy and loamy sand to sandy loam textured layers of the investigated soil profiles.

Organic bound cobalt

Table 5 shows that the organic bound Co in the investigated soil profiles varied from 0.06 to 0.28 mg/kg with a mean value of 0.17 mg/kg. The lowest content was recorded in the deepest layer of profile No.8whereas the highest one was associated with the deepest layer of profile No.1and subsurface layer of profile 5. The values of organic bound, Co as percentage of the total Co form ranged from 2.29 to 9.52%.

When the variations of textural classes among the layers of the studied profiles were taken into account, it was found that organic bound Co ranged from 0.06 to 0.28 mg/kg and from 0.13 to 0.26 mg/kg in the sandy and loamy sand to sandy loam textured layers, respectively, *i. e* 3.57 to 9.52 % and 2.29to 6.98 % of the corresponding total soil Co in the sandy and loamy sand to sandy loam textured layers, respectively.

Residual cobalt

Table 5 shows that soluble Co values varied from o.50 to 5.0 mg/kg with a mean of 2.37 mg/kg. The lowest content was found in the deepest layers of profile No.2, while the highest onewas associated with the surface layer of profile No.4. In other words; residual Co constitutes 34.01 to 82.90 % of total Co.

When textural variations of soil layers in the studied profiles were taken into account, it was found that the residual Co ranged from 0.50 to 4.50 mg/kg and from 1.52 to 5.0 mg/kg in the sandy and loamy sand to sandy loam-textured layers, respectively. Thus,residual Co wassubstantially higher in the loamy sand to sandy loam layers than in the sandy ones. When residual Co was calculated as percentage of total Co, the residual Co constituted 34.01 to 82.90% and 58.91 to 81.70 % of total Co in sandy and loamy sand to sandy loam textural soil layers, respectively.

Frequency distribution of Co-forms in the studied soils

The frequency distribution of total Co, (Fig. 3) reveals that Log_{10} histogram was more convenient in clarifying the Co range, mean and standard deviation. Moreover, the range of Co abundance was also appraised. Depthwise distribution, revealed that total Co displayed three patterns where total Co tended to decrease downwards (profiles No.3, 4 and 6); increased with depth (profile No.7) and followed an irregular pattern for the rest of the soil profiles.

The frequency distribution of chemically extractable Co was illustrated as histograms (Fig. 3) of which Log_{10} histogram was the more convenient where it clarified range, the mean and a low standard deviation. The range of abundance was also clarified. Depthwise distribution of the chemically extractable Co values in the studied profiles revealed three patterns: a tendency of Co to decrease with depth (profiles No. 2, 4, 6 and 8), a tendency of Co to increase downwards (profile No.7) and an irregular distribution of extractable Co downward at the rest of soil profiles,which displayed a pronounced increase of Co in the subsurface layer.

Regarding the frequency distribution of soluble Co, the Log_{10} histogram, depicted in Fig. 3**,** was considered to be more convenient. This histogram explained the distribution range of soluble Co, its mean and the standard deviation as well as the range of soluble Co abundance in the studied soils.

The vertical distribution of soluble Co, exhibited three patterns; a tendency of decrease with depth (profiles No. 3, 4 and 6), a tendency to increase downwards (profile No.7), and an irregular distribution pattern with a relative increase in the subsurface layers for the rest of the studied soil profiles.

The frequency distribution of exchangeable Co was demonstrated in Fig. 3, of which Log_{10} histogram was the more convenient as it represented the range of exchangeable Co with its mean and standard deviation beside the range of exchangeable Co abundance.Depthwise distribution of exchangeable Co indicated that this Co form followed three patterns: a tendency of decrease with depth (profiles No.3 and 6), a tendency of increase downwards (profiles No.5 and 7) and an irregular distribution with relative increase of exchangeable Co in the subsurface layers for the rest of soil profiles.

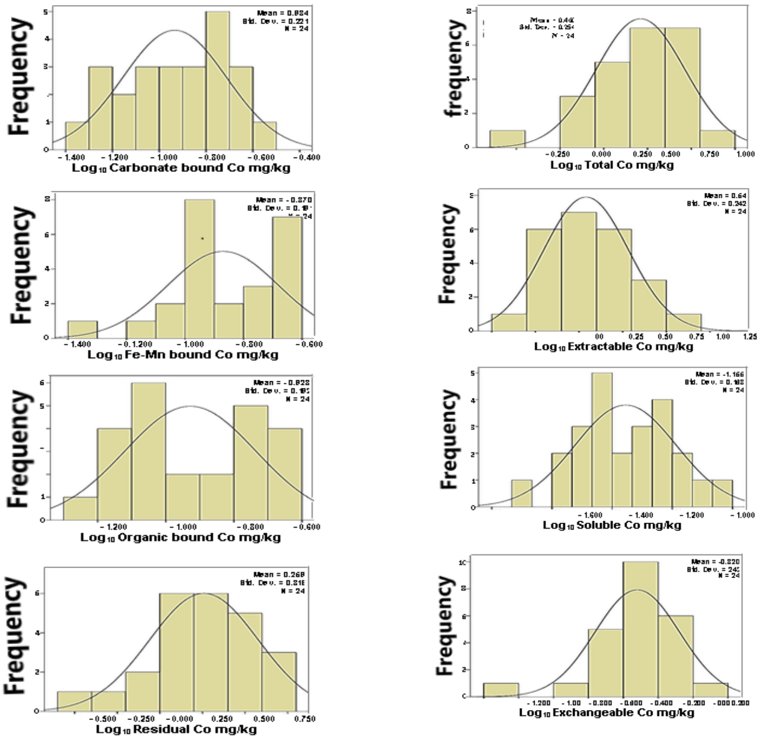


Fig. 3. Frequency distribution of Co forms of the 10thof Ramadanstudied soils

The frequency distribution, illustrated in Fig. 3, revealed that Log_{10} histogram of carbonate bound Co was more convenient since it represented the range, mean and standard deviation. Furthermore, it clarified the range of abundance.Depthwise distribution of carbonate bound Co, indicated that this Co form followed three patterns; a tendency of decrease with depth (profiles No.2, 4, 6 and 8), a tendency of increase downwards (profile No.7) and an irregular distribution with a relative increase of carbonate bound Co in the subsurface layers for the rest of soil profiles.

Regarding the frequency distribution of Fe-Mn bound Co, Fig. 3 illustrates histograms, of which Log_{10} histogram was shown to be the more convenient since it represented the range of this Co form and standard deviation. Moreover, the range of abundance of Fe-Mn bound Co was also clarified.Depthwise distribution of Fe-Mn bound Co, displayed two patterns; a tendency of decrease of the content of Fe-Mn bound Co with depth (profiles No.3, 4 and 8) and an irregular distribution downwards for the rest of soil profiles with relative increase in the subsurface layers of the examined profiles.

The frequency distribution of organic bound Co was manifested in Fig. 3. Log_{10} histogram was shown to be more convenient, as it expressed the range of organic bound Co, the mean and the standard deviation. Moreover, it clarified the range of abundanceof this Co form in the studied profiles. The vertical distribution of organic bound Co in the studied profiles, displayed three patterns, where this Co form values tended to increase downward the soil profiles No.1 and 7 and to decrease with depth (profiles No.6 and 8), while it revealed an irregular distribution the subsurface layers.

Relationships among forms of Cobalt

To figure out the relationship between total Co andeach of its forms, statistical evaluation was carried out. The obtained correlations,Fig. (4),revealed that total Co was highly significantlyand positively correlated with soluble Co (r = 0.822**), exchangeable Co (r= 0.541**), carbonate bound Co (r= 0.758**), Fe-Mn bound Co (r= 0.944**) and organic bound Co (r= 0.597**). To figure out the relationship between soluble Co and Co forms, statistical analysis was carried out (Fig. 4). The obtained correlation coefficients revealed that soluble Co was highly significantly and positively correlated with total Co (r= 0.822**).

To substantiate the relationship between carbonate bound Co and Co forms (Fig. 4), statistical analysis was performed. The obtained correlation coefficients revealed that carbonate bound Co was highly significantlyand positively correlated with total Co (r= 0.758**), soluble Co (r= 0.747**) and exchangeable Co (r=0.641**). Therefore, the bioavailability of cobalt directly depended on the stability of corresponding minerals (Yousefi et al., 2015).

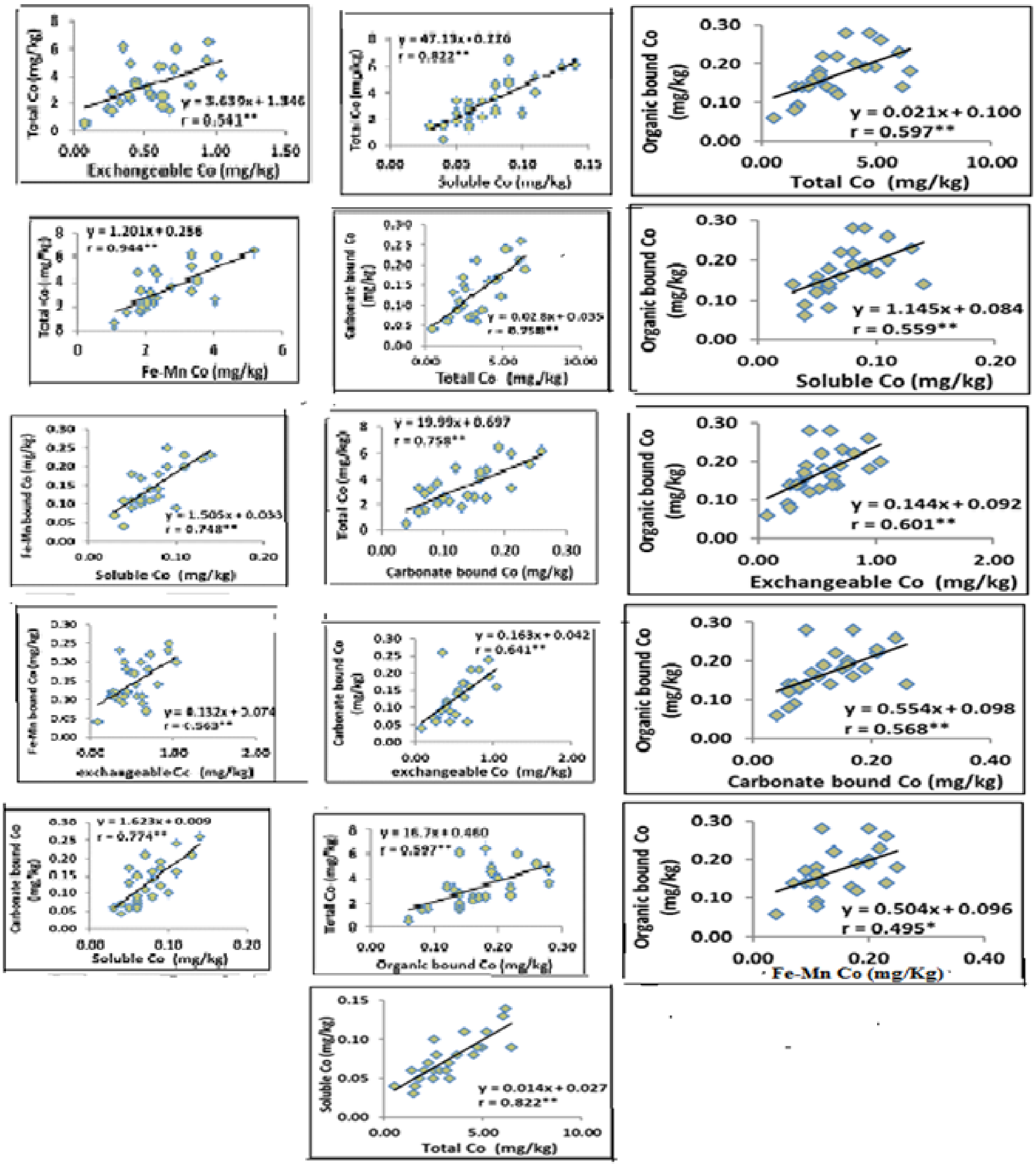


Fig. 4. Relationshipsamong forms of Coof some soils in the 10thof Ramadan city

Furthermore, Fe - Mn bound Cowas highly significantlyand positively correlated with total Co (r=0.944**), soluble Co (r=0.748**), exchangeable Co (r=0.563**) and carbonate bound Co (r=0.696**).Tosubstantiate the relationship of organic bound Co and other Co forms, the obtained correlation coefficients revealed that organic bound Co is highly significantlyand positively correlated with total Co (r= 0.597**), soluble Co (r= 0.559**), exchangeable Co (r= 0.601**) and carbonate bound Co (r= 0.568**) and significantly positively correlated with Fe-Mn bound Co (r= 0.495*).

Relationship amongsoil minerals and forms of Cobaltof the studied soils

Statistical analysis showed highly significant positive correlation coefficient between kaolinite mineral and Fe-Mn bound (Co) % (r = 0.837**), significant positive correlation coefficientbetween kaolinite and organic bound (Co)%(r = 0.755*), while it significantlybut negatively correlatedwith total Co% (r=-0.799*).Furthermore, montmorillonite mineral was significantly and positively correlated with residual (Co) % (r = 0.730*),butsignificantly and negatively correlated withDTPA-extractable (Co)% (r=-o.730*) (Fig. 5).

To substantiate the relationship between accessory minerals and Co forms, statistical analysis (Fig. 5)**.** Revealed that calcite mineral was highly significantly and negatively correlated with total (Co) % (r = -0.840**), pyrite mineral was significantly and positively correlated with carbonate bound (Co) % (r = 0.729*) and, magnetite mineral wassignificantly and negatively correlated with exchangeable (Co) % (r = -0.773*).

TABLE 6. Correlation coefficients (r) among the studied Co forms and some corresponding variables of the 10th of Ramadan studied soils

Variables	**Variables mgkg^{-1}**						
	Total (Co)	**DTPA-extractable (Co)**	**Soluble (Co)**	**Exchangeable (Co)**	**Carbonate (Co)**	**Fe-Mn Bound (Co)**	**Organic Bound (Co)**
Gravel (%)							
Coarse sand (%)	-0.502*		-0.587**	-0.476*	-0.525**	-0.434*	-0.696**
Fine sand (%)							0.602**
Silt (%)		0.435*		0.427*	0.409*		
Clay(%)	0.598**	0.463*	0.480*	0.610**	0.687**	0.606**	
pH							
EC (dS/m)	0.431*	0.722**				0.451*	0.514*
$CaCO_3$(gkg^{-1})	0.409**	0.510*	0.446*	0.612**	0.641**	0.584**	0.635**
OM (gkg^{-1})							
Soluble Na^+(mmol$_c$L^{-1})		0.901**				0.413*	
Soluble K^+(mmol$_c$L^{-1})	0.512*	0.681**		0.410*	0.490*	0.508*	
Soluble Ca^{+2} (mmol$_c$L^{-1})	0.408*	0.556**				0.426*	
Soluble Mg^{+2} (mmol$_c$L^{-1})							
Soluble HCO_3^- (mmol$_c$L^{-1})	0.476**		0.442*	0.627**	0.438*	0.484*	0.498*
Soluble Cl^-(mmol$_c$L-1)		0.890**					
Soluble SO_4^{-2}(mmol$_c$L^{-1})							
CEC (cmol$_c$kg^{-1} soil)	0.791**	0.546**	0.572**	0.518**	0.610**	0.706**	

(1) Significant correlations only are shown in the table.
(2) Levels of significance 5 % (*) and 1 % (**).

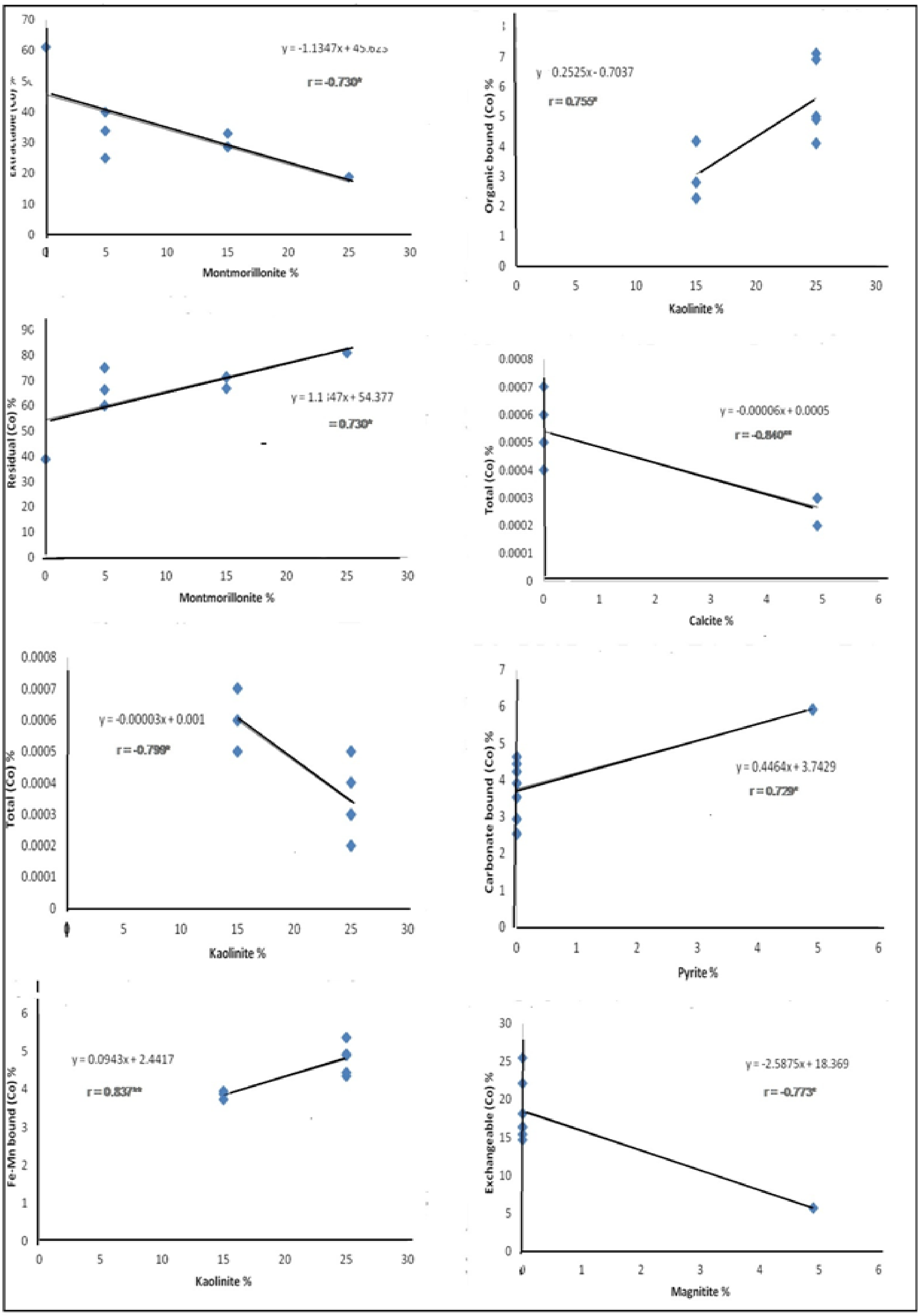


Fig. 5. Relationshipsamong soil minerals and forms of Co of the investigated soils inthe 10th of Ramadan City

Conclusion

The obtained results revealed that the types of clay mineral could affect, to some extent, the distribution of the trace element Co among the different soil fractions. This conclusion was achieved due to the detected highly positive significant correlation between kaolinite mineral and each of Fe-Mn bound Co and organic-bound Co fractions beside of its negatively significant correlation with total Co fraction .Furthermore, a positive significant correlation was detected between montmorillonite mineral and content of the residual Co fraction. Likewise, montmorillonite significantly but negatively correlated with exchangeable Co fraction. A similar significant and negative relationship was detected between calcite mineral and total Co fraction. Also, pyrite mineral positively and significantly correlated with carbonate-bound Co fraction while themagnetite mineral was negatively and significantly correlated with exchangeable Co fraction.

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توزيع وصور الكوبلت وعلاقتها بالتركيب المعدنى فى أراضى مدينة العاشر من رمضان، مصر

نبيل محمدعبداللطيف بهنساوى[١]، عبدالسلام علوه[١]، ليلى عيسى صدقى[١]، تماضرالعيسوي[٢]
[١]مركزبحوث الصحراء- القاهرة و [٢]كلية العلوم - جامعة بنها - بنها - مصر.

تهدف الدراسة إلى معرفة توزيع وصور الكوبلت وعلاقتها بالتركيب المعدنى في أراضى مدينة العاشر من رمضان، مصر.ولهذا تمإختيار ثمانيةقطاعات أرضيه تمثل أراضى منطقة الدراسة. أوضحت النتائج أن قوام التربة يتراوح من الرملى إلى الطميي الرملى.وكان تفاعل التربة يتراوح من (٦,٩٨-٨,٦٨). كما تراوحت قيم التوصيل الكهربائىمن (٠,٨- ٨,١٢ ديسميتر فى٢٥درجه مئوية). وكانت الكاتيونات السائدة تتبع الترتيب التنازلى كما يلى: الكالسيوم> الماغنسيوم > الصوديوم > البوتاسيومبينماكان التركيب الأنيونى السائدهو التالى : الكبريتات> الكلوريد> البيكربونات.وأوضحت النتائج أن معادن الطين السائده هى: الكاؤولينيت > المنتموريلونيت> الإليتبينما المعادن المصاحبه هى:الكوارتز> الجبس >الدولوميت > الكالسيت > الأراجونيت > الهيماتيت > الماجنتيت > الجوثيت > البيوتيت >> المسكوفيت > الفلسبارات البوتاسى.كماوأوضحت النتائج أن المحتوى الكلى للكوبلت يتراوح من (١,٤٢ إلى ٦,٤٦ مجم لكل كجم), والمستخلص كيميائياً يتراوح من (٠,٦٥ إلى ١,٨٠ مجم لكل كجم).ولتجزئة صورالكوبلت من المحتوى الكلى تم إجراء الاستخلاص المتتابعالذى أوضح أن الصورةالمتبقية من الكوبلت هى الأكثر إنتشاراً.وتراوحت قيم الصور القابله للذوبان والمرتبطة بالكربونات والمرتبطة بالحديد والمنجنيز والمرتبطة بالمادة العضويةمن (١,٥١ إلى ٤,٢٤٪) ،(١,٨١, إلى ٧,٣٢٪) ، (٢,٦٣ إلى ٧,٧٧٪) ، و (٢,٢٧ إلى ٩,٤٦٪)على التوالي.وعموماً فقد أوضحت النتائج أن صور وتجزئة الكوبلت هى: المتبقي>> المتبادل > المرتيط عضوياً> المرتبط بالحديد والمنجنيز > المرتبط بالكربونات > الصورة الذائبة. كما أوضحت النتائج أيضاً أنه هناك علاقه بين صور الكوبلت والتركيب المعدنى للأراضى المدروسة.