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EXTRACTABLE TRACE METALS IN SOILS OF SIWA OASIS AS RELATED TO SOIL VARIABLES AND PRODUCTIVITY

Kandil, S.A.
Soil Chemistry and Physics Department, Desert Research Center, El-Matareya, Cairo, Egypt.

Nine soil profiles were chosen to represent the pedological and productivity variations along Siwa Oasis, from which 27 soil samples were collected from the subsequent depths. The relevant morphological, physical and chemical characteristics of soils were presented. Nine trace metals (Fe, Mn, Zn, Co, Ni, Sr, and Cd) were chemically extracted using DTPA.

The results indicate that the amounts of chemically extractable Fe, Mn, Zn and Co are relatively higher in the medium - textured soils while the contents of the other studied trace metals are more pronounced in the coarse - textured soils. Except for chemically extractable Fe, the highest contents of trace metals characterize the poorly productive soils. In all cases, Cd is below the detection level. Depthwise distribution of extractable trace metals does not portray any specific pattern pertaining to locality, soil variations, productivity level and specify of metal except in few cases.

Computation of the weighted means of the studied trace metals reveals that the medium-textured soils attain relatively higher weighted means of Fe, Mn, Cu, Zn and Co while the reverse is true for Ni, Pb and Sr. This could be explained on basis of soil genesis, formation, intermixing of multi-parent materials and multi-depositional regimes of the studied soils. Moreover, weighted means of trace metals are generally higher in the moderately and poorly productive soils with few exceptions. Nevertheless, none of the studied trace metals approached the maximum acceptable concentrations for environmental pollution.

To figure out the relationship between chemically-extractable heavy metals and soil variables, statistical analyses were performed. These analyses reveal that Fe, Zn, Co, and Pb are negatively correlated with soil PH while Fe, Zn, Pb and Sr are positively correlated with HCO_3^-. Cobalt is positively correlated with Fe while being negatively correlated with Mg. Nickel is the only heavy metal that has a highly significant positive correlation with $CaCO_3$ (Fig. 15). Strontium exhibits positive correlations with soil salinity and its individual components except for HCO_3^-. Moreover, Mn and Co are highly significant positively correlated with silt and clay while Zn and Pb are positively correlated with sand.

Keywords: Siwa Oasis, DTPA, trace metals, vertical analysis, vertical distribution, statistical analysis, multiple regression, weighted mean.

Heavy metals accumulation and remobilization in soils are key aspects to understand pollution potential toxicity, possible human and animal health hazards and ecological system disturbance. Among these heavy metals, some have been shown to be of biological significance, i.e., essential for plants, animals and human beings but the essentiality of few others has not been established. Additionally, it is apparent that heavy metals content of soil is dependent almost entirely on the parent rocks of soils and the geochemical and pedochemical weathering processes to which soil-forming materials has been subjected. In addition, aerial sources, fertilizers, manures, pesticides, seepage water and sewage-derived materials have added to heavy metals pool in soils while depletion by crops or stock is also occurred.

Total reliance on heavy metals concentration may also provide an impression on anthropogenic loadings in the environments. This led previous investigations to focus on heavy metals, particularly Pb and Cd in surface soils because of their long residence time and their potential toxicity. But limited attention was given to heavy metals concentration in the subsurface and deeper layers of soils in the closed environmental system of Siwa. Therefore, this study was designed to explore the depthwise chemically-extractable concentrations of nine heavy metals in soils having varying degrees of productivity and characteristics along the environmental media of Siwa Oasis. This is conducted through monitoring the levels of these metals in soils to find out whether their likely accumulation is harmless, or not, which is of great environmental concern.

MATERIALS AND METHODS

Study Area and Sampling

Among the large depressions and oases of the Western Desert of Egypt, Siwa Oasis represents an important elongated closed north-western basin, situated 300km southwest Mersa Matruh city, 50km south EL-

Salloum, east the Egyptian – Libyan frontier, between long. 25° 18' and 26° 05' E and lat. 29° 05' and 29° 21' N (Fig.1) occupying an area of about 1100km^2. Siwa oasis has an irregular elongated shape extending in east-west direction for about 75km but narrowing westward with a width that varies between 9 and 28 km.

The climate is hyper-arid, characterized by mild rainless winter and hot rainless summer, highest mean temperature (25.8°c), high relative humidity (30-60%) and relatively low evaporation (5.5-17.5 mm/day). The lakes in Siwa Oais cover 9000 feddan in winter and decreased abruptly to 3700 feddan in summer due to the increase of evaporation (DRC, 1989). Value of Lang's rain factor, Mayer's N/S Quotient and Emberger coefficient indicate severe aridity prevailing in the depression.

The stratigraphy of exposed rocks in Siwa depression, from oldest to youngest are Middle Eocene, Upper Eocene, Oligocene, Miocene, recent and sub recent deposits, Parsons (1962) the floor of the depression is partly covered with salt lakes and sabkhas, Metwally (1953). Edward (1956) showed that the entire western Siwa area, extending over a large area northwest, west and southwest is composed of Middle Miocene rocks while Blair (1957) showed that the eastern Siwa area is composed of Middle Miocene with Upper and Middle Eocene sediments exposed in or adjacent to Siwa and Qattara depressions.

Topographically, the depression floor lies between 10 and 18 m below the sea level. The topographical features of the depression are related to geological, lithological, structural and climatic conditions. Siwa Oasis occupies a large area of the Great Sand sea with an altitude sinks, some meters below sea level.

Concerning soils, two soil orders (Aridisols and Entisols) have been identified according to U.S. Soil Taxonomy, (Harga *et al.*, 1975). Those orders are further differentiated into Typic salorthids, Salorthic-Calciorthids, Aquic Calciorthids under the order Aridisols, and Salorthic Psammaquents and Typic Torripsamments under the order Entisols. The soils of the oasis exhibit some degradation due to water logging and excess irrigation water which is reflected on their productivity. Several efforts are therefore undertaken to estimate water budget and soil salinization and deterioration in order to increase agricultural potentialities of soils and water resources.

Worthmentioning that the only source of water is groundwater discharging from Miocene bedrock, mostly from the underlying Nubian Sandstone reservoirs. The principal crops in Siwa are dates, olives, citrus, barley and vegetables.

Nine profiles were dug in soil of variable productivity within each locality to represent the variations encountered in the pedological features along Siwa Oasis on the eastern (profiles 1, 2 and 3), western (profiles 4, 5 and 6) and northern (profiles 7, 8 and 9) portions of the Oasis (Fig.1).

Twenty seven soil samples were collected from the subsequent depths according to the conspicuous features within each profile. The morphological description of the studied profiles is given in table (1). The collected soil samples were air-dried, crushed, and sieved through a 2mm sieve, then kept for analysis.

Soil Analysis

The physical and chemical properties of the studied soils were determined according to Black (1965). Following DTPA extraction (Lindasy and Norvell, 1978), the extractable contents of nine trace metals (Fe, Mn, Cu, Zn, Co, Ni, Pb, Sr and Cd) were determined by atomic absorption spectrophotometer, Perkin Elmer, 2380. Data were subjected to statistical analysis according to Snedecor and Cochran (1982) using "Costat Program". Simple correlation and regression analysis were computed. The polynomial lines regression analysis and correlation coefficients between soil variables (dependent) and trace metals (independent) are also computed.

RESULTS AND DISCUSSION

Soils Characteristics

Nine representative profiles (Fig.1) were chosen to cover the widest possible ranges of soils variation within the area under consideration. The soil studies include morphological description of these profiles, summed up in table (1). These descriptions were amplified by factual data about the physical and chemical characteristics of the subsequent layers in each profile, tables (2 and 3).

The obtained data revealed that all the examined soil profiles are moderately deep except for profile 7 which is very shallow. Soil texture is dominated by coarse texture, being sand to loamy sand in six profiles (2,4,5,6,7 and 8) while being sandy loam to clay loam in the rest of profiles (1,3 and 9). Soil Moisture holding properties at field capacity and critical level coincide well with soil texture class. Soil reaction varies considerably as shown by PH values, being neutral to mildly alkaline in profiles 2,4,5,6 and 9 while being alkaline in other soil profiles. The soils are non saline to slightly saline in general as indicated by ECe values except for the surface layer of profiles 5 and 6 while being extremely saline in profile 7. Salinity tended to concentrate in the surface layer of most profiles. Soluble cations are mostly in the order $Na^{+} > Ca^{++} > Mg^{++} > K^{+}$ while soluble anions follow the order $Cl^{-} > SO_4^{--} > HCO_3^{-}$ except in few cases where K^{+} slightly exceeded Mg^{++} (the deeper layers of profile 2 and the top layer of profile 3) and SO_4^{--} exceeds Cl^{-} (the top layer of profile 9). $CaCO_3$ content dictated that the soils are generally of calcareous to highly calcareous nature. Depthwise distribution of $CaCO_3$ showed two distinct patterns where $CaCO_3$ tends to increase downwards within profiles 2,3,5,6 and 8 while the converse is true in other profiles.

TABLE (1). Summary of soil morphological description of the studied soil profiles.

Profile No	Location		Depth cm	Colour		Texture	Structure	Pedological Features
	longitude	latitude		Dry	Moist			
1	29° 9' 26''	25° 48 37	0-25	Light gray(10YR7/2)	Brownish gray(10YR6/2)	S.C.L.	Mod. med. Sb.a.b.	Fine and coarse healthy roots, Strong. Cal.
			25-70	White (10YR8/2)	Light gray(10YR7/2)	C.L.	Weak fine. Sb.a.b.	Fine medium, big died roots, Strong. Cal.
2	29° 8' 33''	25° 47' 1''	0-30	Very pale brown(10YR8/4)	Very pale brown(10YR7/4)	S.	Single grain	Some big and fine healthy roots, Cal.
			30-60	Very pale brown(10YR8/4)	Very pale brown(10YR8/4)	S.	Massive	Many fine and big healthy roots, Mod. Cal
			60-110	Very pale brown(10YR8/4)	Very pale brown(10YR7/4)	S.	Massive	Many fine and big healthy roots, Mod. Cal.
3	29° 9' 51''	25° 46' 38''	0-20	Gray(10YR6/1)	Dark gray(10YR4/1)	S.L.	Weak fine Sb.a.b.	Some fine roots, Strong. Cal
			20-50	Gray(10YR6/1)	Gray(10YR5/1)	S.C.L.	Moderate medium Sb.a.b.	Many fine and big roots, Strong. Cal.
			50 90	Light gray(10YR7/1)	Gray(10YR6/1)	S.C.L.	Moderate medium Sb.a.b.	Many fine and coarse roots, Strong. Cal.
4	29° 11' 8''	25° 34' 59''	0-20	Very pale brown(10YR7/4)	Pale brown(10YR6/4)	S.	Massive	Rich in fine and medium roots, Mod. Cal.
			20-60	Very pale brown(10YR8/4)	Pale brown(10YR7/4)	S.	Massive	Rich in fine big roots, Mod. Cal.
			60-150	Very pale brown(10YR8/4)	Very pale brown(10YR7/4)	S.	Massive	big roots, Mod. Cal.
5	29° 11' 30''	25° 34' 19''	0-20	White (2.5YR8/2)	Light gray(2.5YR7/2)	L.S.	Massive	Few yellowish nodules, Strong Cal.
			20-60	Very pale brown(10YR7/3)	Pale brown(10YR6/3)	L.S.	Massive	Rich in big roots, few yellowish spots Strong. Cal.
			60-110	Grayish brown(2.5YR5/2)	Dark grayish brown(2.5YR4/2)	L.S.	Massive	Common big roots, few yellowish spots, Strong Cal.
6	29° 11' 29''	25° 34' 13''	0-20	Black yellow (2.5YR7/4)	Light yellowish brown (2.5yR6/4)	L.S.	Massive	Strong. Cal.
			20-60	Light gray(10YR7/2)	Light brown. gray(10YR6/2)	L.S.	Massive	Rich in big roots, Strong. Cal.
			60-110	Light gray(10YR7/2)	Light brown. gray(10YR6/2)	L.S.	Massive	Common big roots, Strong. Cal.
7	29° 13' 34''	25° 28' 5''	0-10	Light gray(10YR7/2)	Light brownish gray(10YR6/2)	L.S.	Massive	Common Strong. Cal.
			10-30	n.d.	Gray (10YR6/1)	L.S.	Massive	Strong. Cal.
8	29° 14' 13''	25° 28' 36''	0-20	Very pale brown(10YR7/3)	Pale brown(10YR6/3)	S.	Massive	Common fine roots, Strong. Cal.
			20-50	Very pale brown(10YR8/3)	Very pale brown(10YR7/3)	S.	Massive	Common roots, Strong. Cal.
			50-80	Very pale brown(10YR8/4)	Very pale brown(10YR7/4)	S.	Massive	Common big roots, Strong. Cal.
			80-120	Yellow(10YR8/6)	Yellow(10YR7/6)	S.	Massive	Common big roots, Strong. Cal.
9	29° 14' 5''	25° 28' 50''	0-20	Light gray(10YR7/2)	Light brownish gray(10YR6/2)	L.S.	Massive	Some fin roots, Strong. Cal.
			20-50	Light brownish gray(10YR6/2)	Grayish brown (10YR5/2)	S.L.	Massive	Some fine roots, Strong. Cal.
			50-80	Pale brown(10YR6/2)	Brown(10YR5/3)	L.	Massive	Common Strong. Cal.
			80-110	n.d.	Light brownish gray(10YR6/2)	S.C.L.	n.d.	Some grayish mottling, Strong. Cal.

Sb.a.b.: Sub angular blocky Cal.: Calcareous Strong. Cal.: strong Calcareous Mod. Cal.: Moderately calcareous n.d.: not detected

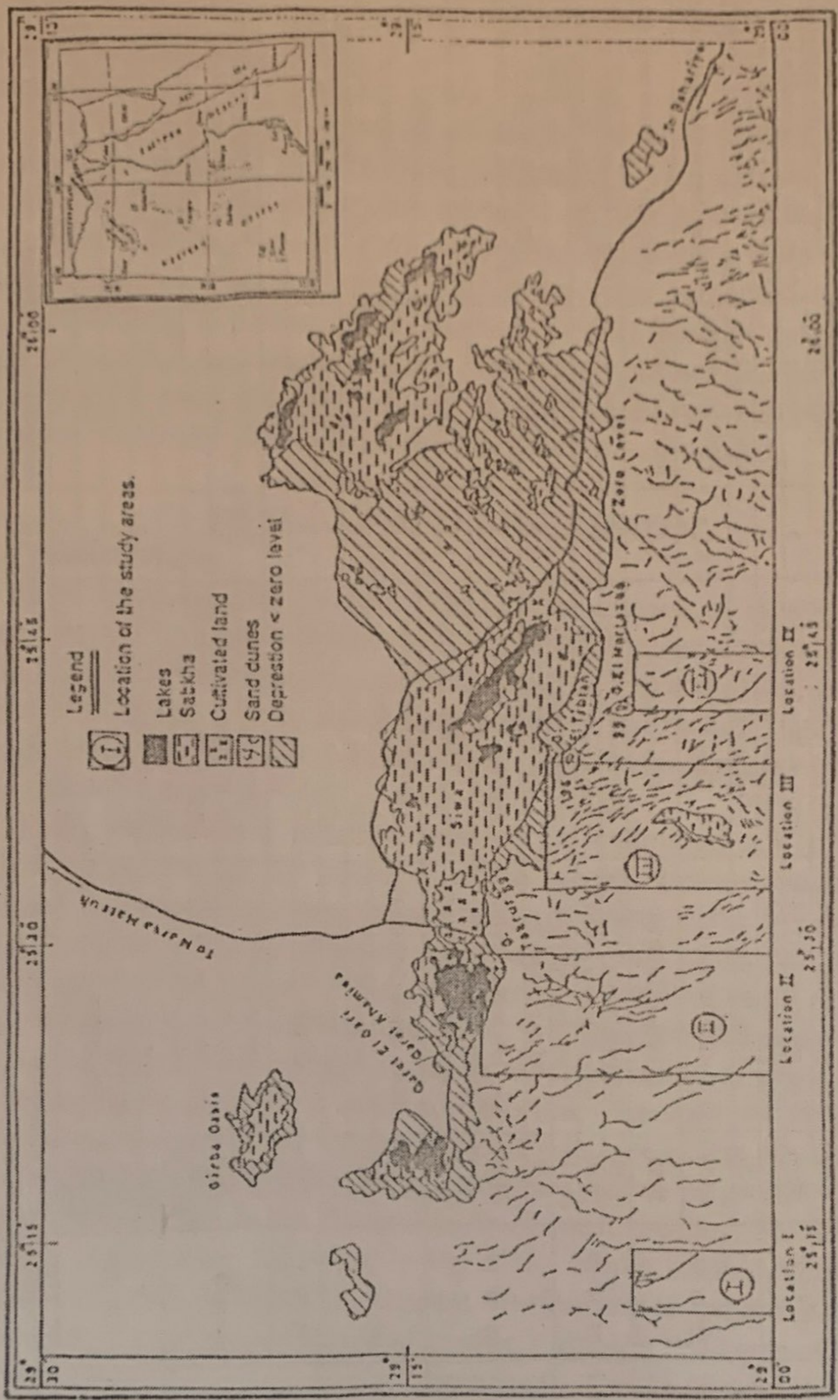

Fig.1. location of the study area.

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TABLE (2). Chemical composition of the studied soils.

Profile No.	Depth cm	Ca CO_3 %	pH (soil paste)	E.C dSm^{-1}	Soluble cations (me/l)				Soluble anions (me/l)			
					Na^+	K^+	Ca^{++}	Mg^{++}	$CO_3^=$	HCO_3^-	Cl^-	$SO_4^=$
1	0-25	28.18	8.15	1.13	7.17	0.64	2.55	0.95	-	2.38	4.96	3.97
	25-70	24.87	8.61	0.48	3.91	0.43	1.50	1.25	-	1.80	3.16	2.13
2	0-30	9.79	9.01	0.15	1.15	0.20	0.67	0.33	-	0.38	1.50	0.47
	30-60	10.71	8.78	0.13	0.91	0.18	0.74	0.06	-	0.52	0.71	0.66
	60-110	12.97	8.84	0.23	1.15	0.20	0.94	0.06	-	0.58	0.94	0.83
3	0-20	30.12	8.30	1.27	11.43	0.83	3.76	0.45	-	1.57	9.00	5.90
	20-50	34.63	8.40	1.35	11.30	0.56	2.50	1.05	-	1.79	7.62	6.00
	50-90	40.00	8.41	1.10	10.00	0.59	1.79	0.97	-	1.79	6.41	5.15
4	0-20	12.38	7.90	0.35	1.89	0.31	1.33	0.67	-	0.38	2.20	1.62
	20-60	12.55	8.25	0.20	0.87	0.22	0.77	0.48	-	0.39	1.16	0.79
	60-150	7.03	7.41	0.26	1.15	0.18	0.88	0.59	-	0.39	1.31	1.10
5	0-20	17.73	7.48	3.95	23.48	0.54	16.65	4.60	-	2.98	24.29	18.00
	20-60	18.32	7.41	2.02	14.04	0.92	5.99	2.01	-	2.98	16.00	3.98
	60-110	22.50	7.31	1.40	8.65	0.72	5.93	2.06	-	2.98	12.00	2.38
6	0-20	18.30	7.70	14.60	86.96	6.14	49.95	31.30	-	3.57	130.80	39.98
	20-60	19.32	7.03	2.36	9.35	0.90	8.26	5.98	-	4.17	12.30	8.02
	60-110	19.44	7.00	1.24	8.78	0.87	3.55	1.45	-	2.98	7.62	4.05
7	0-10	28.28	8.35	86.60	765.22	0.36	54.90	27.20	-	2.34	550.00	276.34
	10-30	24.51	8.85	50.90	377.62	35.00	66.20	30.18	-	2.98	442.84	63.18
8	0-20	31.46	8.21	1.06	8.57	0.63	2.05	1.45	-	2.95	7.00	2.75
	20-50	44.02	8.86	0.57	5.09	0.43	1.78	1.22	-	1.76	4.31	2.45
	50-80	49.60	8.56	0.65	5.35	0.43	1.94	1.31	-	1.98	4.05	3.00
	80-110	52.96	8.57	0.90	6.65	0.40	1.61	1.64	-	1.98	5.03	3.29
9	0-20	28.53	7.68	2.17	16.29	0.41	3.31	1.69	-	3.57	2.16	5.97
	20-50	27.44	7.41	0.96	7.17	0.54	2.33	1.42	-	1.74	5.13	4.59
	50-80	24.85	7.34	1.53	12.26	0.66	2.72	1.78	-	2.76	9.02	5.64
	80-110	26.19	7.48	1.17	11.30	0.56	2.33	1.92	-	2.36	8.04	5.71

TABLE (3). Physical properties of the studied soils.

Profile No.	Depth cm	Moisture content %		Available soil water %	Particle size distribution %			Texture class
		Field capacity	Wilting point		Sand	Silt	Clay	
1	0-25	38.78	13.85	24.93	41.22	24.15	34.63	CL
	25-70	35.20	12.57	22.63	43.52	24.48	32.00	CL
2	0-30	6.12	2.55	3.57	97.27	0.68	2.05	S
	30-60	7.78	3.24	4.54	97.47	0.66	1.87	S
	60-110	10.08	4.20	5.88	97.39	0.76	1.85	S
3	0-20	24.07	10.03	14.04	64.06	19.87	16.07	SL
	20-50	30.97	11.06	19.91	51.53	17.55	30.92	SCL
	50-90	41.24	14.73	26.51	39.10	25.46	35.44	CL
4	0-20	6.55	2.73	3.82	97.37	1.24	1.39	S
	20-60	7.78	3.24	4.54	97.64	0.71	1.65	S
	60-150	9.72	4.05	5.67	97.39	2.28	0.33	S
5	0-20	16.54	6.89	9.65	85.49	4.45	10.06	LS
	20-60	17.00	6.37	10.63	84.42	4.96	10.62	LS
	60-110	10.58	4.41	6.17	88.38	8.22	3.40	LS
6	0-20	16.82	7.01	9.81	84.60	8.25	7.15	LS
	20-60	18.14	7.56	10.58	87.46	6.17	6.37	S
	60-110	14.47	6.03	8.44	86.44	2.16	10.90	S
7	0-10	16.77	6.45	10.32	86.35	3.41	10.24	LS
	10-30	14.69	6.12	8.57	84.15	6.56	9.29	LS
8	0-20	9.67	4.03	5.64	90.68	1.80	7.52	S
	20-50	10.78	4.49	6.29	92.32	3.86	3.82	S
	50-80	10.54	4.39	6.15	87.42	4.98	7.60	S
	80-110	8.45	3.52	4.93	89.76	5.52	4.72	S
9	0-20	10.13	4.22	5.91	93.20	2.55	4.25	S
	20-50	23.74	9.89	13.85	70.97	12.31	16.72	SL
	50-80	19.85	8.27	11.58	72.20	12.89	14.91	SL
	80-110	20.26	8.44	11.82	71.75	11.19	17.06	SL

S: Sand CL: Clay Loam
C: Clay LS: Loamy Sand
SL: Sandy Loam SCL: Sandy Clay Loam

Chemically Extractable Trace Metals in Soils East of Siwa Lake

Table (4) presents the chemically extractable amounts of the studied trace metals in the representative soil profiles. From these data one can figure out that chemically extractable trace metals in soils east of Siwa lake are as follows.

Chemically extractable Fe in soils east of Siwa lake (profiles 1,2 and 3) varies widely from about 0.80 to 19.02 ppm with an appreciable increase in the uppermost surface layer. The highest content characterizes the top layer of profile 1 (soils of higher productivity) while the lowest content is that of the subsurface layer of profile 3 (poorly productive land). The common increase of Fe in the top layer could exhibit its affinity to form organic complexes or chelates which accumulates due to the sandy clay loam texture that prevent its migration downwards.

Chemically extractable Mn also varied considerably, being in the range of 2.56 ppm 2.70 in profile 2 (moderately productive land)and increased considerably to reach up to 44.42 ppm in the deepest layer of profile 3 which represents the poorly productive land in this locality. The fairly productive land (profile 1) attains moderate amounts of chemically extractable Mn with a pronounced increase in the top surface. Depthwise distribution of Mn indicates three patterns where Mn tends to accumulate in the top layer of profile 1 while being almost constant in profile 2 and increased abruptly downwards profile 3.

Chemically extractable Cu constituted about 0.05 to 0.29 ppm , being at its lowest content in the moderately productive soil of profile 2 while being at its maximum in the poorly productive soil (profile 3) and of moderate level in the top layer of fairly productive soils (profile 1). Depthwise distribution of Cu shows relative accumulation in the subsurface layers of profile 1 and 3 while being constant in profile 2.

Chemically extractable Zn ranged within a narrow limit, from 0.26 to 0.61 ppm with its highest concentration in the top layer of the poorly productive soil (profile 3). The vertical distribution of Zn indicates a pronounced increase of its content in the uppermost surface layer with a tendency of decrease downwards.

Chemically extractable Co ranged from 0.04 to 0.35 ppm. Its lowest content characterized the moderately productive soil (profile 2) while its highest content was associated with the poorly productive soil (profile 3) and the soil of higher productivity (profile 1) attained moderate levels. Likewise, extractable Ni ranged between 0.01 and 0.31 ppm with a distribution pattern quite similar to that already mentioned for Co. The vertical distribution of both metals was quite similar where their extractable contents increased in the top layer of highly productive soil (profile1) while showed a tendency of increase downward the profiles representing the moderately and poorly productive soils.

Chemically extractable Pb ranged from 0.04 to 0.27 ppm with a tendency of decrease downward the soil profiles. Its distribution pattern in regard to land productivity resembles those of Co and Ni irrespective of magnitude.

TABLE (4). Chemically extractable trace metals in the studied soils.

Profile No.	Depth cm	Trace elements, ppm								
		Fe	Mn	Cu	Zn	Co	Ni	Pb	Sr	Cd
1	0-25	19.02	26.46	0.14	0.39	0.22	0.16	0.18	4.87	n.d.
	25-70	9.58	17.73	0.22	0.34	0.17	0.14	0.11	6.05	n.d.
2	0-30	1.53	2.70	0.05	0.42	0.04	0.01	0.13	1.39	n.d.
	30-60	0.80	2.56	0.05	0.26	0.05	0.03	0.04	1.45	n.d.
3	0-20	7.36	30.54	0.25	0.61	0.23	0.15	0.27	6.48	n.d.
	20-50	3.18	42.76	0.29	0.53	0.34	0.28	0.25	6.94	n.d.
	50-90	2.71	44.42	0.22	0.44	0.35	0.31	0.16	6.79	n.d.
4	0-20	9.53	8.69	0.08	1.27	0.07	0.02	0.29	3.32	n.d.
	20-60	2.99	4.33	0.06	1.48	0.04	0.01	0.81	1.67	n.d.
	60-150	5.99	0.79	0.09	1.40	0.04	0.01	0.23	1.42	n.d.
5	0-20	7.36	33.44	0.49	2.18	0.23	0.18	0.91	11.38	n.d.
	20-60	14.43	44.80	0.23	3.81	0.29	0.25	1.10	9.24	n.d.
	60-110	17.17	31.86	0.27	4.29	0.25	0.17	1.38	6.40	n.d.
6	0-20	2.97	6.48	0.14	7.06	0.07	0.05	1.85	21.62	n.d.
	20-60	11.85	11.28	0.18	4.85	0.15	0.10	1.34	8.76	n.d.
	60-110	22.01	16.64	0.72	5.05	0.20	0.13	1.08	4.23	n.d.
7	0-10	0.19	1.40	0.17	4.26	0.02	0.08	1.06	33.56	n.d.
	10-30	2.12	1.66	0.09	1.39	0.03	0.08	0.29	34.36	n.d.
8	0-20	14.75	11.37	0.06	3.53	0.14	0.06	0.74	4.37	n.d.
	20-50	2.60	13.56	0.15	3.41	0.14	0.14	0.71	3.31	n.d.
	50-80	2.07	11.99	0.39	2.42	0.09	1.09	0.57	2.98	n.d.
	80-110	2.23	11.86	0.18	3.96	0.10	0.12	1.16	3.52	n.d.
9	0-20	17.03	14.58	0.08	1.76	0.19	0.11	0.64	4.51	n.d.
	20-50	16.70	15.65	0.08	1.50	0.21	0.16	0.66	3.86	n.d.
	50-80	30.16	16.58	0.11	1.57	0.21	0.18	0.36	5.41	n.d.
	80-110	24.99	15.16	0.15	1.82	0.21	0.23	0.59	4.23	n.d.

n.d. = not detected

Chemically extractable Sr varied from 1.39 to 6.94 ppm with a tendency of increase downward the studied profiles. Its distribution pattern in regard to soil productivity was, more or less, typical to those already mentioned for Co, Ni and Pb regardless of magnitude. In all cases, Chemically extractable Cd is below the detection level in all profiles and samples.

Chemically Extractable Trace Metals in Soils West of Siwa Lake

Data set out in table (4) showed that chemically extractable Fe varied from 2.97 ppm up to 22.01 ppm. The lowest content was found in the top layer of profile 6 (least productive land) and the subsurface layer of profile 4 (highly productive land) while the highest content is associated with the deepest layer of profile 6. Depthwise distribution of Fe indicated a tendency of increase downwards in profiles 5 and 6 while being irregular in profile 4. The increase of Fe in profiles 5 and 6 reflects the water-logged conditions which stimulate the reduction of Fe^{3+} to Fe^{2+}, thus increases iron solubility.

Chemically extractable Mn also varied widely from 0.68 ppm in the deepest layer of profile 4(highly productive land) up to 44.8 ppm in the subsurface layer of profile 5 (moderately productive land). Depthwise distribution of Mn showed an abrupt decrease from the surface downwards in profile 4 while displayed an appreciable increase in the subsurface layer (profile 5) or deeper (profile 6). It is also apparent that the highly productive soil attains the least amount of extractable Mn.

Chemically extractable Cu ranged from 0.06 to 0.72 ppm with the lowest contents in the highly productive soil of profile 4 and the highest content in the deepest layer of the least productive soil of profile 6. Depthwise distribution of Cu exhibited an irregular pattern in all profiles.

Chemically extractable Zn ranged between 1.27 and 7.06 ppm. The lowest content was associated with the highly productive soil, represented by profile 4 and increased progressively in the moderate and poorly productive soils to reach its maximum in the top surface of the latter soil (profile 6). Depthwise distribution of Zn indicates an irregular pattern in profiles 4 and 6 while showed a continuous increase with depth in profile 5.

Chemically extractable Co varied from 0.04 to 0.15 ppm. The lowest content was found in the subsurface and deepest layers of profile 4 which represents the fairly productive land while the highest content characterizes the subsurface layer of the poorly productive land (profile 6). Depthwise distribution of Co revealed relative increase in the surface of profile 4 and the subsurface layers of profiles 5 and 6.

Chemically extractable Ni varied from 0.01 to 0.25 ppm. The lowest content characterized the fairly productive soil (profile 4) while the highest content was associated with the moderately productive soil (profile 5). Depthwise distribution of Ni did not show any specific pattern in the representative profiles, while being concentrated in the top surface of profile 4, it tended to increase progressively in profile 6 and distributed irregularly in profile 5.

Chemically extractable Pb ranged from 0.2 to 1.9 ppm. The lowest content was found in the deepest layer of profile 4 (fairly productive land) while the highest content was found in the top surface of profile 13 (poorly productive land). Depthwise distribution of Pb showed an irregular pattern in profile 4, progressive increase with depth in profile 5 while tended to decrease with depth in profile 6.

Chemically extractable Sr ranged widely from 1.42 to 21.62 ppm, being at its lowest level in the fairly productive land (profile 4) while reached its maximum in the top surface of poorly productive land (profile 6). Depthwise distribution of Sr showed a unique pattern where its content tended to decrease progressively with depth. Chemically extractable Cd was usually below the detection level in all profiles.

Chemically Extractable Trace Metals in Soils South of Siwa Lake

Table (4) revealed that chemically extractable Fe ranged widely from 0.19 to 30.16 ppm. The lowest content was found in the 0-10cm layer of profile 7 (fairly productive land) while the highest content characterized the 50-80cm layer of profile 9 (poorly productive land). A striking feature was the apparent homogeneity of Fe in the deeper layers of profile 8 and the top layers of profile 9, in contrast to their top surface and deeper layers respectively which displayed an appreciable increase in extractable Fe.

Chemically extractable Mn varied from 1.3 to 16.58 ppm. The lowest content was found in the 0-10 cm depth of the fairly productive soil (profile 7) while the highest content was associated with the 50-80 cm layer of the poorly productive soil (profile 9). Noteworthy to mention that the latter layer attained the highest content of Fe, indicating Fe- Mn association in such soil. It was also evident that the amounts of extractable Mn in each profile lie within the same range of magnitude. Moreover, the increase of Fe and Mn contents follows a pattern quite opposite to that of productivity.

Chemically extractable Cu ranged from 0.05 to 0.39 ppm. The lowest content was found in the surface layer of profile 8 (moderately productive soil) while the highest content was associated with the subsurface layer of the same profile. Depthwise distribution of Cu revealed relative concentration in the top layer, subsurface, and deepest layers of profiles representing fairly productive, moderately and poorly productive soils, respectively.

Chemically extractable Zn ranged from 1.39 to 4.26 ppm with the lowest and highest contents in the subsurface and top surface, respectively of profile 7 which represented the fairly productive soil. Depthwise distribution indicated the dominancy of an irregular pattern with a close coincidence between productive soils (profiles 8 and 9) while Zn content decreased abruptly in the subsurface layer of the fairly productive soil (profile 7).

Chemically extractable Co varied from 0.02 to 0.21 ppm with a tendency of gradual increase on passing from fairly productive soil to poorly productive one. A striking feature was the uniformity of Co contents throughout depth in profiles 7 and 9 which represent the fairly productive and poorly productive soils while Co displayed an irregular pattern in the moderately productive soil (profile 8).

Chemically extractable Ni varied widely from 0.05 to 1.09 ppm. The lowest and highest contents were strictly confined to the surface and subsurface layers of the moderately productive soil. Depthwise distribution of Ni indicated a constant level in the fairly productive soil (profile 7), a tendency of Co increase with depth in the poorly productive soil (profile 9) and an irregular pattern in the moderately productive soil (profile 8).

Chemically extractable Pb ranged from 0.29 up to 1.16 ppm. The lowest content was found in the subsurface layer of profile 7 (fairly productive soil) while the highest content was that of the deepest layer of profile 8 (moderately productive soil). Depthwise distribution indicated a tendency of Pb decrease with depth in the fairly productive soil and an irregular pattern of Pb in other soils.

Chemically extractable Sr in each of the studied soil profiles varied within a narrow limit, being at its highest level in the fairly productive soil (profile 7) while being at a lower level within the same range of magnitude in other soil profiles of moderate and poor productivity.

Chemically extractable Cd was usually below the detection level in all the studied soil profiles.

To figure out the relationship between chemically extractable heavy metals and soil variables, the data were subjected to statistical analysis according to Snedecor and Cochran (1982) using the "Costat program". Simple correlation and regression analyses were also computed for the significant relations.

Statistical analyses reveal that Fe, Zn, Co and Pb are negatively correlated significantly with soil pH where r =-0.689, -0.448, -0.370 and -0.502, respectively (Figs. 2,5,3 and 4).

This was expected since the solubility of trace metals is often shown as a function of pH affected by the amount and kind of organic matter. This doesn't exclude the other soil factors such as CEC, carbonates, Fe and Mn hydrous oxides and clay minerals which are known to play a significant role in the behaviour of trace elements: Fe, Zn, Pb and Sr are positively correlted significantly with HCO_3^- where r = 0.406, 0.575, 0.572 and 0.407, respectively (Figs.3,7,15and22). Cobalt was shown to be highly significant positively correlated with Fe (r = 0.551) due to the high selective adsorption by Fe oxides which eliminates its migration in soluble phase, which is reflected on the Co distribution and behaviour in soil profiles showing similar pattern of Fe and Co in soil layers. In contrast, Co is negatively correlated significantly with Mg (r = -0.392, Fig. 10). A striking feature is that Ni is the only heavy metal which has a highly significant positive correlation with $CaCO_3$ (Fig.13), this may be due to organic matter which is able to mobilize Ni from carbonates and decrease its sorption on clays , however Ni bonding to organic ligands could not be particularly strong.

Strontium exhibited highly significant positive correlations with soil salinity and its individual components(Figs.17to24) except for HCO_3^- which is the only insignificant, where r = 0.886,0.846 ,0.652, 0.883, 0.822, 0.909 and 0.766 with EC, Na^+, k^+, Ca^{++}, Mg^{++}, Cl^- and SO_4^{--} , respectively. These results confirm that Sr distribution in soil profiles follows the general trends of soil solution circulation, being easily mobile in light- textured soils such as those predominating in the study area.

Considering the soil mechanical fractions as related to chemically extractable heavy metals, statistical evaluation indicates that Mn and Co are highly significant positively correlated with silt (r=0.643 and 0.683, Figs.21 and 22), and clay (r = 0.666 and 0.713, Figs. 20 and 19). This means that clay and silt contents are important factors that govern Mn and Co distribution and behaviour. On the other hand, Zn and Pb are the only heavy metals that have highly significant positive correlation with sand fraction (Figs. 23 and 24) where r = 0.477 and 0.473, respectively. This may be due to the occurrence of Zn and Pb as readily released constituents from the sand fraction which probably contains Zn and Pb bearing minerals inherited from the soil parent materials.

Multiple regression program is further applied (Forward stepwise multiple regression) and the obtained results are summed up hereafter.

$Fe = 68.065 - 7.685\ PH - 0.461\ Mg^{++} + 2.29\ HCO_3^- + 0.256K^+$.

$Mn = 2.21 - 4.96\ Mg^{++} + 3.09\ HCO_3^- + 3.17\ Ca^{++} - 0.102\ Cl^- - 0.913\ K^+ + 0.34\ CaCo_3$.

$Cu = 0.937 - 0.106\ PH + 0.0041\ CaCO_3$.

$Zn = 5.098 + 0.641\ HCO_3^- + 0.339\ Mg^{++} - 0.0771\ K^+ - 0.124\ Ca^{++} - 0.553\ PH$

$Co = 0.074 + 0.00005\ Cl^- + 0.054\ HCO_3^- - 0.00724\ Mg^{++}$.

$Ni = - 0.0929 + 0.0101\ CaCO_3$.

$Pb = 1.55 + 0.155\ HCO_3^- - 0.164\ pH + 0.0463\ Mg^{++} - 0.0432\ K^+ - 0.0027\ SO_4^{--}$.

$Sr = 1.76 + 0.515\ Ca^{++} + 0.126\ E.C + 0.912\ HCO_3^- - 0.349\ Mg^{++}$.

TABLE (5). Weighted means of the trace metals in the studied soils.

Profile No.	Fe	Mn	Cu	Zn	Co	Ni	Pb	Sr
1	12.95	20.85	0.189	0.361	0.116	0.148	0.131	5.63
2	1.16	2.63	0.049	0.339	0.043	0.021	0.084	1.42
3	3.90	40.78	0.249	0.507	0.319	0.266	0.45	6.77
4	5.66	2.78	0.080	1.404	0.047	0.015	0.388	1.74
5	14.39	36.85	0.294	3.732	0.261	0.199	1.164	8.34
6	14.85	12.84	0.417	5.346	0.157	0.104	1.315	9.04
7	1.47	1.57	0.118	2.347	0.027	0.081	0.542	34.09
8	4.35	12.24	0.205	3.367	0.114	0.359	0.829	3.47
9	22.69	15.58	0.122	1.652	0.206	0.175	0.557	4.87

Fig. (2) Relationship between Fe and pH.

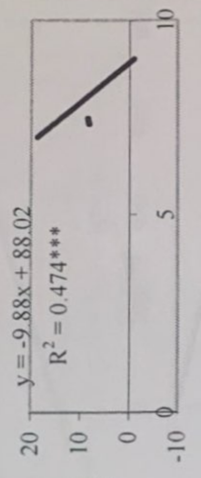


Fig. (3) Relationship between Co and pH .

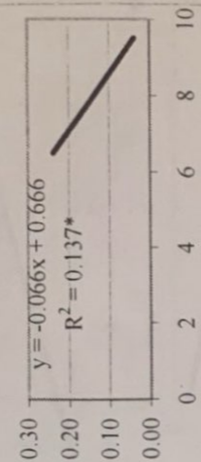


Fig. (4) Relationship between Pb and pH .

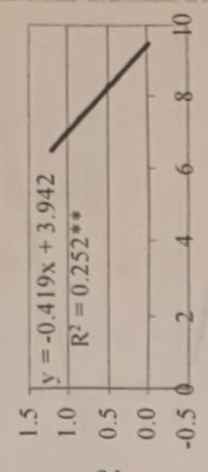


Fig. (5) Relationship between Zn and pH .

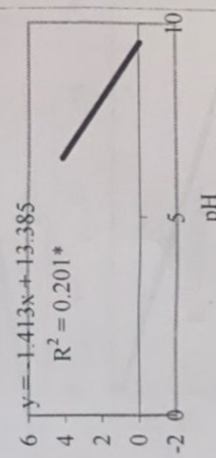


Fig. (6) Relationship between Sr and EC_e .

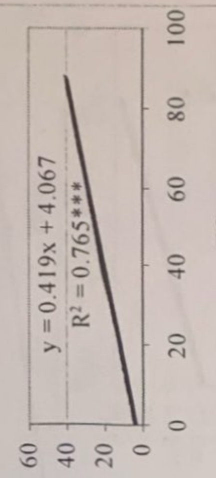
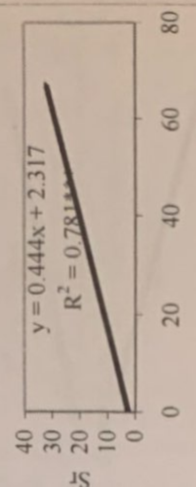


Fig. (7) Relationship between Sr and Ca++ .



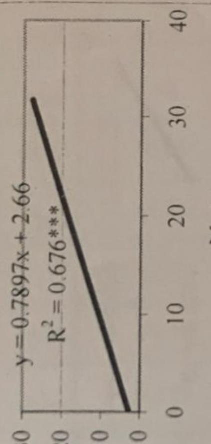


Fig. (8) Relationship between Sr and Mg++.

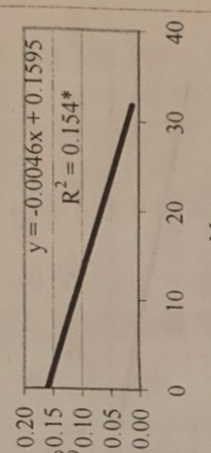


Fig. (9) Relationship between Co and Mg++.

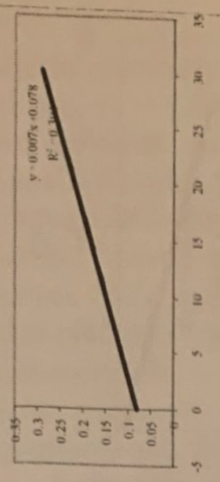


Fig. (10) Relationship between Co and Fe.

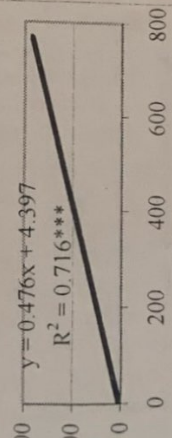


Fig. (11) Relationship between Sr and Na+.

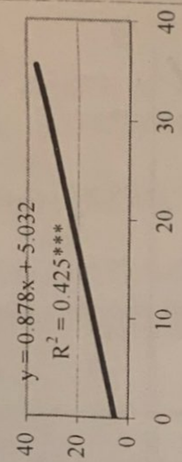


Fig. (12) Relationship between Sr and K+.

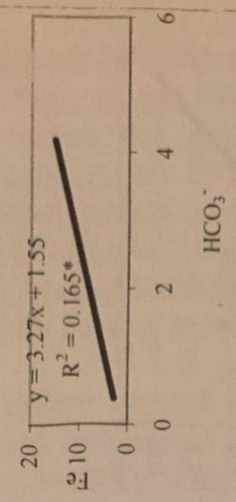


Fig. (13) Relationship between Fe and HCO_3^-.

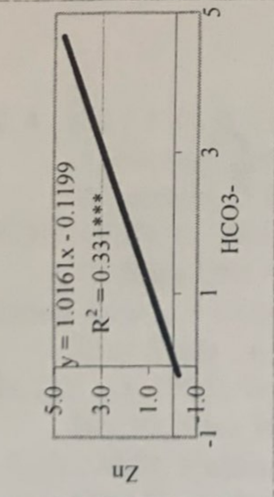


Fig. (14) Relationship between Zn and HCO3-.

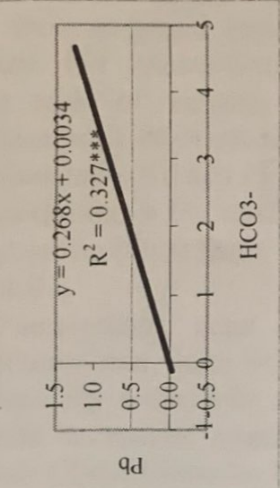


Fig. (15) Relationship between Pb and HCO3- .

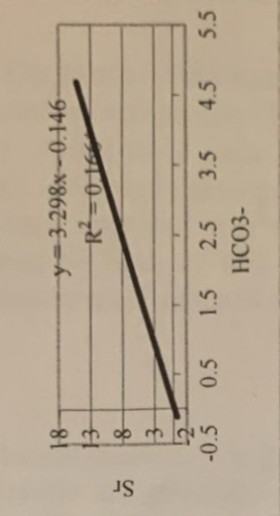


Fig. (16) Relationship between Sr and HCO3-.

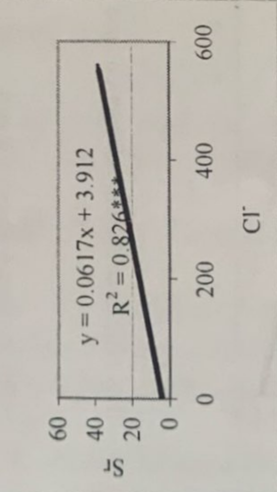


Fig. (17) Relationship between Sr and Cl^- .

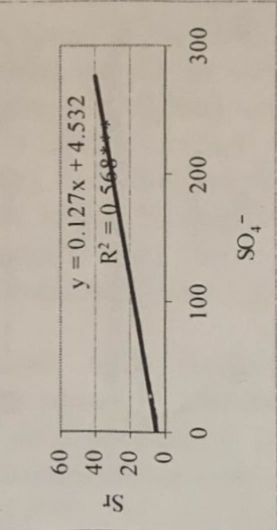


Fig. (18) Relationship between Sr and $SO_4^{=}$.

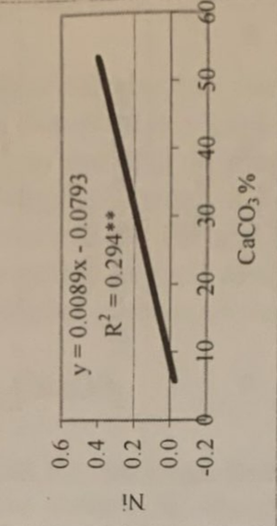


Fig. (19) Relationship between Ni and $CaCO_3$.

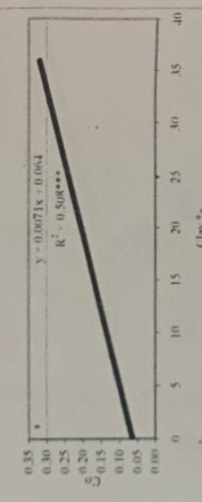


Fig. (20) Relationship between Co and clay .

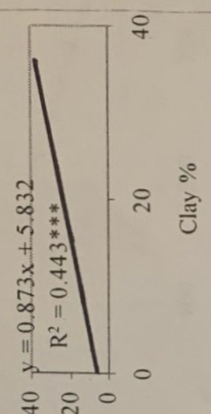


Fig. (21) Relationship between Mn and clay .

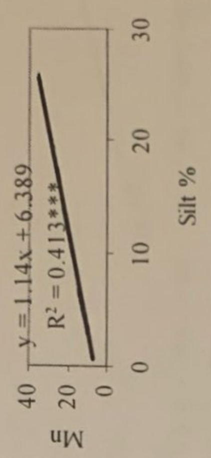


Fig. (22) Relationship between Mn and Silt .

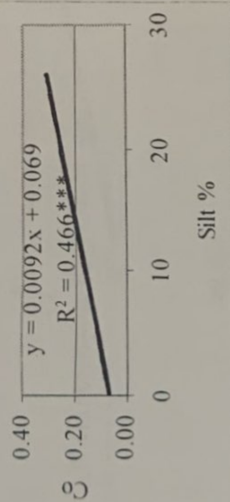


Fig. (23) Relationship between Co and silt .

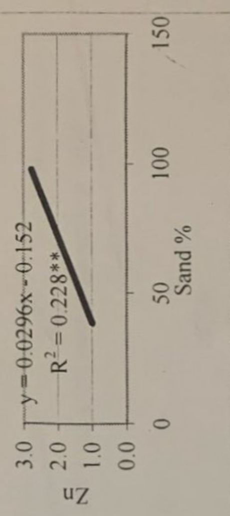


Fig. (24) Relationship between Zn and sand .

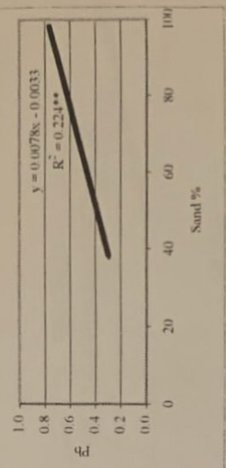


Fig. (25) Relationship between Pb and sand .

For further information about trace metals, their weighted means are computed in each profile (Table 5) and discussed in regard to soil matrix and locality. From these data, it is quite obvious that in most cases medium-textured soils attain relatively higher weighted means of Fe, Mn, Zn and Sr while have relatively low weighted means of Ni, Pb, and Sr. This could be explained on basis of soil genesis, formation as well as the intermixing of multi-parent materials and multi-depositional regimes of the studied soils.

CONCLUSION

In conclusion, it is quite clear that the weighted means of the studied trace metals are generally higher in the moderately and poorly productive soils in the areas under consideration, with few exceptions such as Fe (East Siwa), Pb (west Siwa) and Sr (North Siwa) in the fairly productive soils where their weighted means are superior relative to other soils in these localities. For convenience, the maximum weighted means among the studied soils of variable productivity are associated with the poorly productive soils of North Siwa lake (Fe), East Siwa lake (Mn and Co) and West Siwa lake (Cu and Zn). In addition, Ni and Pb weighted means reached their maximum in the moderately productive soils, North Siwa lake, while the highest weighted mean of Sr is recorded in the fairly productive soils of such locality.

Furthermore, none of the studied trace metals approached the concentration that cause pollution of the soil environments. In other words, the chemically extractable amounts of such trace metals do not exceed the maximum acceptable concentrations in agricultural soils reported by UN Economic Commission for Europe and FAO (1987) and WHO(1989).

REFERENCES

Black,C.A. (ed.) (1965). In *"Methods of soil analysis"*, parts (1 and 2). Agronomy series 91-1572. Am. Soc. Agronomy, Madison, Wisconsin, U.S.A.

Blair, R.W. (1957). In *"Sahara Petroleum Comp"*. Final Geologic Rep. No. 16, Siwa East Area Project.

DRC, Desert Research Center (1989). In *" Project of biological drainage in Siwa Oasis"*. (Arabic Rep.), Desert Res. Center, Egypt. 150pp.

Edwards, D.C. O.(1956). In *"Sahara petroleum comp"*. Final Geologic Rep. No. 10, Siwa West Area Project.

Harga, A. A.; M.M. Hammad and M. A. Abdel Salam (1975). The soils of Siwa Oasis, Egypt. *Desert Ins. Bull., Egypt*, 25 (1,2):173-86.

Lindasy, W.L. and W.A. Norvell (1978). Development of DTPA soil test for Zn, Fe, Mn. *Soil Sci. Soc. Am. J.*,42:421-8.

Metwally, M. (1953). Physiographic features of Oases of Libyan Desert. *Extrait du bull. L'Inst. De Desert D' Egypte.* 3(2):143.

Parsons, R.M. (1962). In *"The Ralph M. Parsons Engineering Comp"*. Final Rept. Oasis Area, New Vally Project, Western Desert of Egypt.

Snedecor, G. W. and W.G. Cochran (1982). In *"Statistical methods"*. 7th ed., Iowa State Univ. Press, Iowa, U.S.A., 593pp.

UN Economic Commission for Europe and FAO (eds.) (1987) In *"The utilization of secondry and trace elements in agriculture"*. ISBN 90-247-3546-7.

WHO (1989). In *"Agiculture and Aquaculture: Health guidelines for the use of wastewater"*. Report of WHO Scientific Group, World Techni. 778, WHO, Geneve, Switherland.

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العناصر الصغرى المستخلصة فى أراضى سيوة وعلاقتها بمتغيرات التربة وإنتاجيتها

سيد أبوزيد قنديل
قسم كيمياء وطبيعة الأراضى - مركز بحوث الصحراء- المطرية- القاهرة- مصر

اختيرت تسعة قطاعات أرضية تمثل التغيرات البيدولوجية والإنتاجية عبر واحة سيوة حيث أجريت الدراسة على ٢٧عينة أرضية ممثلة للتعاقب الطبقى فى القطاعات حيث تمت دراسة أهم الصفات المورفولوجية والطبيعية والكيمائية واختير تسع عناصر صغرى هى الحديد- المنجنيز- النحاس- الزنك- الكوبالت- النيكل- والرصاص والاسترانشيوم والكادميوم حيث تم استخلاصها كيمائيا باستخدام DTPA

وقد أوضحت النتائج أن كمية العناصر المستخلصة كيمائيا كانت مرتفعة نسبيا من الحديد- المنجنيز والكوبالت فى الأراضى متوسطة القوام. بينما كانت كميات العناصر الأخرى المستخلصة أعلى فى الأراضى الخشنة القوام وفيما عدا الحديد المستخلص كيمائيا كانت نسبة العناصر الصغرى أعلى فى الأراضى ضعيفة الإنتاجية كذلك كان محتوى الكادميوم دون مستوى تقدير. وقد أوضح توزيع العناصر رأسيا بعمق القطاع عدم وجود اتجاه مميز للموقع أو متغيرات التربة أو إنتاجياتها أو خصوصية العنصر إلا فى بعض الحالات القليلة.

وبحساب المتوسط الوزنى للعناصر الصغرى المدروسة تبين أن الأراضى متوسطة الانتاجية وضعيفة الانتاجية ذات متوسط وزنى مرتفع نسبيا من الحديد- المنجنيز- النحاس و الزنك والكوبلت بينما سلكت عناصر النيكل والرصاص والاسترنشيوم مسلكا عكسيا. ويمكن تفسير ذلك على أساس اختلافات أصل ومنشأ وتكوين التربة وتعدد مواد الأصل وظروف الترسيب فى الأراضى المدروسة.كذلك كان المتوسط الوزنى للعناصر المدروسة عال نسبيا فى الأراضي متوسطة وضعيفة الإنتاجية مع بعض الاستثناءات القليلة. وبالرغم من ذلك لم يصل مستوى العناصر الصغرى المستخلصة إلى التركيزات القصوى المسموح بها للتلوث البيئي.

ولإيضاح العلاقة بين العناصر الصغرى المستخلصة كيمائيا ومتغيرات التربة أجرى التحليل الاحصائى والذى أظهر أن الحديد والزنك والكوبلت والرصاص ترتبط سلبيا مع pH بينما الحديد والزنك والرصاص والاسترنشيوم ترتبط ايجابا مع HCO_3^- . ويرتبط الكوبلت ارتباطا موجبا مع الحديد بينما يرتبط سلبا مع الماغنسيوم. كما أن النيكل هو العنصر الثقيل الوحيد الذى تربطه علاقه موجبه عاليه مع كربونات الكالسيوم. ويرتبط الاسترنشيوم ارتباطا معنويا موجبا مع ملوحة التربة ومكوناتها الأيونيه عدا البيكربونات. وزيادة على ذلك فان المنجنيز والكوبالت ترتبطان ارتباطا معنويا موجبا وعاليا مع كل من محتوى الطين والسلت. بينما يرتبط كل من الزنك والرصاص ارتباطا معنويا موجبا مع محتوى الرمل. هذا وقد تم تسجيل الانحدار المستقيم المتعدد ومعاملات الارتباط ومعادلات الانحدار المتعدد للنتائج المتحصل عليها.