
GEOCHEMICAL ASSESSMENT OF THE QUATERNARY SOIL IN SIWA OASIS, WESTERN DESERT, EGYPT

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El Awady, M. A. M.⁽¹⁾; Abd-Elwahed. A. G.⁽²⁾; Garamoon, H. K.⁽²⁾
and El Malky, M. G.⁽³⁾

1) Environmental Monitoring Department, Research and Development Sector, Nuclear Power Plant Authority 2) Geology Department, Faculty of Science, Ain Shams University 3) Basic Environmental Science Department, Institute of Environmental Studies and Research, Ain Shams University

ABSTRACT

The physicochemical parameters, major ions and heavy metals of the Quaternary cultivated and uncultivated soils in Siwa Oasis were quantitatively determined. Bivariate and multivariate statistical analyses were applied to clarify the relationship between the investigated metals and soil properties and identify the potential sources of these metals in Siwa Oasis soils

The geochemical characteristics of SiwaOasis soils are controlled by several factors, including the nature of parent rocks, geographic location, soil-forming processes, extent of drainage and leaching, effects of saline near-surface groundwater and agriculture practices.

Key words: Egypt, Western Desert, Siwa Oasis, Quaternary soils, geochemical assessment.

INTRODUCTION

Egyptian agricultural lands are increasingly strained due to limited water resources and significant urban encroachment. Nowadays, Egypt is vulnerable to confrontation a serious problem of the shortage in clean and fertile agricultural soil. Recently many efforts were harnessed to increase the agricultural area in Egypt by reclaiming new lands and strict legislation. The Egyptian Ministry of Agriculture announced an effort to reclaim approximately 1.5 million acres (607,028 ha) of marginal or desert lands for agricultural use.

Siwa Oasis is a promising area for agricultural extension and the associated industrial activities. It comprises a great historic interest due to the presence of Romanic and Pharoanic monuments. Hence, Siwa Oasis is attractive site for tourism. Moreover, the Siwa Oasis is rich in palm and olive trees. Therefore, in recent years, great attention has been directed towards building, agricultural improvement and the construction of agriculturally related industrial projects in this area especially after increasing the population and number of tourists in this area (El-Khoriby and Issa, 1998). Agriculture represents the main activity in Siwa Oasis. Currently, about 88 km² (20940 acres) of the oasis are cultivated. This activity depends on the availability of groundwater from about 1199 wells and springs, which give a total annual discharge of about 255 million m³ (Samy, 2010; Elnaggar *et al.*, 2016; El-Saied, 2017). The cultivated lands in Siwa Oasis suffer from salinization problem. The soil salinization is very high in low lands due to high salinity in groundwater, quick capillary rise of water in soil surface, poor workmanship of pumping water, high evaporation and the high activity of salt weathering (Abdallah, 2007).

Soil chemical properties can be used as chemical attributes to assess soil quality (Heil and Sposito, 1997). This is important in evaluating the condition and sustainability of soil and to guide soil research, planning and conservation policy (De la Rosa and Sobral, 2008; Mastro *et al.*, 2008). Assessing the concentration of potentially harmful heavy metals in the soil is imperative in evaluating its potential risks (Chen *et al.*, 2005).

The Quaternary soils in Siwa Oasis were subjected to a few pedogenetic, textural and mineralogical studies by earlier workers (e.g. Saleh, 1970; Harga *et al.*, 1975; Aziz and Fanous, 1979; Abdou *et al.*, 1980 and 1981; El-Khoriby and Issa, 1998; Omran, 2002; Bahanasawy, 2006). The geochemistry of Siwa Oasis soils received attention of recent workers dealing only with soil salinity and degradation (Ismail *et al.*, 2006; Azzam and Salem, 2007; Aly, 2014; Badawy *et al.*, 2015; Elnaggar *et al.*, 2016; Rashed, 2016a and 2016b; Rafie, 2017).

Most of the previous studies on Siwa Oasis soils were concerned almost entirely with the soil salinity problem and there is no comprehensive geochemical study. Therefore, the aims of the present work are: (1) to investigate the detailed geochemical characteristics of the various soil types in Siwa depression and assess their possible pollution by toxic metals.

MATERIAL AND METHODS

1) Study area: Siwa Oasis, almost unique on its own, represents the last virgin oasis in the Western Desert of Egypt. It extends between latitudes 29° 05' and 29° 24' and between longitudes 25° 14' and 26° 06' (Fig. 1). It is located about 560 km west of Cairo and 300 km south of the Mediterranean Sea coast. The Siwa depression is about 82 km long, 21 km wide with a total area of about 1000 km². It lies at about 18 m below the sea level being completely surrounded by the Sahara Desert (Badawy *et al.*, 2015). The climate of Siwa exhibits extreme aridity from April to November and very low rainfall from December to March (10 mm/yr on average), and its population increased from about 8,000 residents in 1980 to 28,000 residents in 2016.

Geomorphologically, the region comprises mainly closed flat depressions bounded from the north by the Marmarica limestone Plateau with a steep escarpment running E–W and from the south by areas of mobile sand dunes. Playas, saline lakes, and cultivated land are the main habitats of the closed flat depressions (Abdel-Motelib *et al.*, 2015).

From a geological point of view, three main lithologic units of the Middle Miocene age are extensively exposed in Siwa: a lower older Siwa Oasis Member, forming the floor of the depression and consisting mainly of shale and marl; a middle Siwa Escarpment Member, forming the escarpment and the slope of the detached hills; and an upper El-Diffa Plateau Member, occupying the upper surface of the plateau. The escarpment and the plateau consist principally of chalky limestone, limestone, and dolomitic limestone (Gindy and El-Askary, 1969). Structurally, Siwa Oasis occupies a regional NNW–SSE synclinal fold and is characterized by well-developed NW–SE and ENE–WSW

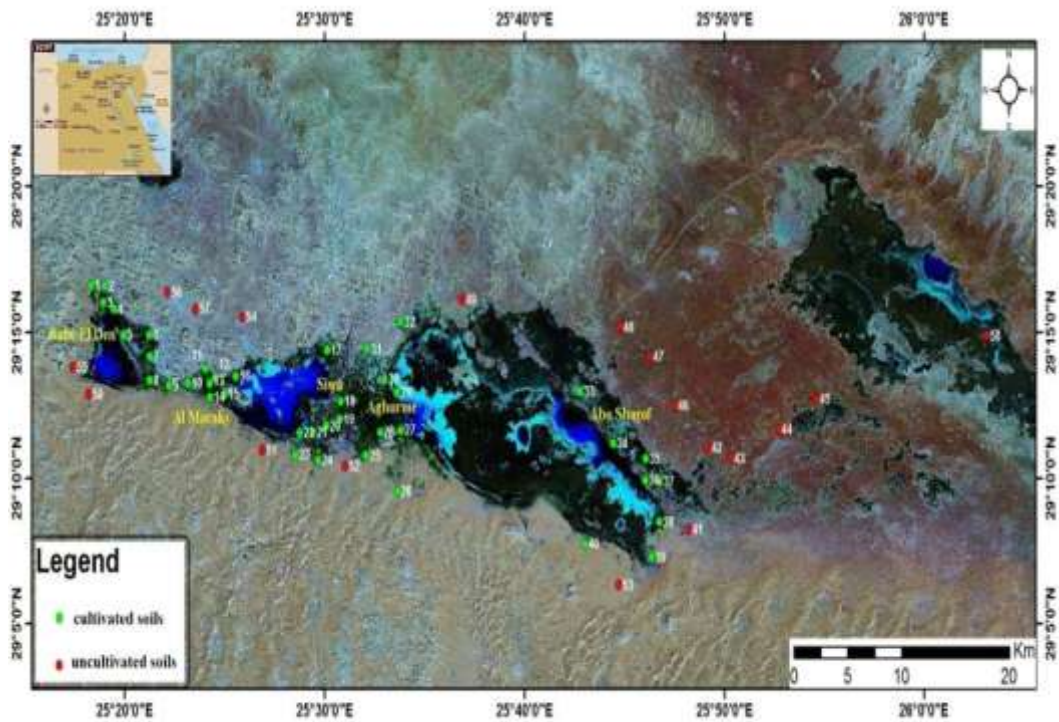


Figure 1 Location map of the Siwa Oasis showing the sampling sites.

Structural lineaments (El Shazly *et al.*, 1978). The tectonic evolution in the Siwa area indicates a complicated geologic history of uplift and subsidence with developed folds, horsts, and grabens (Rizkalla and Awad, 1990).

2) Sampling: A total of fifty-eight top soil samples (0-20 cm depth) were collected from the study area. Forty samples were collected from the cultivated land representing the main suburbs in the Siwa Oasis; eighteen samples were collected from the barren areas representing the uncultivated soils with special attention to the north-eastern part (Fig. 1). From every sampling point, up to 5 subsamples (50×50 m²) were collected and aggregated to obtain a bulk sample; weighting up to 500 g. Soil sample was collected in sealed

polyethylene bags using a clean stainless steel shovel to avoid any contamination.

3) Samples treatment and chemical analysis: After removal of recognizable plant debris and stones, the air-dried soil sample was sieved through 2 mm sieve before analysis. Soil organic matter content (OM) was measured by loss in ignition followed the procedure adopted by Van Reeuwijk (2002). Clay content was measured using pipetting analysis followed the procedure adopted by Lewis and McConchie (1994). pH and EC were determined in aqueous soil suspensions (1 soil:2.5 water) followed the procedure adopted by Pansu and Gautheyrou (2006).

These samples were subjected to chemical analysis. The concentrations of the major cations were determined in the soil extract (1:2.5) using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with ultrasonic Nebulizer (USN) (Perkin Elmer Optima 3000, USA). Major anions were determined using Ion Chromatography (IC) applying model DX-500 chromatography system. Total metals content were extracted using microwave digestion techniques as reported by Littlejohn *et al.* (1991).

4) Statistical treatment: Descriptive statistics and multivariate statistical analysis were determined for the studied soils by using SPSS (version 21). Sampling sites locations in the study area were presented by using Arc GIS (version 9.3). Pearson correlation coefficient matrix was calculated to define the correlations between the different heavy metal pairs and interrelationship between heavy metal levels and OM % and clay content in soil samples. Also,

Cluster analysis (CA) was used to identify the sources contributing to the soil heavy metal contamination and their controlling factors.

RESULTS AND DISCUSSION

1) Physicochemical parameters: Organic matter (OM) could play a significant role in the retention of heavy metals in soils due to its strong adsorption (Guo *et al.*, 2006; Micó *et al.*, 2006). Among the various grain size classes' clay size plays a significant role in distribution of heavy metal in soil samples. Table (1) and Figure (2) show that Soil organic matter (OM%) and clay%

Table (1): The descriptive statistical parameters of the investigated physicochemical properties, major ions and heavy metals.

Soil Type Sample	Cultivated												Uncultivated (N=18)											
	Baba El Dea (N=9)			Al Murrakhy (N=9)			Sima (N=9)			Aghurme (N=9)			Abo Sharof (N=9)			All Cultivated (N=40)								
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
OM %	1.44	7.61	4.34	2.13	7.19	3.93	1.42	3.96	3.19	1.34	5.22	2.86	1.83	8.66	6.55	1.34	8.66	4.17	0.75	2.13	1.40			
Clay %	1.65	11.56	7.37	2.90	8.68	5.29	1.58	9.68	6.27	1.86	8.33	5.02	2.12	18.67	10.51	1.58	18.67	6.89	0.62	1.91	1.48			
pH	8.08	8.67	8.34	8.14	8.42	8.29	7.10	7.97	7.38	7.11	8.45	7.87	7.73	8.56	8.13	7.10	8.67	8.00	7.92	9.05	8.39			
EC ds.m ⁻¹	0.62	1.90	1.07	0.61	1.38	1.05	0.59	2.70	1.10	0.52	1.77	0.82	0.55	3.58	1.55	0.52	3.58	1.12	0.32	2.36	1.04			
Na ⁺	41.00	113.00	69.38	27.00	104.00	76.75	21.00	163.00	81.00	10.00	160.00	49.00	17.00	186.00	91.25	10.00	186.00	73.48	40.00	180.80	94.78			
K ⁺	5.00	39.00	14.38	4.00	14.00	9.13	4.00	33.00	13.38	2.00	40.00	10.63	8.00	44.00	18.88	2.00	44.00	13.28	5.85	65.00	20.61			
Ca ²⁺	85.60	156.20	112.43	22.40	143.60	104.88	66.20	106.40	88.08	76.60	133.80	102.45	91.80	264.20	161.93	22.40	264.20	113.95	10.00	130.00	51.11			
Mg ²⁺	44.40	181.32	93.59	39.24	118.44	84.12	26.40	156.84	81.10	12.12	105.48	55.67	7.44	175.92	111.685	7.44	181.32	86.26	7.92	156.84	42.40			
Cl ⁻	71.00	284.00	150.88	71.00	213.00	133.13	71.00	639.00	195.25	71.00	426.00	115.38	71.00	994.00	319.13	71.00	994.00	182.75	64.90	355.00	171.30			
HCO ₃ ⁻	37.20	122.00	74.80	32.20	122.00	77.23	24.40	73.20	54.90	48.80	97.60	67.10	48.80	97.60	64.05	24.40	122.00	67.62	30.50	305.00	116.27			
SO ₄ ²⁻	63.00	181.20	121.88	87.00	150.00	114.65	51.00	420.00	124.00	55.00	240.00	99.43	65.50	560.00	233.01	51.00	560.00	138.59	9.60	650.00	169.68			
Al	1635	10720	6153	1964	7210	3497	1453	8125	5391	1765	7630	4131	1856	23274	11372	1453	23274	6109	744	1354	991			
Cd	0.02	0.26	0.10	0.02	0.51	0.19	0.05	0.59	0.30	0.02	0.52	0.26	0.02	0.35	0.12	0.02	0.59	0.19	0.02	0.35	0.07			
Co	0.02	2.41	0.85	0.02	4.31	1.15	0.09	5.51	1.62	0.02	5.23	2.71	0.02	3.56	1.16	0.02	5.51	1.50	0.02	4.14	0.80			
Cr	9.50	29.50	20.70	10.90	23.20	15.66	9.30	26.50	18.19	10.10	22.90	16.01	10.60	35.50	24.29	9.30	35.50	18.97	8.10	10.50	9.52			
Cu	18.30	37.90	27.44	18.60	28.30	21.30	18.30	33.60	24.39	19.70	29.30	23.54	18.10	50.30	35.14	18.10	50.30	26.36	15.20	19.10	17.12			
Fe	963	5943	2848	1064	2465	1411	932	3120	2013	92	2876	1682	1135	9945	5636	932	10460	2719	850	1056	954			
Mn	53.00	664.00	351.88	98.00	314.00	174.13	51.00	398.00	226.88	53.00	326.00	162.50	99.00	775.00	447.13	51	775	273	42.00	101.00	71.56			
Ni	0.02	3.45	1.09	0.51	5.24	2.39	0.04	6.15	1.70	0.02	5.49	2.27	0.02	5.46	1.85	0.02	6.15	1.86	0.02	2.24	0.46			
Pb	0.02	7.13	3.47	0.87	7.56	4.50	0.52	8.13	2.97	0.05	7.19	3.48	0.51	7.15	3.85	0.02	8.13	3.65	0.02	4.51	1.91			
V	14.30	45.00	33.76	15.90	37.90	22.46	13.90	40.90	29.66	16.40	37.90	26.76	16.80	69.10	42.89	13.90	69.10	31.11	11.90	18.50	14.22			
Zn	25.20	59.50	47.43	29.10	52.60	36.89	25.90	55.50	43.61	28.30	53.10	40.69	29.30	85.30	57.03	25.20	85.30	45.13	13.40	31.20	25.07			

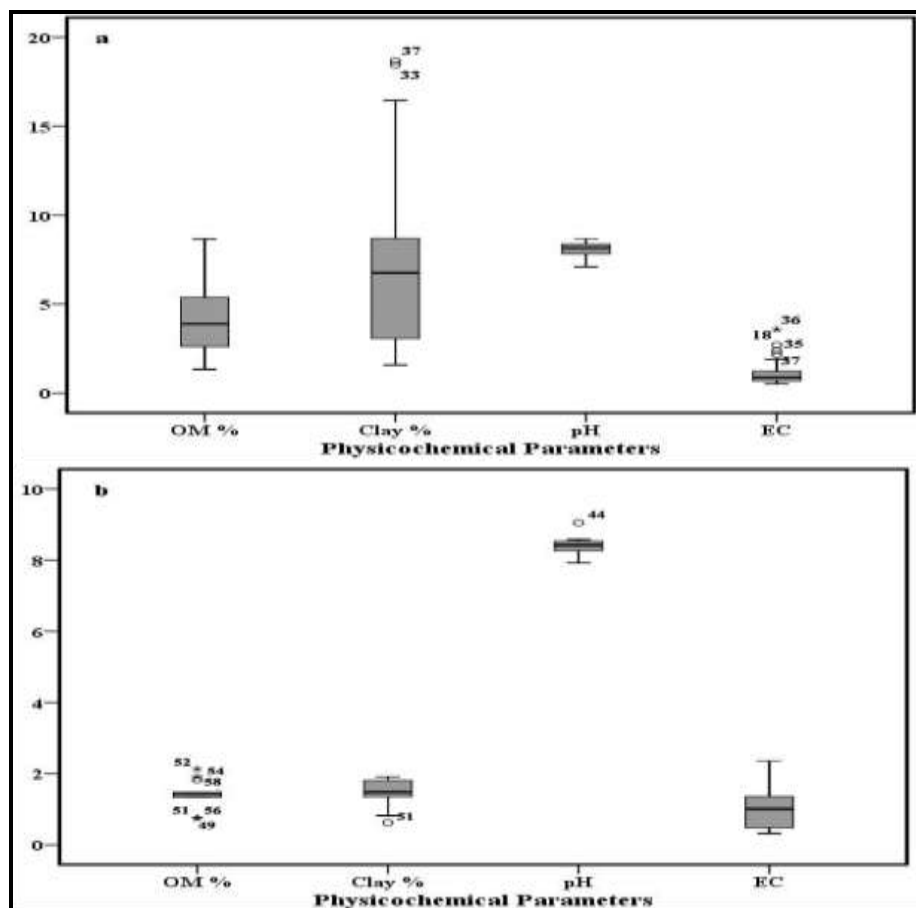


Figure (2): Boxplots of the physicochemical parameters in the studied cultivated (a) and uncultivated (b) soils of Siwa Oasis.

of the cultivated soil samples range from 1.34 to 8.66 %, with an average value of 4.17 % and from 1.58 to 18.67 %, with an average value of 6.89 %, respectively. On the other hand, the uncultivated soil samples show low content of OM and clay ranging from 0.75 to 2.13 %, with an average value of 1.40 %, and from 0.62 to 1.91 %, with an average 1.48 %, respectively.

pH is one of the most important soil properties that affect the availability of elements. The cultivated and uncultivated soils in Siwa Oasis are slightly

alkaline having pH values ranging from 7.10 to 8.67 and 7.29 to 9.02; respectively. The alkalinity of these soils is related to the composition of the soil parent rocks which mainly composed of limestone and shale. On the other hand, these soils exhibit a wide range of EC values of the cultivated soils (0.52-3.58, average 1.12 dsm^{-1}) are slightly higher than those of the uncultivated soils (0.32-2.3, average 1.04 dsm^{-1}).

Based on their slight alkalinity, significant varying salinity and development under hyper-arid conditions, the Siwa soils belong to the saline desertic subgroup of the intrazonal group in the world pattern of soils (Ollier, 1979).

2) Major ions: Differences in chemistry of Siwa soils are expressed by differences in the relative abundances of the major cations (Ca^{++} , Mg^{++} , Na^+ and K^+) and anions (Cl^- , HCO_3^- and SO_4^-). These differences are attributed primarily to differences in mineral composition. The recorded cations and anions constitute the major parts of clay minerals, calcite, dolomite, halite and gypsum which exist in different proportions in the different soil types as reported by Bahanasawy(2006).

Ca^{++} and Mg^{++} are the most dominant major cations in the cultivated soils of Siwa Oasis (Table 1 and Fig. 3). They are followed by Na^+ and K^+ . On the other hand, the uncultivated soils are characterized by the marked dominance of Na followed by Ca^{++} , Mg^{++} and K^+ . The depletion of the cultivated soils in Na may be due to the dissolution of halite by irrigation water and/or cation exchange with Ca^{++} and Mg^{++} . The major anions in the cultivated and uncultivated Siwa soils are arranged in the order of decreasing abundance Cl^- , SO_4^- , and HCO_3^- (Fig. 4).

The recorded high concentrations of Ca and Mg may be inherited from the exposed rocks which mainly composed of limestone and shale. The relatively high salinity expressed by high concentrations of Na⁺, Cl⁻ and SO₄⁻ recorded in these soils is related to the saline near-surface underground waters and/or inadequate drainage rather than their proximity to playa lakes.

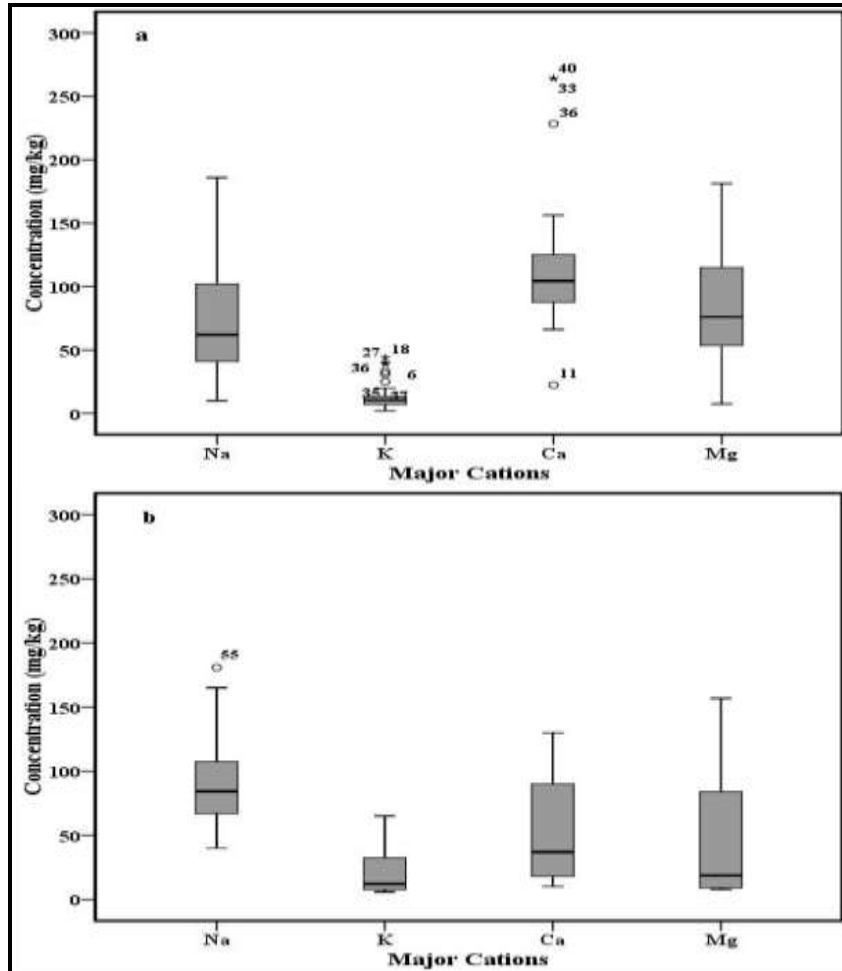


Figure (3): Boxplots of the major cations in the studied cultivated (a) and uncultivated (b) soils of Siwa Oasis.

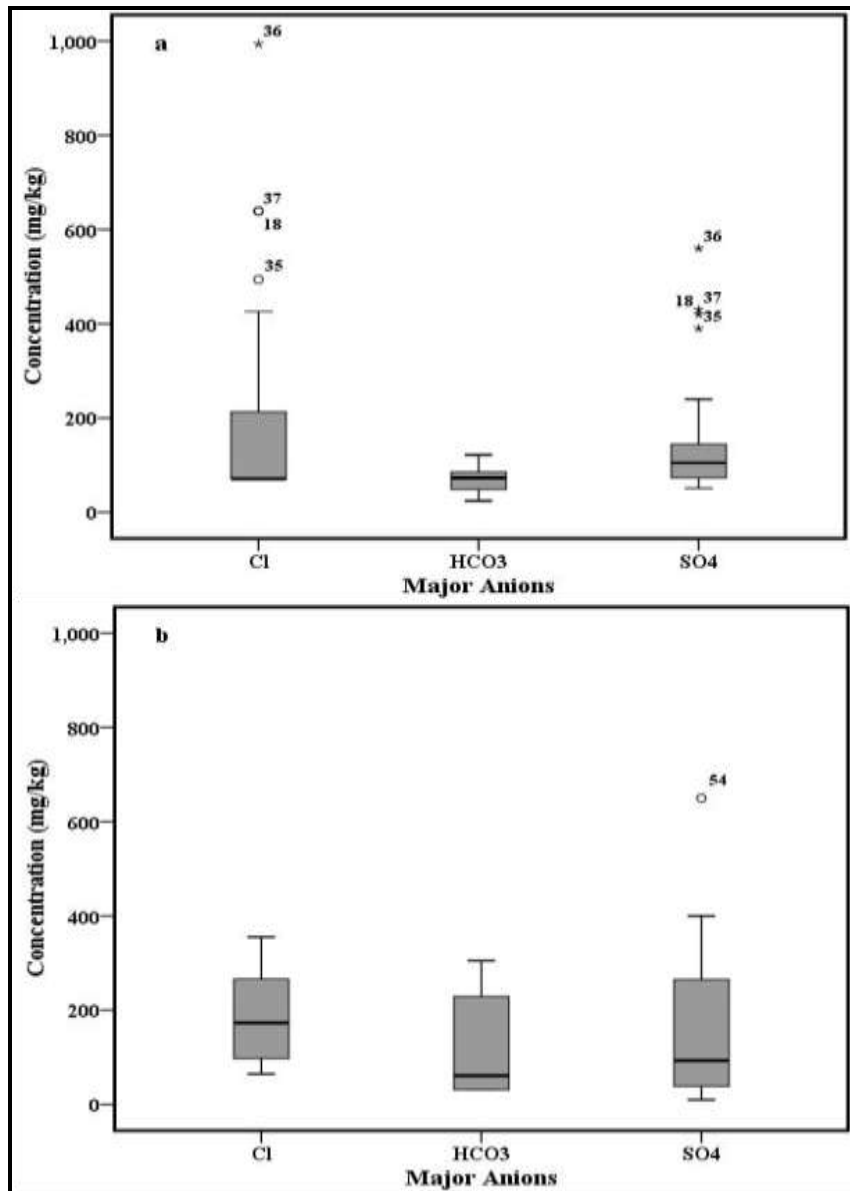


Figure (4): Boxplots of the major anions in the studied cultivated (a) and uncultivated (b) soils of Siwa Oasis.

3) Metal Distribution: Table (1) shows that Al, Fe and, to a much lesser extent, Mn are the most abundant metals in the Siwa cultivated and uncultivated soils. Zn, V, Cu and Cr exist in minor concentrations. Generally, the concentrations of the investigated metals (fig 5) Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the cultivated soils range from 1453 to 23274, 0.02–0.59, 0.02–5.51, 9.30–35.50, 18.10–50.30, 932–10460, 51–775, 0.02–6.15, 0.02–8.13, 13.90–69.10, and 25.20–85.30 ppm, respectively. On the other hand, they range from 744 to 1354, 0.02–0.35, 0.02–4.14, 8.10–10.50, 15.20–19.10, 850–1056, 42–101, 0.02–2.24, 0.02–4.51, 11.90–18.50, and 13.40–31.20 ppm in the uncultivated soils, respectively.

The mean concentrations of these metals in the cultivated soils followed the order Al > Fe > Mn > Zn > V > Cu > Cr > Pb > Ni > Co > Cd; while those of the uncultivated soils followed the order Al > Fe > Mn > Zn > Cu > V > Cr > Pb > Ni > Co > Cd (Fig.4). Interestingly, the concentrations of all investigated metals are higher in the cultivated soils than the uncultivated soils. Also, their concentrations don't exceed the maximum allowable limits for metal in agricultural soil (Table 2).

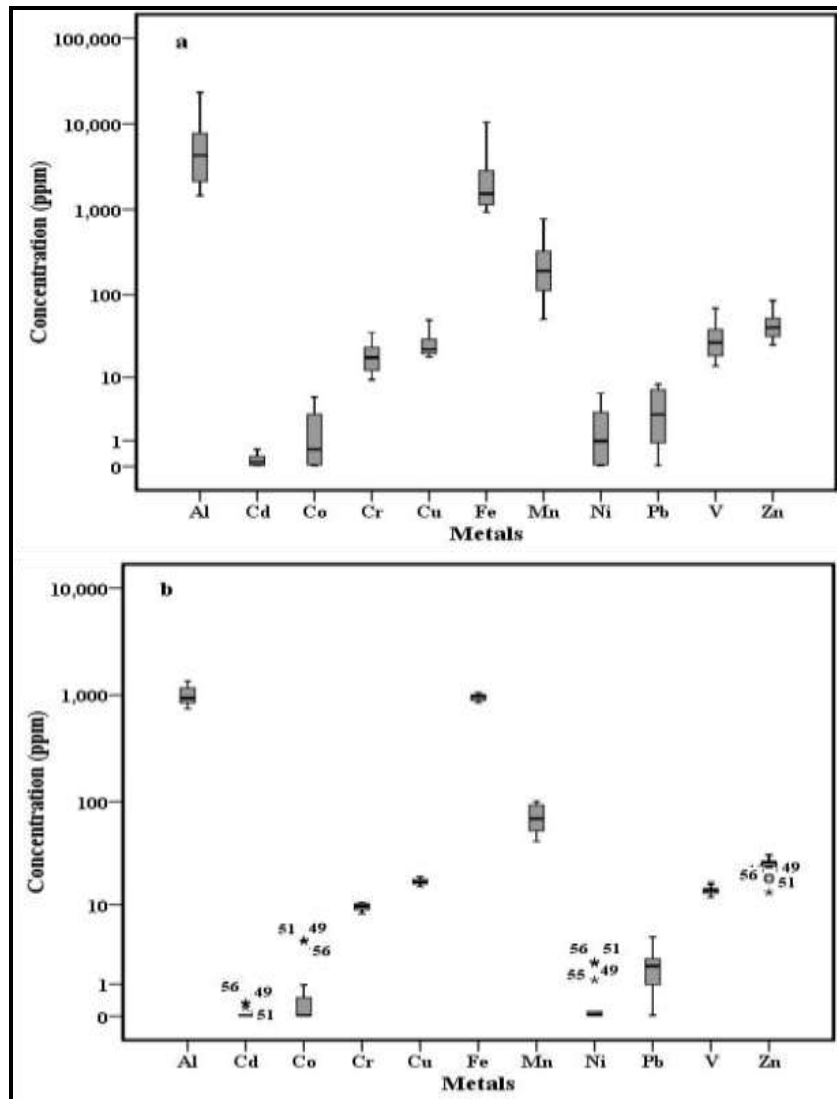


Figure (5): Boxplots of the metals in the studied cultivated (a) and uncultivated (b) soils of Siwa Oasis.

Table (2): Values of maximum allowable limits (M.A.L.) for heavy metals in soil (ppm) used in different countries (in Kabata-Pendias, 1995)

Metal	Austria	Canada	Poland	Japan	UK	Germany
Cd	5	8	3	-	3	2
Co	50	25	50	50	-	-
Cr	100	75	100	-	50	200
Cu	100	100	100	125	100	50
Ni	100	100	100	100	50	100
Pb	100	200	100	400	100	500
V	100	130	100	150	100	200
Zn	300	400	300	250	300	300

4) Metal Sources and Interaction: Bivariate and multivariate statistical analyses are used to clarify the relationship between the recorded metals and soil properties in addition to metal sources in the studied soils, these analyses are Pearson's correlation coefficient (PCC), and hierarchical cluster (HCA). The most of the recorded metals (Table 3) had a significant positive correlation (>0.5) with OM %, clay % and with each other. On the other hand Cd, Co, Ni and Pb had a significant positive correlation (>0.5) with each other and negative correlation with OM %, clay % and the rest of metals. This conclusion indicates that these metals possibly originated from different sources.

Table (3): Pearson's correlation coefficient for the studied variables (n=58)

	Clay%	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
OM %	.68	.65	-.58	-.53	.67	.67	.65	.69	-.45	-.46	.67	.66
Clay %		.97	-.70	-.67	.98	.96	.92	.95	-.71	-.66	.98	.98
Al			-.60	-.56	.92	.96	.95	.91	-.59	-.54	.96	.96
Cd				.86	-.73	-.60	-.52	-.64	.82	.74	-.68	-.69
Co					-.70	-.55	-.46	-.61	.82	.74	-.62	-.64
Cr						.96	.86	.96	-.75	-.73	.96	.96
Cu							.93	.97	-.58	-.56	.96	.95
Fe								.88	-.48	-.39	.92	.91
Mn									-.62	-.59	.94	.93
Ni										.92	-.71	-.73
Pb											-.67	-.68
V												.99

(HCA) (Fig. 6) generated similar results with those of PCC. HCA can be divided into two major clusters (A and B): Cluster (A): can be split into A⁻¹ subcluster (Cu, Zn, Cr, V, and OM %) and A⁻² subcluster (Al, Fe, clay % and Mn). A⁻¹ subcluster indicates that the Cu, Zn, Cr and V associated with soil OM and possibly originated from natural source. The heavy metals of A⁻¹ subcluster have the affinity for allumino-silicate phase and soil's Fe-Mn oxides which are important products of parent rock weathering. Cr⁺³ may exist as a substituent of Fe⁺³ and/or Al⁺³ in their compounds. Also, V may be admitted in the crystal structures of ferric compounds. Cluster (B) includes Cd, Co, Ni and Pb which indicated that these heavy metals were possibly originated anthropogenically from the agricultural practices and newly constructed industrial activities. This conclusion is confirmed by the significant negative correlation between heavy metals of cluster (B) and OM, clay, Al, Fe and Mn of cluster (A).

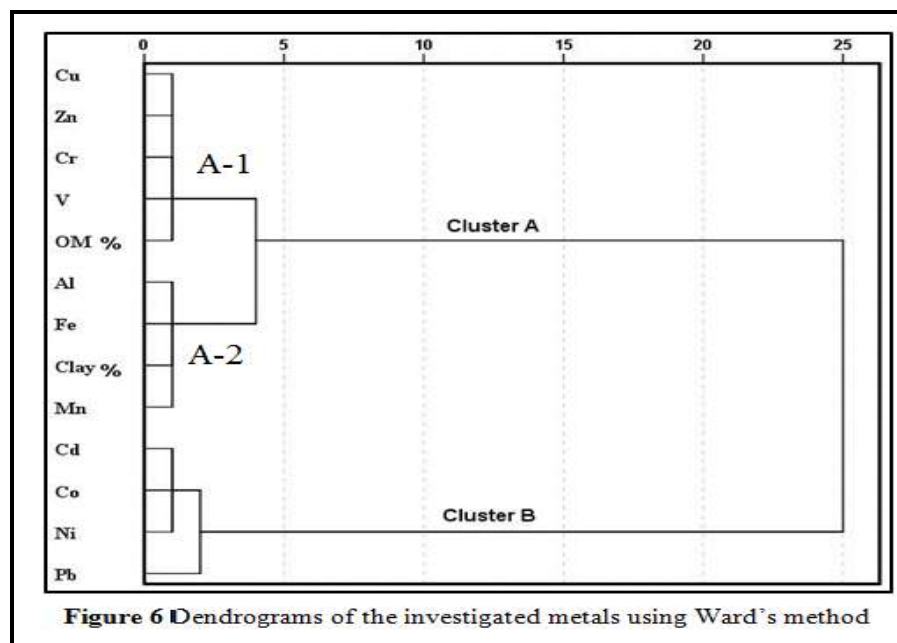


Figure 6 Dendrograms of the investigated metals using Ward's method

CONCLUSIONS

The development of Siwa Oasis Quaternary soils under hot dry climatic conditions resulted in their slight alkalinity and considerable salinity. Differences in their chemical constituents are attributed to the differences in parent rocks as well as local conditions such as location, extent of drainage and leaching, effects of near-surface saline groundwater and agriculture practices.

The cultivated Siwa soils are invariably more enriched with heavy metals than the uncultivated soils. The associations that exist between the soil components in Siwa Oasis indicate their inheritance from geogenic and anthropogenic sources by the effects of weathering processes and agricultural and industrial activities which enhance the accumulation of heavy metals.

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تقييم جيوكيميائي لتربة الحقب الرباعي في واحة سيوة، الصحراء الغربية، مصر

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محمد أحمد محمد العوضي^(١) - أحمد جاد عبد الواحد^(٢) - حسن كامل جرامون^(٣)
محمد غريب المالكي^(٣)

(١) إدارة المراقبة البيئية، قطاع الدراسات والتطوير، هيئة المحطات النووية (٢) قسم الجيولوجيا، كلية العلوم، جامعة عين شمس (٣) قسم العلوم الأساسية البيئية، معهد الدراسات والبحوث البيئية، جامعة عين شمس

المستخلص

تم التحديد الكمي للمعاملات الفيزيقيو- كيميائية والأيونات الرئيسية والعناصر الثقيلة لتربة الحقب الرباعي المزروعة وغير المزروعة في واحة سيوة. كما تم تطبيق التحليلات الأحصائية ثنائية المتغيرات والمتعددة المتغيرات وذلك لتوضيح العلاقة بين العناصر الثقيلة المقاسة وخواص التربة وتحديد المصادر المحتملة لهذه العناصر في تربة واحة سيوة.

تتأثر الخصائص الجيوكيميائية لأراضي واحة سيوة بعدة عوامل والتي تشمل، طبيعة صخور المصدر، الموقع الجغرافي، وعمليات تكوين التربة، ومدى التصريف والرشح، تأثير المياه الجوفية المالحة القريبة من السطح والأنشطة الزراعية.

الكلمات الدالة: مصر، الصحراء الغربية، واحة سيوة، تربة الحقب الرباعي، التقييم الجيوكيميائي.