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Geochemical characteristics of agricultural soils, Assiut governorate, Egypt



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Abstract

Background: The geochemical investigation of agricultural soil is a great demand because of its help in the characterization of soil and its suitability for cultivation. The urbanization, cultivation, and industrial activities at Assiut Governorate have adversely impacted the chemical composition of soil, especially its content of heavy metals. The study area includes El-Madabgh sewage station and many big industries; cement, fertilizers, and pharmaceutical.

Results: The Nile Valley soils are very comparable in composition and composed mainly of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, and TiO₂ which represent about 88% of its chemical composition. The chemical composition gave an indication about the mineralogical assemblage of soil; quartz, clay minerals, and calcite. The results pointed to the mixed source (geogenic and anthropogenic) of Fe, Co, Cu, Ni, Zn, Zr, and Cr and the anthropogenic source of As, Pb, and Cd (especially phosphatic fertilizers) in the studied soil.

Conclusion: The studied soil chemistry affected mainly by the agricultural practices (application of fertilizers, pesticides, manure, and wastewater irrigation), industrial inputs, and atmospheric deposition. Generally, the Egyptian soil needs more geochemical studies to monitor its quality and enhance of its productivity.

Keywords: Geochemistry, Anthropogenic activities, Heavy metals, Pollution

Introduction

Soil is a complex heterogeneous mixture of organic and inorganic matter, as well as different components that determine its physical, chemical, and biological properties. There are 12 major and minor elements (Si, Al, O, Ca, Fe, K, Ti, Mg, Mn, Na, Cr, Ni) representing about 99.4% of its total composition and at least 68 trace elements account for the rest. However, local or regional geochemistry plays an important role in the soil composition (Galinha et al. 2010). The major elements generally occur in minerals, so can be used as a tool of discriminating element-mineral associations (Liu et al. 2001 and Salman 2008). The Al, K, Na, and Mg elements are expected to be dominantly contained in Al-silicates such as various clay minerals, chlorite, micas, and feldspars, whereas the other elements can occur in non-Al-bearing mineral phases (Salman 2013).

Soil chemical composition is controlled mainly by lithogenic and pedogenic weathering. The Egyptian soil

chemistry is mainly related to the chemistry of parent rocks (mafic/ultramafic rocks) in the Ethiopian highlands. The Nile Valley sediments contains about 53.4%, 16.5%, 11.8%, 3.7%, 2.5%, 1.1%, 121 ppm, 152 ppm, 114 ppm, and 178 ppm of SiO₂, Al₂O3, Fe₂O₃, CaO, MgO, TiO₂, Cr, Ni, Cu, and Zn, respectively (Omer 1996). Iron (Fe) content in alluvial soils at El-Saff reached 16.6% in the surface deposit which irrigated with liquid industrial wastes (Rabie and Abd El-Sabour 1999) and Ni recorded 55.3 ppm in alluvial soils at El-Fayoum (El-Sayed and Hegazy 1993). Mohamed et al. (2013) pointed out the overload of dust fall with about 3.30, 26.46, 22.33, 235.00, 4.53, and 3.80 ppm of As, Cu, Pb, Zn, Cd, and Hg; respectively around Assiut Fertilizer Plant. Elgharably et al. (2014) stated that soils at Assiut are polluted with Fe, Mn, Zn, Cu, Pb, Cd, and Ni as a result of the application of sewage wastewater for irrigation.

Nowadays, pollution is considered as one of the main grave problems in the world, because the pollutants are potentially hazardous to human and animal life. The industrial practices may be causing redistribution of some hazardous elements in the environment; air, water, and



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surface soil. Some of these elements are vital, whereas others are toxic metals (Samuding et al. 2009). Thus, the industrial zones are probably the majority significant source of soil and plant contamination with heavy metals (Mohamed et al. 2015). Thus, the content and type of these metals depend on the nature of industrial activities.

Thus, the aim of this study was to assess the geochemical characters of the soil in the studied area. In addition, indicating the source of the heavy metals into the soil and try to give some recommendations to improve its nature.

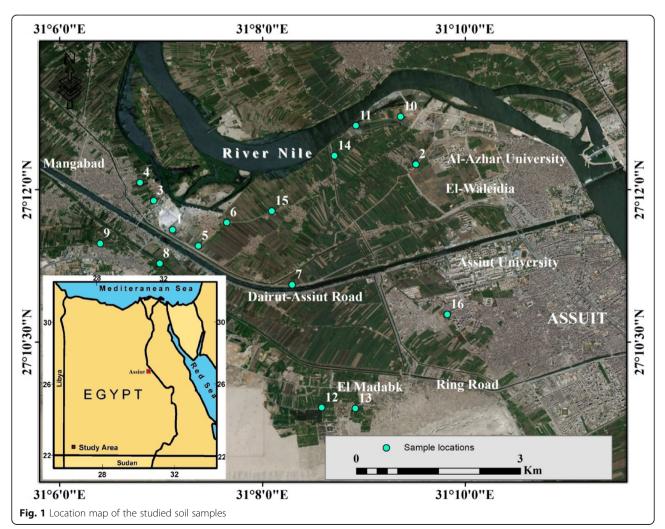
Materials and methods

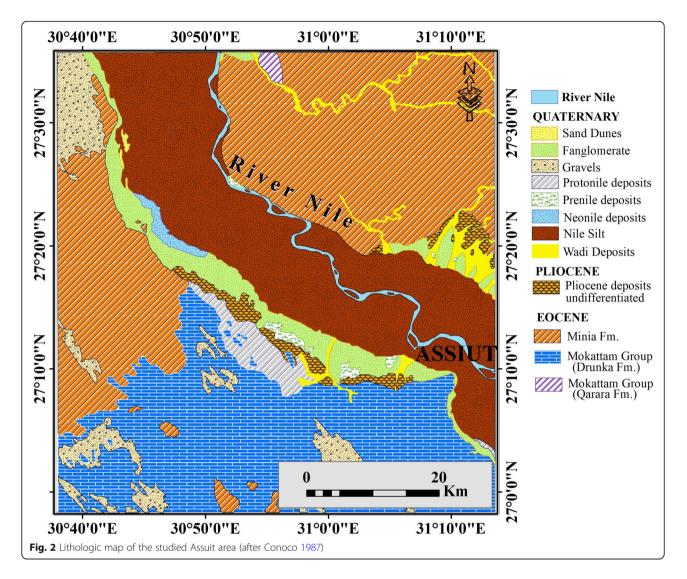
The study area

Assiut is located between latitudes 26° 50′ and 27° 40′ N and longitudes 30° 40′ and 31° 32′ E which borders at the River Nile on both eastern and western sides and the cultivated soil extends along the two banks of the Nile Valley (Fig. 1). It comprises part of the Nile Valley and parts of the surrounding plateaus. Assiut Governorate contains many big industries, such as cement chemical, fertilizers, detergents, and food. The study area includes mainly the relative wide stretch extending to the west of the Nile River.

Many authors studied the geology (Fig. 2) and structural geology of the area (Said 1962; Said 1981; Omer 1996; Osman 1980; Khalifa et al. 2004). The area of study is distinguished into the following three main geomorphic units:

- The young alluvial plain (Holocene silty clay): it represents the cultivated lands bordering the western side of the Nile. It is dissected by irrigation canals and drains running from south to north parallel to the River Nile. The cultivated lands to the west of the River Nile in Assiut are generally much wider than those lands to the east.
- The old alluvial plain (Quaternary sand and gravel): it is represented by terraces with various elevations between the calcareous plateau and the young alluvial plain. It contains some elongated sand dunes which cover the eastern areas of the scarp of the carbonate plateau. It takes mainly the northwest-





southeast direction and threats the cultivated lands of the alluvial plains. The old terraces cover a considerable area and formed mainly of travertine conglomerate with gravel, sandstone, and clay.

- The calcareous plateau: The eastern slope of the western calcareous plateau in the area of study represents the eastern fringes of the Nile Valley. It has an elevation higher than floodplain varies from south to the north respectively. It is built of Eocene limestone covered by drift sands, flints, and the boulder of carbonate. The surface is formed into gravelly plains of black to dark brown color occupying areas of the surface.

Sampling and analyses

Sixteen soil samples (30 cm depth) were collected around the industrial activities in the study area, which is represented the young alluvial plain. The XRF analysis was used to determine the main and trace elements in the studied soils in order to reveal the geogentic and anthropogenic enrichments of elements nearby the industrial activities.

The XRF analysis was made by using Axios Sequential WD_XRF Spectrometer, Analytical 2005 in the National Research Center laboratories. ASTM E1621 standard guide was used for elemental analysis by wavelength dispersive X-ray fluorescence spectrometer and ASTM D7348 standard test methods for loss on ignition (LOI) of solid combustion. The samples were ground to <63 μ m in diameter.

Results

Generally, the Nile Valley soils are very comparable in composition, since they are created from the same sources of weathered sedimentary and magmatic rocks. However, resulting of the anthropogenic input, the percentage of exact trace elements can change obviously depending on the land utilize (cultivated, urban, or industrial). The average concentration of the major oxides (wt%) in the studied soils are 50.06, 13.58, 12.01, 6.44, 2.65, 1.83, 1.3, 0.82, 0.69, 0.52, and 0.09 for SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂, K₂O, Na₂O, P₂O₅, SO₃, and Cl; respectively, as well as LOI = 9.55 (Table 1). The average levels of trace elements in the studied area are as follows in decreasing order: Mn, Zr, Zn, Cr, Ni, Pb, Co, Cu, As, and Cd are ~ 1181, ~ 266, ~ 119, ~ 117, ~ 84, ~ 38, ~ 35, ~ 32, 15.41, and 1.37 ppm, respectively (Table 2).

Discussion

The major elements

The major element oxides generally occur in minerals. Thus, major oxides analysis is useful as a tool for discriminating element-mineral associations (Liu et al. 2001 and Salman 2008). Abou El-Anwar et al. (2018) stated that Assiut soil is composed mainly of quartz, anorthite, calcined albite, calcite, montmorillonite, vermiculite, and illite mineral assemblages. Melegy and El-Agami (2004) stated that the mineralogical composition of soil at Bahtim, Egypt is mainly quartz, plagioclase, amphibole, smectite, kaolinite, and illite. Also, Salman (2013) mentioned that Sohag soils are mainly composed of quartz, feldspars, calcite, montmorillonite, and kaolinite. Al, K, Na, and Mg elements are expected to be dominantly contained in Al-silicate minerals; clay minerals, chlorite, micas, and feldspars, while the other elements can also occur in the non-silicate mineral phases (Van der Veer 2006).

High SiO_2 content in the studied soils is possibly due to the abundance of quartz (Hussein et al. 2004 and Salman 2008) in agreement with the mineralogical studied for the same studied samples with Abou El-Anwar et al. (2018). This is supported by the strong significant positive correlation between SiO₂ and sand content (r = 0.77) as well as negative correlation (-0.81) between SiO₂ and Al₂O₃ (Table 3).

To further investigate the role of Al-minerals for the distribution of different major elements, a simple linear regression analysis was performed (Table 3). The results of this regression indicate that the concentrations of K, Fe, Ti, and Mg are primarily related to Al, and as such, these elements are dominantly controlled by clay minerals and/or by minerals associated with clays during sedimentation. Sample No. 10 recorded the highest percentages of Al_2O_3 , Fe_2O_3 , and TiO_2 (16.26, 15.51, and 2.48%; respectively Table 1) which referred to the abundance of vermiculite mineral, its agreements with the mineralogical studies Abou El-Anwar et al. (2018).

Iron (Fe₂O₃) content ranges from 4.58 to 15.52% and averages 12.01%, which is strongly higher than that of the values UUC (5.04%) recorded by Rudnick and Gao (2014). Thus, the enrichment of iron in the studied soils may be strongly controlled by the source rock composition, where they are derived principally from the Ethiopian basaltic plateau (Omer 1996; Abou El-Anwar and Samy 2013; Abou El-Anwar et al. 2018). Fe₂O₃ is positively correlated with silt and clay content (r = 0.64 and 0.57; respectively), and not correlated with carbonate content (r = 0.09). Thus, the unusually high concentration of Fe₂O₃ recorded in most samples might be attributed to effluents from Seed Pharmaceutical, Mangabad factories, sewage station in the studied area.

Table 1 Major oxides contents and LOI in the studied soil samples (%)

SN	Sand	Silt	Clay	CaCO ₃ %	CaSO ₄ %	SiO_2	AI_2O_3	Fe_2O_3	CaO	MgO	${\rm TiO}_2$	K_2O	Na ₂ O	P_2O_5	SO_3	Cl	LOI
1	22.5	43.5	34	1	8.8	44.8	14.2	13.2	6.6	2.7	2.0	1.2	0.9	2.1	3.5	0.1	8.3
2	19.5	47.25	32.75	5	0.4	48.2	15.7	14.4	4.2	2.6	2.2	1.5	0.9	0.5	0.2	0.0	9.2
3	9.75	61.75	27.5	7.5	0.4	44.1	15.0	13.1	5.1	3.1	1.9	1.4	0.8	0.7	0.2	0.0	14.1
4	11	53.25	35	7	0.2	46.0	16.4	12.9	4.1	3.3	2.1	1.1	0.8	0.3	0.1	0.0	12.3
5	32	39.25	27.5	25	0.2	46.5	14.5	14.4	5.8	2.9	2.3	1.3	1.0	0.9	0.2	0.0	9.6
6	6.25	56	35	5	0.2	44.7	15.6	13.3	3.9	3.2	2.0	1.1	1.0	0.6	0.1	0.0	13.9
7	33.48	32.5	32.5	5	0.4	50.1	14.9	13.6	4.3	2.8	1.7	1.6	0.8	0.4	0.2	0.0	9.2
8	72.5	3.5	24	7.5	0	55.5	12.5	11.0	8.8	2.1	1.8	1.4	0.5	0.5	0.2	0.0	5.3
9	58.88	21.25	20	12.5	0	56.1	12.3	10.1	6.1	2.3	1.6	1.4	0.6	1.1	0.3	0.1	7.7
10	66.45	18.75	16.25	0.5	0.2	48.1	16.3	15.5	5.3	3.0	2.5	1.5	0.9	0.4	0.1	0.0	6.0
11	46.25	35.25	19	34	0	50.8	13.6	12.3	5.7	3.0	1.9	1.3	0.9	0.3	0.3	0.0	9.3
12	71.2	10	17.5	10	0.5	58.7	8.4	5.9	14.4	1.9	1.0	1.1	0.6	1.1	0.8	0.2	7.6
13	82.5	2.75	16	0.5	0	77.1	7.6	4.6	2.9	1.0	0.6	1.1	0.3	0.8	0.3	0.0	3.3
14	17.75	50	32.5	7.5	0.5	43.4	14.3	13.3	7.1	3.2	2.2	1.2	0.8	0.4	0.1	0.0	13.1
15	60	16	24	6	1	48.0	12.3	11.7	9.1	2.9	1.7	1.4	1.3	0.4	0.9	0.6	8.3
16	17.23	51.5	31.5	10	11.4	38.8	13.8	13.0	9.6	2.6	1.6	1.3	0.9	0.5	0.9	0.2	15.7
Mean	39.2	33.9	26.6	9.0	1.5	50.1	13.6	12.0	6.4	2.7	1.8	1.3	0.8	0.7	0.5	0.1	9.5

SN	Fe	Mn	Zn	Zr	As	Pb	Cd	Со	Cr	Cu	Ni
1	29,041.3	1310.8	134.2	277.4	20.5	38.5	2.4	39.9	154.6	35.4	92.4
2	30,826.4	1249.7	135.3	290.0	19.8	37.3	1.1	43.5	130.3	36.7	91.2
3	34,023.6	1753.0	143.2	300.3	13.4	38.4	1.2	48.2	131.5	45.7	113.9
4	35,347.4	1712.5	135.3	305.9	15.4	37.6	1.1	47.3	151.7	41.7	102.6
5	28,583.8	1124.2	117.8	276.4	4.8	35.0	1.7	43.6	136.5	31.2	91.2
6	35,746.1	1899.3	144.4	308.6	15.4	34.3	1.8	42.6	148.1	34.9	85.9
7	25,148.2	988.4	108.9	264.9	15.6	36.0	1.6	39.6	117.0	31.4	93.5
8	10,690.4	647.5	69.3	232.3	16.8	28.9	1.6	13.8	114.0	13.3	43.0
9	14,277.9	643.9	133.0	265.2	17.5	43.7	1.1	21.0	67.6	28.9	62.2
10	20,150.1	944.6	88.5	232.0	13.2	33.3	1.2	41.4	103.7	32.5	83.9
11	26,990.5	1297.2	111.9	288.4	15.3	32.1	1.7	35.2	151.0	34.0	81.8
12	6958.4	331.2	144.6	212.6	18.4	55.7	0.8	14.7	45.3	23.6	140.3
13	5127.5	238.5	84.4	101.9	16.7	30.4	0.4	11.9	36.6	12.1	28.3
14	31,139.5	2381.9	124.0	278.7	15.5	35.5	1.3	46.9	120.1	38.8	97.1
15	16,269.6	792.7	90.2	369.5	13.2	38.3	1.8	27.9	126.6	20.9	51.8
16	27,070.4	1573.9	144.4	254.3	15.2	59.2	1.3	48.6	133.3	44.3	88.1
Mean	23,586.9	1180.6	119.3	266.2	15.4	38.4	1.4	35.4	116.7	31.6	84.2

Table 2 Heavy metals (ppm) contents in the studied agriculture soil

Table 3 Correlation matrix of the major oxides in the studied agricultural soils

	Sand	Silt	Clay	CaCO ₃ %	CaSO ₄ %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K ₂ O	Na_2O	P_2O_5	SO_3	Cl	LOI
Sand	1																
Silt	98**	1															
Clay	88**	.78**	1														
CaCO ₃	- 0.02	0.10	- 0.19	1													
CaSO ₄	- 0.30	0.29	0.35	- 0.15	1												
SiO ₂	.77**	_ 0.77**	_ 0.67**	- 0.12	- 0.40	1											
AI_2O_3	73**	0.72**	0.64**	0.02	0.06	_ 0.81**	1										
Fe ₂ O ₃	65**	0.64**	0.57*	0.09	0.15	_ 0.85**	0.96**	1									
CaO	0.32	- 0.33	- 0.25	0.11	0.28	- 0.06	_ 0.45	_ 0.33	1								
MgO	72**	0.73**	0.56*	0.20	- 0.01	_ 0.87**	0.87**	0.85**	- 0.20	1							
TiO ₂	56*	0.56*	0.48	0.12	- 0.01	- 0.78**	0.92**	0.95**	- 0.30	.85**	1						
K ₂ O	0.09	- 0.08	- 0.09	0.06	- 0.10	- 0.19	0.33	0.44	- 0.12	0.15	0.32	1					
Na ₂ O	- 0.47	0.47	0.39	0.23	0.20	_ 0.74**	0.57*	.67**	0.02	0.74**	0.60	0.18	1				
P_2O_5	0.03	- 0.06	0.04	- 0.18	0.43	0.12	- 0.26	_ 0.22	0.17	- 0.30	- 0.19	- 0.29	- 0.19	1			
SO_3	- 0.07	0.03	0.19	- 0.23	0.70**	- 0.14	_ 0.10	_ 0.03	0.25	- 0.10	- 0.05	- 0.23	0.12	.82**	1		
Cl	0.26	- 0.29	- 0.14	- 0.09	0.16	- 0.06	_ 0.29	_ 0.16	0.50*	- 0.04	- 0.22	0.10	0.49	- 0.07	0.20	1	
LOI	88**	0.89**	0.69**	0.14	0.35	78**	0.54*	0.49	- 0.02	0.68**	0.38	- 0.12	0.49	- 0.22	- 0.08	- 0.04	1

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed)

 Fe_2O_3 is strongly to medium correlated with Al_2O_3 , TiO₂, MgO, NaO, and K₂O (r = 0.96, 0.95, 0.85, 0.67, and 0.44; respectively) (Table 3). This indicates that montmorillonite is the main bearer for Fe (Al-Gamal 2011; Salman 2013; Abou El-Anwar et al. 2018). The high concentration of Fe₂O₃ may be attributed to the presence of other iron-bearing phases in the soil such as ferromagnesian minerals (amphibolies and pyroxene), iron oxides (magnetite and hematite), and chlorite. Where Sohag soil contains a significant amount of chlorite (Bekir 1997). The high average percentage of iron content (12.01%) may be reacted with the montmorillonite in suitable media and produced the vermiculite (Mg, Fe, Al-silicate) which is in agreement with the mineralogical studied for the same studied samples with Abou El-Anwar et al. (2018). This is also supported by the positive relation between MgO and LOI (r = 0.68) (Table 3), where montmorillonite is unstable at high temperature.

Also, the higher average content of Mn (\sim 1181 ppm) is attributed to its high level in the parent source rocks mainly the basaltic rocks of the Ethiopian plateau, where Mn is substituted with iron in the ferromagnesian silicate minerals (Table 2).

The negative correlation between CaO and all major oxides indicates that Ca is present mainly in the form of carbonate minerals. High levels of calcite were identified by the XRD results (Abou El-Anwar et al. 2018) and chemical analysis (Table 1). The very low correlation between CaO and both of LOI (r = -0.02) and CaCO₃ (r = 0.10) (Table 3) suggests other sources for Ca than carbonate minerals; Ca-albite (Abou El-Anwar et al. 2018).

The higher content (1.83%) of TiO₂ than the world soil (0.55%) (Kabata-Pendias and Mukherjee 2007) point to the presence of abundance Ti-bearing minerals. The very strong positive relation between TiO₂ and both of Fe₂O₃ (r = 0.95) and MgO (r = 0.85) indicated the role of ferromagnesian minerals in Ti distribution. Also, the strong positive relation of TiO₂ with Al₂O₃, silt, and clay (r = 0.92, 0.56, and 0.48; respectively) indicated another source of Ti; clay minerals.

The Na₂O content is positively correlated with Al₂O₃, Fe₂O₃, MgO, and TiO₂ with correlation coefficients of r= 0.56, 0.67, 0.74, and 0.60, respectively (Table 3), suggesting that Na is mainly associated with silicate minerals (Querol et al. 1998). This result is in accordance with the mineralogical results (Abou El-Anwar et al. 2018) for the same studied samples which indicate the presence of significant amount of albite. Small amounts of Na can be incorporated in the crystal lattice or adsorbed on the clay mineral surfaces. As indicated from the positive relation between Na₂O versus silt and clay (r = 0.47 and 0.39, respectively), this supports the confinement of Na in feldspars particles which are largely removed from the clay fraction. Sulfur (SO₃) shows no clear relation with Al₂O₃, indicating that their occurrence is largely conquered by gypsum and/or phosphatic fertilizer, which is confirmed with the positive correlation (r = 0.70 and 0.82, respectively) between SO₃ and both of gypsum (CaSO₄) and P₂O₅ (Table 3). Also, Cl has a positive relationship with Na₂O (r = 0.49, Table 3) which revealed that Cl may mainly come from irrigation water. P₂O₅ contents range from 0.26 to 2.11%. Sample No. 1 represented the highest values of both P₂O₅ and SO₃ (2.11 and 3.5%, respectively), where this sample is located south of Mangabad fertilizer factory.

Loss on ignition (LOI) ranges from 3.31 to 15.74% with an average of 9.55% (Table 1). The main contributors to LOI are fine particle (silt and clay) minerals. This is confirmed from the significant positive correlation between LOI versus silt, clay, Al_2O_3 , Fe_2O_3 , MgO, Na_2O , and TiO₂ (r = 0.89, 0.69, 0.54, 0.49, 0.68, 0.49, and 0.38, respectively) (Table 3). The higher LOI values confirm the content of montmorillonite while lower values confirm high kaolinite content, which is in agreement with Al-Gamal (2011).

Gypsum is a characteristic mineral in the soil of arid and semi-arid regions. Gypsum is a moderately soluble source of the essential nutrients for the plants (Choudhary et al. 2004). It is formed from the oxidation of pyrite in the environment rich in calcium carbonate or leaching of hillslope sediments rich in gypsum (Herrero and Porta 2000). It is one of the soluble salts that have dangerous effects on the soils, buildings, and earth structures if occurred in high quantities (Razouki and Kuttah 2006). Gypsum contents vary from null to 11.4% in the investigated soil samples (Table 1). Soils can be classified as gypsiferous soil if gypsum constitutes > 50% (Al-Marsoumi et al. 2008). It was observed that more than 69% of the studied samples contain less than 0.5% gypsum. Consequently, gypsum may be derived from the weathering of the limestone plateau in the western side of the study area.

The statistical analysis supported the control of major oxides in the mineralogical composition of the soil. Where five principal components (PCs) were extracted (Table 4 and Fig. 3). The PC1 has 43.76% of the variance and represent the role of clay minerals where Al, Ti, Fe, Na, Mg, silt, and clay are loaded in this PC. In PC2, gypsum, CaO, P_2O_5 , and SO₃ were loaded and indicated the role of used fertilizers and have 17.76% of the variance. The PC3 represented 12.6% of the variance and indicated the role of marine sediment where it loads Ca, Na, and Cl.

The trace elements

Trace metals can be accumulated in soils as a result of human activities and consequentially affect human health. The values of maximum allowable limits (MAL) must be taken into consideration for the assessment of heavy metal pollution in soils (Ji et al. 2012).

The average concentrations of the trace elements Mn, Zr, Zn, Cr, Ni, Pb, Co, Cu, As, and Cd are ~ 1181, ~ 266, ~ 119, ~ 117, ~ 84, ~ 38, ~ 35, ~ 32, 15.41, and 1.37 ppm, respectively (Table 2). The average concentrations in worldwide soil were 437, 300, 63, 54, 22, 25, 7.9, 20, 5, and 0.5 ppm, respectively (Kabata-Pendias and Mukherjee 2007). It was observed the enrichment of the studied soils with these elements than the world soil. Heavy

503 P205 1.0 CaSO4 Component 2 0.5CaC Clav 0 Sand TiO2 O Na2O 20300 0.0 0 AI203 CaCO3 MgO -0.5 -1.0* 1.01.0 0.5 0.0 -0.5 -1.0 -1.0 -0.5 0.0 0.5 Component Component 1 Fig. 3 Component plot in rotated space

metals are one of the most soil, water, and plant pollutants (Elnazer et al. 2015; Salman et al. 2017), owing to their persistent, non-biodegradable, and toxic characteristics (Massas et al. 2009).

Contamination of agricultural soils by heavy metals may result from the use of fertilizers, chemicals, irrigation water, and dust-fall (Salman et al. 2017). This led to trace metals concentrated in foodstuff and potential hazard to human health (Lu et al. 2015). Many studies pointed out the pollution of agricultural soil heavy metals in different localities in Egypt. Darwish and Pollmann (2015) recorded 19.69, 38.17, 133.1, 47.2, and 31.69 ppm of Cd, Co, Cr, Cu, and Pb, respectively in the agricultural soil of Aswan. Also, the agricultural soil was found polluted with Cd in Kafr El-Sheikh, El-Fayoum, El-Mehala El-Kobra, and Kafr El-Zayat and they recorded high concentration of Cd (Al Naggar et al. 2014). Salman (2013) pointed out the pollution of agricultural soils at Sohag Governorate with Cd (22 ppm). On the northern part of the study area at El Minya Governorate, the agriculture soil contains about 1.19 ppm (Asmoay 2017). The exposure to polluted soil with heavy metals has a diverse effect on human health (Karim et al. 2015). Also, polluted soil with Cd, Cu, Cr, and Pb has a negative effect on the yield of oats (Wyszkowska et al. 2006). These metals have a negative effect on soil fertility, water quality, and could be transported to human food chain causing great health risk (Elnazer et al. 2015; Salman et al. 2017).

The high average concentration of Zr, Zn, Cr, Ni, Pb, Co, Cu, As, and Cd (Table 2) indicated an anthropogenic input. Zr, Zn, Cr, Ni, Pb, Co, and Cu are strongly positively correlated with silt, clay fractions, and iron (Table 5). Thus, they may be adsorbed with the clay minerals and/or iron oxy-hydroxides minerals. As, Pb, and Cd are positively correlated with P_2O_5 (Table 5), which indicated that the phosphatic fertilizer plays a vital role in the pollution of soil with these metals. Also, these elements are positively correlated with each other; consequently, these may be indicating that they concentrated under the same environmental conditions.

Generally, the cultivated soil is affected mainly by (a) agricultural anthropogenic input, such as fertilizers, pesticides, green manure, wastewater irrigation, etc., and (b) atmospheric deposition.

Sample numbers (1, south Mangabad fertilizer factory), (2, 10, 11, and 14, north El-Waleidia electricity station), (12 and 13, west El-Madabk Sewage Station), and (16 south Seed Pharmaceutical factory) represented the highest concentrations in As, Zn, and Pb (Table 2).

Also, sample numbers (1) in north, 12 and 13 in south, and 16 nearby the Seed Pharmaceutical factory represented high concentration in all the heavy and toxic elements (Table 2). In addition, samples number 3 and 4

Table 4 Principal component matrix of the extracted factorscontrolling major oxides

controlling ma	ajor oniacs				
	PC1	PC2	PC3	PC4	PC5
Sand	- 0.860	- 0.209	0.302	0.251	0.132
Silt	0.853	0.158	- 0.288	- 0.284	- 0.058
Clay	0.750	0.324	- 0.292	- 0.081	- 0.298
CaCO ₃	0.101	- 0.279	0.271	- 0.544	0.680
CaSO ₄	0.202	0.811	0.073	0.089	0.058
SiO ₂	- 0.917	- 0.210	- 0.248	0.059	- 0.026
Al ₂ O ₃	0.946	- 0.173	- 0.083	0.198	0.033
Fe ₂ O ₃	0.933	- 0.120	0.106	0.267	0.125
CaO	- 0.323	0.405	0.599	- 0.248	0.070
MgO	0.920	- 0.125	0.165	- 0.130	0.012
TiO ₂	0.873	- 0.176	0.077	0.213	0.206
K ₂ O	0.216	- 0.401	0.370	0.636	0.138
Na ₂ O	0.698	0.108	0.582	- 0.102	- 0.073
P ₂ O ₅	- 0.204	0.760	- 0.249	0.203	0.368
SO3	- 0.003	0.903	0.018	0.240	0.211
Cl	- 0.156	0.265	0.817	- 0.018	- 0.404
% of variance	43.76	17.76	12.6	7.5	6.3

	Sand	Silt	Clay	CaCO ₃ %	Fe_2O_3	P_2O_5	Fe	Mn	Zn	Zr	As	Pb	Cd	Со	Cr	Cu	Ni
Fe	- 0.95**	0.96**	0.79**	0.13	.78**	-0.14	1										
Mn	- 0.88**	0.90**	0.73**	0.06	.65**	- 0.24	0.90**	1									
Zn	- 0.70**	0.73**	0.50	0.09	0.16	0.28	0.56*	.50*	1								
Zr	- 0.58*	0.56*	0.53*	0.21	.66**	-0.18	0.64**	.54*	0.32	1							
As	0.07	- 0.11	0.07	- 0.44	- 0.33	0.29	- 0.19	- 0.12	0.18	- 0.19	1						
Pb	- 0.12	0.13	0.04	0.01	- 0.19	0.21	- 0.09	- 0.04	.61*	0.03	0.18	1					
Cd	- 0.37	0.31	0.46	0.18	.58*	0.30	0.44	0.34	0.04	0.63**	- 0.11	- 0.16	1				
Со	- 0.88**	0.90**	0.70**	0.06	.84**	- 0.19	0.93**	0.85**	0.45*	0.56*	- 0.29	0.05	0.35	1			
Cr	- 0.75**	0.73**	0.71**	0.23	.81**	-0.13	0.85**	0.72**	0.24	0.75**	- 0.21	- 0.19	.74**	.76**	1		
Cu	- 0.87**	0.92**	0.60*	0.12	.66**	- 0.09	0.87**	0.81**	.74**	.51*	- 0.08	0.31	0.21	.91**	.62**	1	
Ni	- 0.50*	0.53*	0.31	0.12	0.24	0.12	0.45	0.40	.74**	0.28	0.01	0.50	0.05	0.48	0.20	.64**	1

Table 5 Correlation matrix of the heavy metals in the studied agricultural soils

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed)

recorded high content in Mn, Zn, Zr, As, Pd, Cd, Co, Cu, and Ni which results from the Mangabad fertilizer factory (Table 2). Sample No. (1) recorded the highest percentage of Cd (2.4 ppm), indicating the worst effect of Mangabad fertilizer factory on the soil of cultivated land.

The significant positive correlation (Table 5) is observed between Fe versus Zr, Co, Cr, Cu, and Zn (r = 0.64, 0.93, 0.85, 0.87, and 0.56, respectively). This possibly indicates the adsorption of these elements on Fe-oxy-hydroxide or Fe-rich clay minerals (such as vermiculite mineral, which is detected by the mineralogical studies with Abou El-Anwar et al. (2018). Also, the positive relation between P₂O₅ versus As, Pb, Cd, and Zn (r = 0.29, 0.21, 0.30, and 0.28, respectively (Table 5) revealed that these toxic elements are mostly related to the Mangabad fertilizer factory.

Conclusions

The mean concentrations of the major elements in these soil decrease from Si $> Al > CaCO_3 > Fe > Ca > Mg > OM > Ti > K > Na > P > Mn > S$. The concentrations of K, Fe, Ti, and Mg are primarily related to Al, and as such, these elements are dominantly controlled by clay minerals and/or by minerals associated with clays during sedimentation.

The high concentration of Zr, Zn, Cr, Ni, Pb, Co, Cu, As, and Cd indicated their anthropogenic input. As, Pb, and Cd could be mainly coming from the application of phosphatic fertilizer. The industrial activities (Seed Pharmaceutical and Mangabad fertilizer factories) contributed greatly in the pollution of soil with heavy metals.

The authors mentioned to some recommendations which can decrease the effect of the pollutions: (1) create a barrier of suitable size between the wastewater disposal sites and populated or farming areas where contamination represented a problem, (2) augment the awareness of the government about these problems and to help the people to understand the potential extent of such pollutions on their health and plants, and (3) must treat the wastewater to diminish the possibility of contamination.

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