



Determination of heavy metal content and pollution indices in the agricultural soils using laser ablation inductively coupled plasma mass spectrometry

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Abstract

In this study, we determined the concentrations of heavy metals in the agricultural soils of Kafr El-Zayat city using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The LA-ICP-MS performance was firstly evaluated by analyzing appropriate reference materials and comparing the concentration values found to those of the reference values. LA-ICP-MS was then applied to examine the content of 21 elements (Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Sr, Mo, Sn, Ba, Pb, Th, and U) in 16 collected agricultural soil samples from Egypt. The soil quality was assessed by calculating the contamination factor (CF), enrichment factor (EF), and the geo-accumulation index (I_{geo}) of the measured heavy metals. The average concentrations of V, Cr, Co, Ni, and Cu were higher than the average worldwide background concentrations and exceeded the Canadian soil quality guidelines with values of 162.8, 113.3, 42.2, 88.1, and 70.6 $\mu\text{g/g}$, respectively. Multivariate analysis was applied to investigate the correlation and sources of heavy metals in agricultural soils. Cluster analysis indicated the clustering of heavy metals into three groups: Cr and Mo; Fe and Mn; and V, Ni, Co, Cu, Zn, and Pb. The results of principal component analysis (PCA) agreed with those of the cluster analysis and yielded three components that explained 81.13% of the total variance. The contamination factor (CF) of soils from all sampling sites showed moderate contamination.

Keywords Agricultural soil · LA-ICP-MS · Heavy metals · Kafr El-Zayat city · Pollution

Introduction

Contamination of urban and agricultural soils by heavy metals is a worldwide problem that has severe threats to human and animal health (Adimalla et al. 2019). The soil particles can bind various chemicals and, therefore, can be considered as an

important sink for contaminants that may originate from different sources (Senesi et al. 2009; Shivakumar et al. 2012; Al-Wabel et al. 2017). Heavy metals can get into the soil through natural and anthropogenic sources. Anthropogenic sources of heavy metals include industrial effluents, domestic sewage, vehicle exhaust emissions, and excessive use of fertilizers, herbicides, and pesticides (Pan et al. 2016; Song et al. 2018). Contamination of the agricultural soils may be a reason for the contamination of various food products such as vegetables, fruits, grains, and legumes. Heavy metals in polluted soils can infiltrate into the groundwater reservoirs causing their contamination and spoliation. The uptake and accumulation of heavy metals in plants and their transfer to animals through various food webs can deteriorate human health due to the consumption of polluted products or intake of contaminated water. Therefore, it is of extreme importance to evaluate the content of heavy metals in the agricultural soils to control pollution.

The most common techniques that have been used for the determination of heavy metals in soils and sediments can be categorized into solution-based and direct solid analysis

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instrumental techniques (Moenke-blankenburt et al. 1994; Bacon et al. 2020). The solution-based techniques include inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and atomic absorption spectroscopy (AAS). These techniques are time-consuming and require the use of aggressive acids to dissolve the samples for the total extraction of elements. The total extraction of elements in soil, however, is always difficult and requires the use of hazardous reagents, such as HF and HClO₄, in addition to a well-designed digestion methodology (Moenke-blankenburt et al. 1994). Sample contamination can also be an issue during sample preparation processes if careful measures were not followed. These problems can be minimized or eliminated by using analytical techniques that require no or minimal sample preparation procedures. In direct analytical techniques, the solid samples can be analyzed directly without the need for sample decomposition. These techniques include laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Shaheen et al. 2008, 2012, 2017; Shaheen and Fryer 2010), laser ablation inductively coupled plasma optical emission spectroscopy (LA-ICP-OES) (Musil et al. 2000), laser-induced breakdown spectroscopy (LIBS) (Senesi et al. 2009; Jantzi and Almirall 2011; Aslam Farooq et al. 2013; Tawfik et al. 2015; Farooq et al. 2015, 2020; Suyanto et al. 2017), and X-ray fluorescence spectroscopy (XRFS) (Moenke-blankenburt et al. 1994). XRFS is a useful technique for the determination of minor and major elements in solid samples but not appropriate for the determination of trace or low-atomic weight elements (Jantzi et al. 2019). LIBS is less expensive and faster than LA-ICP-MS and may provide data of a similar quality to that obtained by LA-ICP-MS for some elements. Both techniques are quasi-non-destructive but require careful optimization of the instrumental and operating conditions to reduce spectroscopic and non-spectroscopic interferences (Jantzi and Almirall 2011, 2015; Jantzi et al. 2019). LA-ICP-MS is a rapid multielement analytical technique that has the advantages of minimal sample preparation, high sensitivity, low detection limit, high sample throughput, and wide linear dynamic range, which means the capability of simultaneous analyses of major, minor, and trace elements in the sample (Limbeck et al. 2015). The advantages of LA-ICP-MS allow the determination of all essential trace elements in the soils that may not be possible to determine using other analytical techniques. The disadvantages of LA-ICP-MS include matrix effect, fractionation, and the lack of suitable matrix-matched calibration standards (Shaheen et al. 2012). Fractionation and matrix effect can be minimized by using calibration standards of properties similar to those of the sample (i.e., matrix-matched standard (Guillong and Günther 2002; Hattendorf et al. 2003; Saetveit et al. 2008; Pisonero and Günther 2008; Limbeck et al. 2015; Shaheen et al. 2015) (Limbeck et al. 2015) (Shaheen et al. 2012) (Mao et al. 1998; Krosalakova and Günther 2007; Saetveit et al. 2008).

Heavy metals is a term that is generally used to refer to a group of metals and semimetals (metalloids) that have densities greater than or equal to 3 g/cm³ and can cause harmful biological effects and ecological problems when present in sufficient concentrations (Senesi et al. 2009; Bánfalvi 2011). The most important heavy metals include Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Zr, Ag, Cd, Sn, Sb, Te, Ba, Ce, Pt, Au, Hg, Th, Pb, Bi, and U (Bánfalvi 2011). Trace elements are another term that is widely used in literature to describe elements that exist in the ecosystem at concentrations less than 0.1% (Senesi et al. 2009). Trace elements include most of the heavy metals and elements with a density of less than 3 g/cm³ such as Li, B, Mg, Al, and Si (Bánfalvi 2011). An element is considered a contaminant or pollutant to the environment if found at concentrations higher than its background or natural value (Senesi et al. 2009). In this study, we determined the content of 21 elements in the agricultural soils of Kafr El-Zayat city, Egypt, using LA-ICP-MS.

Methodology

Sampling and sample preparation

Sixteen soil samples were collected from an agricultural region that lies within a populated area close to many industrial facilities in Kafr El-Zayat city. Kafr El-Zayat is an important agricultural and industrial city that belongs to El-Gharbia Governorate, which is located to the west of the Nile Delta in Egypt. The samples were collected during winter 2019 from an area (about 5 km²) cultivated with a clover (berseem) plant. To obtain representative samples, enough amount of soil (about 2–3 kg) was collected at each sampling site from four locations forming a square of 1-m side length using a shovel and ax at a depth between 10 and 25 cm. The four sub-samples were manually mixed to form a single composite sample and packed into a zip-lock polyethylene bag. The samples were air-dried before pulverizing into powders using a mortar and pestle. The pulverized samples were sieved using a 0.2-mm nylon sieve to remove large particles and gravels. The samples were then prepared for LA-ICP-MS by pressing into pellets of 1-cm diameter and 3-mm thickness using a hydraulic press at 15 tonnes pressure. No binders were added during the formation of pellets. The locations of the collected soil samples with landmarks on Kafr El-Zayat city map in Egypt are shown in Fig. 1.

Instrumentation

Laser ablation ICP-MS analyses were conducted at the University of Windsor, Canada, using a Photon Machines ArF excimer laser ablation system coupled to an Agilent 7700 mass spectrometer. The excimer laser operates at a



Fig. 1 Sampling sites in Kafr El-Zayat City, Egypt

wavelength of 193 nm and has a repetition rate of 1–300 Hz. The laser beam can be adjusted to have different shapes (e.g., circle, square, rectangle, and cross-like) with adjustable spot sizes of 3–160 μm. The full description of the laser system can be found in Shaheen et al. (Shaheen et al. 2016, 2021). The laser system was equipped with a Photon Machine HELEX 2-volume ablation cell. Helium was used as a sample carrier gas and mixed with Ar after the ablation cell. LA-ICP-MS signal was acquired for 120 s: 30 s for gas blank collection (i.e., the laser was off) and 90 s for sample signal collection (i.e., the laser was on). The laser beam was scanned over the sample surface at a speed of 5 μm/s to increase the amount of ablated material and to improve the representativeness of the sampling. The instrumental and operating conditions are listed in Table 1. Lake sediment reference material (LKSD-3) was used as a calibration standard for the quantification of 21 elements in marine (MESS-3), stream (STSD-2) reference materials, and the agricultural soil samples using Al as an internal element standard to correct for the variation in the amount of material ablated. The isotopes used for the determination of element concentration in soils and reference materials are listed in Table 1. In all samples, four replicate LA-ICP-MS analyses were conducted on one pellet prepared from each corresponding homogenized composite sample.

To evaluate the LA-ICP-MS as a technique suitable for the analysis of soils, analysis of sediment reference materials (stream STSD-2 and marine MESS-3 sediment samples) was performed to estimate the accuracy and precision of the analyses. All reference materials were obtained in powder form

from the Canada Centre for Mineral and Energy Technology (CANMET). The reference materials were prepared to form solid pellets by pressing using a hydraulic press without using a binder. The precision of analysis was calculated as a relative standard deviation (RSD) based on four replicate analyses.

The concentration of the analyte in the sample C_{AnSAM} was calculated by dividing the signal intensity of the analyte in the sample I_{AnSAM} by the normalized element sensitivity S (cps/ppm) (Longerich et al. 1996):

$$C_{AnSAM} = \frac{I_{AnSAM}}{S} \tag{1}$$

The normalized sensitivity S was calculated from the following equation (Longerich et al. 1996):

$$S = \left[\frac{I_{IS_{SAM}}}{C_{IS_{SAM}}} \right] \left[\frac{I_{AnCAL}}{C_{AnCAL}} \right] \left[\frac{C_{IS_{CAL}}}{I_{IS_{CAL}}} \right] \tag{2}$$

where I and C refer to the signal intensity (cps) and concentration, respectively; the subscripts IS_{SAM} and IS_{CAL} refer to the internal standard element in the sample and in the calibration standard, respectively; and I_{AnCAL} and C_{AnCAL} are the signal intensity and concentration of the analyte in the calibration standard, respectively. The use of internal element standard improves the precision (i.e., reproducibility) and accuracy of the measurement by correcting for the matrix effect and the variation in the amount of material ablated from different samples (Fryer et al. 1995; Hoffmann et al. 1996; Guerra et al. 1999; Jochum et al. 2005).

Table 1 Instrumental and operating conditions used for the analyses of soil samples

Laser ablation system	
Laser model	Photon Machines ArF excimer laser
Wavelength	193 nm
Pulse width	4 ns
Energy	2.9 mJ
Fluence	2.35 J/cm ²
Spot size	25 μm
Scan speed	5 μm/s
Repetition rate	20 Hz
Ablation time	90 s
Gas blank acquisition time	30 s
Mass spectrometer	
Model	Agilent Technologies 7900 ICP-MS
Plasma gas	Ar 16 L/min
Auxiliary gas	Ar 1 L/min
He flow rate through the cell	0.84 L/min
Ar flow rate added after the cell	0.93 L/min
RF power	1400 W
Ablation time	90 s
Gas blank acquisition time	30 s
Measured Isotopes	²⁵ Mg, ²⁷ Al, ²⁹ Si, ⁴³ Ca, ⁴⁴ Ca, ⁴⁷ Ti, ⁵¹ V, ⁵³ Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶² Ni, ⁶⁵ Cu, ⁶⁶ Zn, ⁶⁸ Zn, ⁸⁵ Rb, ⁸⁶ Sr, ⁹⁵ Mo, ¹¹⁷ Sn, ¹¹⁸ Sn, ¹³⁷ Ba, ²⁰⁸ Pb, ²³² Th, and ²³⁸ U

Results and discussion

LA-ICP-MS analysis of reference materials

LA-ICP-MS is a comparative technique that compares the signal intensity of an element of unknown concentration in a sample to that in a standard reference material to calculate the element concentration (Shaheen et al. 2015, 2017). Therefore, the ablation behavior of the sample should be identical or closely similar to that of the reference material for getting accurate concentrations. The ablation behavior (i.e., the amount of ablated material and dry aerosol quality) depends on both the physicochemical properties of the sample and the properties of the laser used for ablation (Shaheen et al. 2012; Limbeck et al. 2015). A practical approach to minimize or eliminate the drawbacks of LA-ICP-MS (e.g., fractionation and matrix effect) is to use a matrix-matched standard for calibration. This would ensure a similar ablation behavior of the sample and the calibration standards and, consequently, accurate analysis.

Table 2 shows the concentrations of 21 elements (Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Sn, Ba, Pb, Th, and U) in marine (MESS-3) and stream (STSD-2) sediment reference materials as determined by LA-ICP-MS using

Al as an internal standard. The measured concentrations of most elements in MESS-3 and STSD-2 were found to lie within 15% of the reference values (Jochum et al. 2005). The precision of most elements in MESS-3 and STSD-2 was better than 10 and 15% RSD (relative standard deviation), respectively. By comparing the elemental concentrations in MESS-3 and STSD-2 measured by LA-ICP-MS to those of the reference values, it becomes clear that LA-ICP-MS could be applied to the determination of elements in the agricultural soils.

LA-ICP-MS analysis of agricultural soils

Table 3 lists a statistical summary of the concentration of major and trace elements in the agricultural soils measured using the energy-dispersive X-ray spectroscopy (EDS) and LA-ICP-MS. The Canadian soil quality guidelines (CSQGs) for agricultural soils are also shown in Table 3. The concentration of Al measured by EDS for each soil sample was used as an internal standard in calculating element concentration in the LA-ICP-MS. The concentrations of V, Cr, and Ni were higher than those of the CSQGs values and varied between 147 to 190 μg/g, 95 to 150 μg/g, and 73 to 133 μg/g with average values of 163, 113, and 88 μg/g, respectively, for all samples. Copper and Co concentrations were slightly higher

Table 2 Concentrations of elements in MESS-3 marine and STSD-2 stream sediment reference material as determined by LA-ICP-MS

Element	MESS-3					STSD-2				
	Published values (µg/g)	Reference values (µg/g)	SD (µg/g)	Measured (µg/g)	SD (µg/g)	Published values (µg/g)	Reference values (µg/g)	SD (µg/g)	Measured (µg/g)	SD (µg/g)
Mg	9950–17,300	16000	...	16,503	431	13,500–20,200	18,800	1000	15,430	353
Al	74,894–99,150	85900	5000	33,400–86,900	83,700	251
Si	250,000–270,000	270000	...	298,962	11069	250,600.00	250,600	...	271,745	17348
Ca	13,800–15,400	14700	600	12,935	1360	11,900–29,000	28,600	2900	31,351	1048
Ti	3912–4400	4400	600	4460	96	870–4870	4870	400	3262	220
V	218.9–250.68	243.00	10	244.48	7.11	58–120	101.00	...	96.66	4.44
Cr	1.1–112	105.00	4	116.41	3.36	43–116	116.00	...	80.52	5.25
Mn	149–348	324.00	12	311.66	25.16	610–1060	720.00	120	904.44	112.03
Fe	6890–57,400	43400	1100	36332	879	38,000–52,000	52000	3000	50574	7136
Co	12.4–14.52	14.40	2	15.46	0.53	16–20	19.00	2	21.42	2.67
Ni	40–51.1	46.90	2.2	42.11	3.11	47–88.9	53.00	6	50.52	6.03
Cu	14.1–40.58	33.90	1.6	28.03	0.83	41.2–52.2	47.00	5	43.57	6.53
Zn	37.5–177	159.00	8	142.91	5.42	193–246	246.00	21	270.24	29.10
Rb	82–137	137.00	20	144.42	1.93	94.3–99	104.00	...	83.70	6.35
Sr	117–144	129.00	11	169.48	12.51	133–499	400.00	65	347.29	54.82
Mo	2.04–2.87	2.78	0.07	2.67	0.27	10.5–1–	13.00	2	12.99	2.16
Sn	0.16–3.6	2.50	0.52	3.10	0.24	4.27–5.07	5.00	...	3.82	0.58
Ba	842–1010	1010	45	1107	32	100–540	540	43	407	34
Pb	8.81–23.94	21.10	0.7	18.63	1.30	63–90.51	66.00	4	77.23	12.75
Th	11.8–11.96	13.19	1.03	14.43–16.1	17.20	...	12.50	2.20
U	2.9–3.98	4.00	...	2.83	0.08	15.6–21.53	18.60	...	16.60	1.61

The published and reference values were obtained from the GeoReM online database (Jochum et al. 2005). SD refers to standard deviation and was calculated based on four replicate analyses.

than those recommended by CSQGs in more than 63% of the samples with concentrations ranging from 52 to 85 µg/g, 34 to 53 µg/g, and an average of 71 and 42 µg/g, respectively. Tin (Sn) had a concentration higher than that of the CSQGs in 44% of the samples with values ranging from 3.27 to 9.76 µg/g and an average of 5.55 µg/g. Molybdenum, Ba, and Pb had concentrations lower than those of the CSQGs in all samples. Figure 2 shows the concentrations of V, Cr, Co, Ni, Cu, Zn, Sn, and Pb in comparison to the Canadian soil quality guidelines (CSQGs) for agricultural soils. The comparison of heavy metal concentrations in the study area to the CSQGs (CCME 2007) indicated a medium contamination level with a soil quality index (SOQI) of 52. The calculations (applied to V, Cr, Co, Ni, Cu, Zn, Sn, Mo, Ba, and Pb) were performed using a spreadsheet calculator (SOQI 1.0) published by the Canadian Council of Ministers of the Environment (CCME; Canadian Council of Ministers of the Environment 2007). According to the CSQGs, soil quality or contamination levels can be divided into five categories depending on the overall soil quality index SOQI (i.e., 90–100, very low; 70–90, low; 50–70, medium; 30–50, high; and 0–30, very high). The

average concentration of heavy metals decreased according to the following order Mn> Ba> V> Cr> Zn> Ni> Cu> Co> Pb> Sn> Mo. The reasons of the increased levels of V, Cr, Co, Ni, and Cu can be attributed to the various agricultural activities (e.g., application of fertilizers and organic manure, irrigation using wastewaters, and application of pesticides) and the atmospheric deposition of contaminants emitted from traffics and industrial facilities located near the sampling area (Simon 2014; El-Bady 2016; Khalifa and Gad 2018).

Pollution indices

The enrichment or depletion of an element in an environmental sample can be evaluated by comparing its concentration in the sample to the average element concentration in the upper continental crust (Gałuszka and Migaszewski 2011). A table of element abundances in the major parts of the earth’s crust was published in 1961 by Turekian and Wedepohl (1961). The concentrations of elements published in this table are widely used to represent the geochemical background concentrations (i.e., natural element concentration without

Table 3 Statistical summary of major and trace elements measured by EDS and LA-ICP-MS in all agricultural soils

	CSQGs (µg/g)	Min (µg/g)	Max (µg/g)	Mean (µg/g)	Median (µg/g)	SD (µg/g)
Major elements determined by EDS (in weight %)						
C	...	1.96	2.87	2.47	2.53	0.33
O	...	48.79	51.10	49.95	49.87	0.68
Na	...	0.81	1.15	0.97	0.97	0.11
Mg	...	2.19	2.58	2.32	2.30	0.10
Al	...	9.05	10.02	9.48	9.52	0.28
Si	...	20.61	23.38	22.34	22.62	0.78
K	...	0.89	1.49	1.14	1.14	0.13
Ca	...	3.06	4.34	3.67	3.62	0.33
Ti	...	0.92	1.25	1.06	1.06	0.09
Fe	...	7.52	8.66	8.14	8.09	0.38
Elements measured by LA-ICP-MS						
Mg	...	17,267	25,093	20,231	20,558	1937
Si	...	239,862	291,640	269,069	272,820	18,951
Ca	...	29,444	50,942	39,947	39,457	5732
Ti	...	6722	10,379	8768	8929	916
V	130	147.32	190.43	162.84	157.79	12.43
Cr	64	94.49	150.27	113.31	111.90	13.28
Mn	...	556	1369	807	781	204
Fe	...	61,954	87810	74510	73252	6770
Co	40	34.06	52.66	42.24	43.17	4.88
Ni	50	73.27	133.34	88.36	83.05	15.15
Cu	63	52.35	85.26	70.55	69.75	11.26
Zn	200	78.82	142.06	106.07	107.39	17.07
Rb	...	32.09	48.94	41.93	42.77	4.93
Sr	...	329	408	366	371	22
Mo	5	0.53	1.42	0.94	0.86	0.30
Sn	5	3.27	9.76	5.55	4.92	2.00
Ba	750	285	464	373	364	55
Pb	70	10.37	37.43	18.20	15.23	7.43
Th	...	4.61	6.48	5.52	5.66	0.55
U	...	0.64	1.25	0.96	1.00	0.19

CSQGs is the Canadian Environmental Quality Guidelines for agricultural soils (CCME 2007). SD refers to standard deviation and was calculated based on four replicate analyses

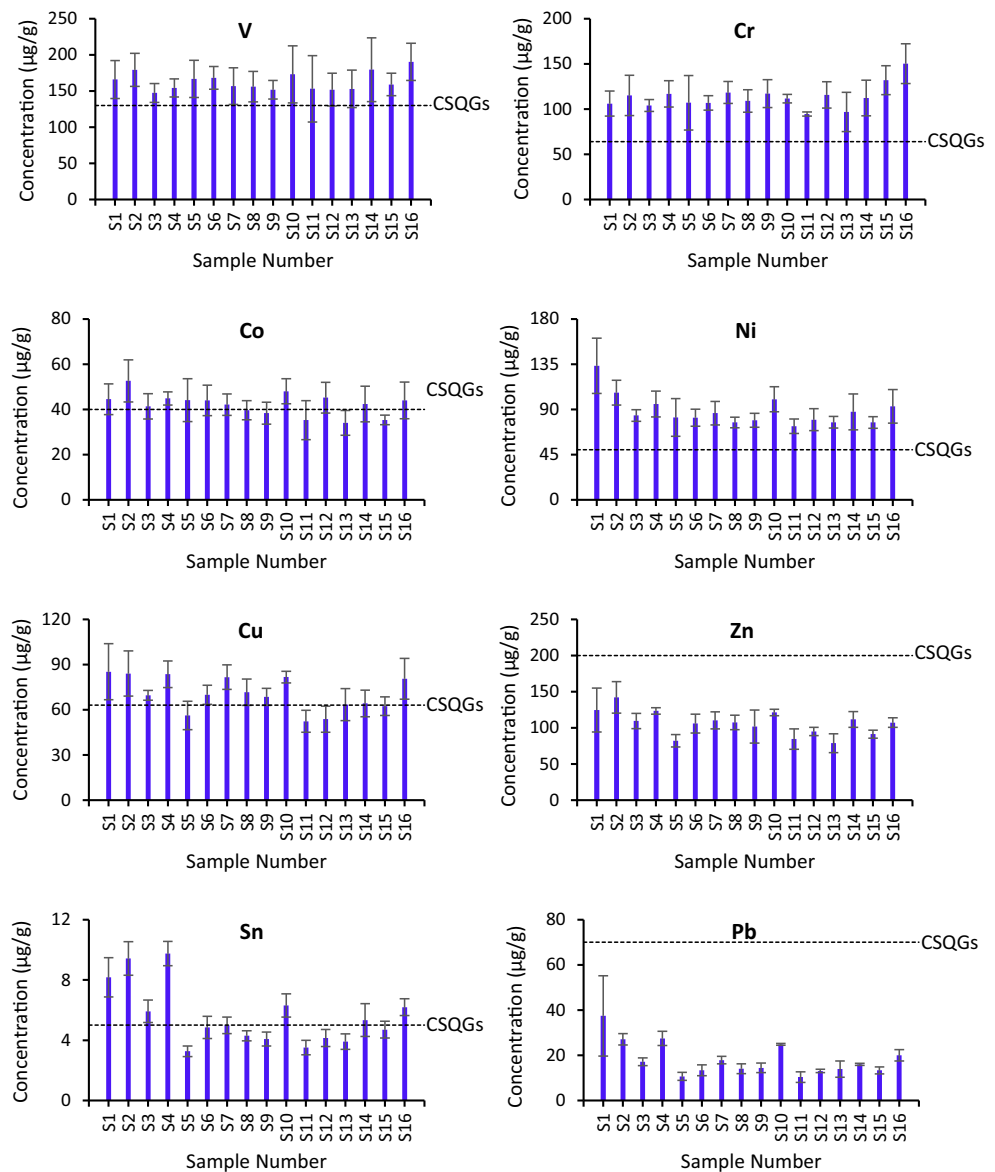
contribution from anthropogenic sources) and can be used to differentiate between natural and anthropogenically affected element concentration (Gałuszka and Migaszewski 2011). The worldwide soil average concentration is also used as a reference (Kabata-Pendias 2011). Various geochemical parameters such as enrichment factor (EF), contamination factor (CF) or pollution index (PI), and geo-accumulation index (I_{geo}) are used to evaluate the quality or pollution levels of elements in environmental samples (Gałuszka and Migaszewski 2011; Adimalla et al. 2019). It is important to know that these geochemical parameters depend on the original concentration of the uncontaminated soil, and therefore, the selection of an appropriate background reference can be a source of error in estimating the degree of soil contamination (Shokr et al. 2016).

The contamination factor (CF), or pollution index (PI), is defined as the ratio of the measured element concentration in the sample $C_{e-sample}$ to the element background concentration C_{e-bkg} (i.e., worldwide average soil concentration) (Gałuszka and Migaszewski 2011; Shokr et al. 2016)

$$CF = \frac{C_{e-sample}}{C_{e-bkg}} \quad (3)$$

The degree of soil contamination can be classified into four categories depending on the value of the contamination factor CF (i.e., $CF < 1$, low contamination; 1–3, moderate contamination; 3–6, considerable contamination; and $CF > 6$, the soil is very highly contaminated) (Gałuszka and Migaszewski 2011; Shokr et al. 2016). Table 4 lists the values of CF for

Fig. 2 Heavy metal concentration in agricultural soil samples compared to the Canadian soil quality guidelines (CSQGs) for agricultural soils



V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Sn, Ba, and Pb. Molybdenum, Ba, and Pb showed low contamination (i.e., a CF < 1) in 75%, 94%, and 81% of the samples, respectively. Vanadium, Cr, Mn, Cu, and Zn showed moderate contamination (i.e., 1 < CF < 3) in all samples. Nickel and Sn showed moderate contamination in 63% and 81% and considerable contamination (i.e., 3 < CF < 6) in 37% and 19% of the samples, respectively. The highest contamination level was observed for Co that showed considerable contamination in all samples.

The enrichment factor EF is defined by the following equation (Gałuszka and Migaszewski 2011):

$$EF = \frac{C_{e\text{-sample}}}{C_{e\text{-bkg}}} \times \frac{C_{\text{ref-bkg}}}{C_{\text{ref-sample}}} \quad (4)$$

where $C_{\text{ref-bkg}}$ and $C_{\text{ref-sample}}$ are the background concentration of the reference element and the concentration of a reference element in the sample, respectively. A reference element is an abundant element in the earth’s crust whose concentration does not change substantially by anthropogenic input (Gałuszka and Migaszewski 2011). Examples of reference elements include Si, Fe, Al, and Ti. The degree of enrichment of an element can be classified into five categories according to the enrichment factor EF (i.e., EF < 2, deficiency to minimal enrichment; 2–5, moderate enrichment; 5–20, significant enrichment; 20–40, very high enrichment; and EF > 40, extremely high enrichment). Table 4 lists the EF values for V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Sn, Ba, and Pb. All heavy metals except for Co and Ni showed enrichment factors smaller than

Table 4 Concentration, contamination factor (CF), enrichment factor (EF), and geo-accumulation index (I_{geo}) of metals in agricultural soil relative to Ti

Element	Statistics	Concentration ($\mu\text{g/g}$)	SAC ($\mu\text{g/g}$) (Turekian and Wedepohl 1961)	WSAC ($\mu\text{g/g}$) (Kabata-Pendias 2011)	CF	EI	I_{geo}
V	Minimum	147.32	1.14	0.88	- 0.39
	Maximum	190.43	1.48	1.35	- 0.02
	Mean	162.84	130	129	1.26	1.02	- 0.25
Cr	Minimum	94.49	1.59	1.38	0.08
	Maximum	150.27	2.53	1.92	0.75
	Mean	113.31	90	59.5	1.90	1.54	0.34
Mn	Minimum	556.10	1.14	0.90	- 0.40
	Maximum	1368.92	2.81	2.21	0.90
	Mean	807.50	850	488	1.65	1.34	0.10
Co	Minimum	34.06	3.01	2.59	1.01
	Maximum	52.66	4.66	4.08	1.64
	Mean	42.24	19	11.3	3.74	3.02	1.31
Ni	Minimum	73.27	2.53	2.04	0.75
	Maximum	133.34	4.60	3.79	1.62
	Mean	88.36	68	29	3.05	2.46	1.01
Cu	Minimum	52.35	1.35	1.13	- 0.16
	Maximum	85.26	2.19	1.81	0.55
	Mean	70.55	45	38.9	1.81	1.45	0.26
Zn	Minimum	78.82	1.13	0.97	- 0.41
	Maximum	142.06	2.03	1.47	0.44
	Mean	106.07	95	70	1.52	1.21	0.00
Mo	Minimum	0.53	0.48	0.43	- 1.64
	Maximum	1.42	1.29	1.10	- 0.22
	Mean	0.94	1.5	1.1	0.85	0.68	- 0.88
Sn	Minimum	3.27	1.31	1.32	- 0.20
	Maximum	9.76	3.90	2.95	1.38
	Mean	5.55	6	2.5	2.22	1.76	0.49
Ba	Minimum	284.61	0.62	0.55	- 1.28
	Maximum	464.17	1.01	0.77	- 0.57
	Mean	372.61	580	460	0.81	0.65	- 0.90
Pb	Minimum	10.37	0.38	0.37	- 1.97
	Maximum	37.43	1.39	1.14	- 0.11
	Mean	18.20	20	27.0	0.67	0.54	- 1.25

SAC shale average concentration (Turekian and Wedepohl 1961), WSAC worldwide soil average concentration (Kabata-Pendias 2011), CF contamination factor, EF enrichment factor, I_{geo} geo-accumulation index

2 in all samples; this indicates deficiency to minimal enrichment. Cobalt and Ni showed moderate enrichment with an average enrichment factor of 3.02 and 2.46, respectively.

Pollution levels can also be assessed using the geo-accumulation index (I_{geo}) according to the following:

$$I_{\text{geo}} = \log_2 \left(\frac{C_{\text{e-sample}}}{1.5 \times C_{\text{e-bkg}}} \right) \quad (5)$$

where $C_{\text{e-sample}}$ and $C_{\text{e-bkg}}$ are the element concentration in the sample and the element background concentration,

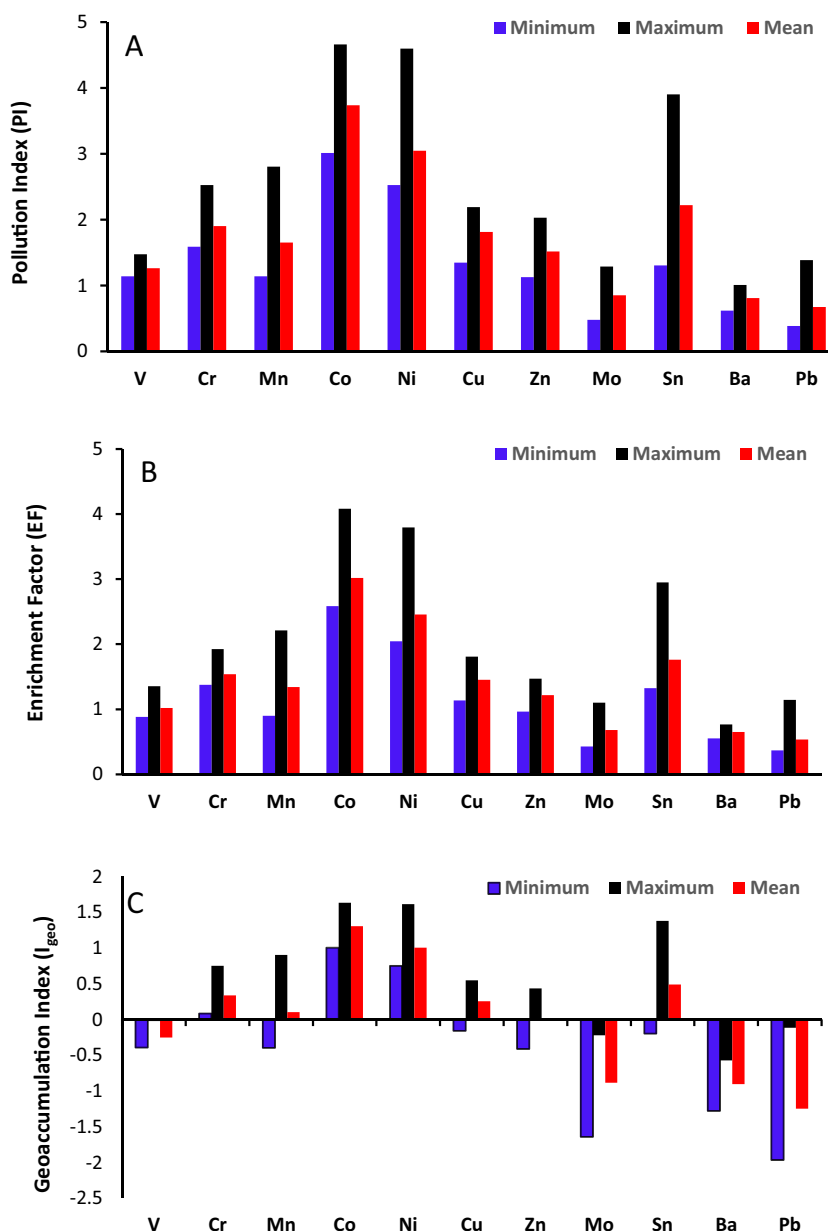
respectively (Adimalla et al. 2019). The soil quality can be classified into 7 categories based on the I_{geo} values (i.e., $I_{\text{geo}} < 0$, uncontaminated; 0–1, uncontaminated to moderate contamination; 1–2, moderate contamination; 2–3, moderate to heavy contamination; 3–4, heavy contamination; 4–5, heavy to extreme contamination; and $I_{\text{geo}} > 5$, extreme contamination) (Adimalla et al. 2019). Table 4 lists the I_{geo} values for V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Sn, Ba, and Pb. All samples were practically uncontaminated with I_{geo} smaller than 1 for V, Mo, Ba, and Pb. Chromium, Mn, Cu, Zn, and Sn showed

uncontaminated to moderate contamination with $0 < I_{geo} < 1$ in 100%, 56%, 81%, 63%, and 60% of the samples, respectively. The rest of the samples were not contaminated. Cobalt and Ni showed moderate contamination with $1 < I_{geo} < 2$ in 100% and 38% of the samples. Nickel showed uncontaminated to moderate contamination ($0 < I_{geo} < 1$) in 62 % of the samples. The CF, EF, and I_{geo} reported in this study were calculated relative to the worldwide soil average concentration reported in reference (Kabata-Pendias 2011) using Ti as a reference element. Figure 3 shows the minimum, maximum, and average values of CF, EF, and I_{geo} .

Many studies have been conducted on the analysis of heavy metals in the agricultural soils of Kafr El-Zayat and nearby cities (Al Nagggar et al. 2014; El-Bady 2016; Shokr

et al. 2016; Khalifa and Gad 2018; Mankoula et al. 2021). Al Nagggar et al. (2014) determined the content of five heavy metals (Cu, Zn, Cd, Pd, and Fe) in the agricultural soil and plant samples collected from four different cities in Egypt, including Kafr El-Zayat, using flame atomic absorption spectroscopy (FAAS). They reported a significant variation in the concentrations of heavy metals with location and season. The concentration values of Cd and Fe were found to exceed the maximum allowable concentration (MAC), while the concentration values of Cu, Pb, and Zn were lower than that of MAC. El-Bady (2016) studied the distribution of heavy metals in the cultivated soils of the Middle Nile Delta. They measured the concentrations of Cr, Co, Fe, Ni, Cu, Zn, and Pb at different depth and various grain sizes in agricultural soils around and

Fig. 3 Minimum, maximum, and the mean value of the contamination factor (a), enrichment factor (b), and geochemical index (c) for heavy metals in agricultural soils



near Tanta and Kafr El-Zayat cities and compared the results with the Canadian soil quality guidelines (CSQGs). The highest concentrations were found in the top surface layers and clay fractions. The average concentrations of Pb and Ba were lower than the corresponding concentrations in both CSQGs and the average shale values. Chromium and Ni showed concentrations higher than that of CSQGs and the average shale values. The concentrations of Co and Zn were found to be lower than that of CSQGs and higher than that of the average shale values, respectively (El-Bady 2016). The authors attributed the high concentration of heavy metals in the surface soils of Kafr El-Zayat and Tanta cities to irrigation using water contaminated with residential and industrial waste (El-Bady 2016). A comparison of heavy metal concentrations in agricultural soils in various areas of Egypt and other countries has been reported in a recent study by Khalifa and Gad (2018). The concentrations of heavy metals varied widely with time and sampling location due to reasons that might be related to the variation of soil treatment (e.g., plowing and fertilization) or the variation in the analytical techniques used for the analysis. This study is the first to apply LA-ICP-MS to the analysis of agricultural soils in Kafr El-Zayat and surrounding areas. The results of our study lie within the values published in reference (Khalifa and Gad 2018). Shokr et al. (2016) studied the distribution of heavy metals in El-Gharbia Governorate using various techniques including X-ray fluorescence (XRF) spectrometry, geographical information systems (GIS), and remote sensing. They reported a concentration of V, Ni, Cr, Cu, and Zn higher than the average global concentration. Nickel and Zn were higher than the recommended values set by the CSQGs, while Zn was under the CSQGs allowable limit. They assessed the environmental risk of the soil by calculating the pollution load index, contamination factor, and the degree of contamination (Shokr et al.

2016). It should be mentioned that comparisons of heavy metal content in different regions are difficult due to the many variables that could affect the measured concentrations (e.g., location, time of sample collection, sampling depth, climate conditions, human activities, irrigation methods, type of crops, soil treatment procedures, type of soils, and the analytical techniques used in the measurements).

Multivariate analysis

Multivariate analysis was conducted using XLSTAT, version 2019.2.2, as a Microsoft Excel add-on statistical software. Principal component analysis (PCA) and cluster analysis (CA) were applied to get information about the sources of pollution in the agricultural soils. Table 5 shows the Spearman correlation coefficient as calculated from the observed elemental concentrations in the collected soil samples considering a significance correlation level of 0.05. The correlation matrix indicates that Pb is significantly correlated with Ni, Cu, Zn, Sn, and Ba. The results also show a significant correlation among Fe, V, and Mn and between Cr and Mo. The high correlation between these groups of elements indicates some common sources of contamination (Pan et al. 2016) (Petrotou et al. 2012).

Table 6 shows the factor loadings of the first three principal components in PCA and their percentage contribution to the total variance for heavy metals in soils. Principal components with eigenvalues greater than one were considered to explain the variability of the data set. Varimax rotation with Kaiser Normalization mode was applied in the analysis of the data set to maximize the variance (Frentiu et al. 2009). The eigenvalues of the first three extracted components for heavy metal concentrations have values greater than one. This suggests a three-component model that explains 81.13% of the total

Table 5 The Spearman correlation coefficient matrix between heavy metal concentrations

Variables	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Sn	Ba	Pb
V	1	0.259	0.382	0.582	0.453	0.529	0.379	0.376	0.050	0.415	0.544	0.309
Cr		1	0.197	0.106	0.194	0.171	0.203	0.188	0.785	0.279	0.285	0.250
Mn			1	0.618	0.344	0.300	-0.050	0.141	0.347	0.050	0.332	0.059
Fe				1	0.126	0.153	-0.132	-0.044	-0.065	-0.082	-0.047	-0.141
Co					1	0.776	0.529	0.624	0.082	0.609	0.624	0.494
Ni						1	0.800	0.832	0.176	0.841	0.576	0.862
Cu							1	0.871	0.265	0.859	0.597	0.932
Zn								1	0.194	0.912	0.694	0.888
Mo									1	0.253	0.232	0.338
Sn										1	0.635	0.909
Ba											1	0.565
Pb												1

Values in bold are different from 0 with a significance level $\alpha = 0.05$

Table 6 Factor loadings of the first three principal components and their percentage contribution to the total variance for heavy metals in soils

	PC1	PC2	PC3
V	0.574	0.541	-0.276
Cr	0.372	0.318	0.773
Mn	0.289	0.800	0.008
Fe	0.074	0.850	-0.304
Co	0.747	0.144	-0.231
Ni	0.921	0.006	-0.205
Cu	0.883	-0.327	-0.007
Zn	0.919	-0.212	-0.094
Mo	0.356	0.213	0.873
Sn	0.921	-0.238	-0.013
Ba	0.774	0.080	-0.019
Pb	0.900	-0.303	0.068
Eigenvalue	5.971	2.128	1.637
Variability (%)	49.757	17.737	13.640
Cumulative %	49.757	67.494	81.134

Varimax rotation with Kaiser Normalization mode was applied in the analysis of the data set

Values in bold correspond to factor loadings greater than 0.55

variance. According to this model, heavy metals in the agricultural soil can be grouped into three principal components. The first principal components (PC1) explains 49.76% of the total variance and includes V, Co, Ni, Cu, Zn, Sn, Ba, and Pb. The concentrations of most elements in PC1 are higher than the reference background values, which indicate that the sources of these elements are of anthropogenic origin. Anthropogenic sources arise from various agricultural activities and practices that are applied by individual farmers to

serve agricultural land. The excessive use of chemical (e.g., phosphate) and organic (e.g., animal manures and sewage sludges) fertilizers, pesticides, and irrigation by untreated water contribute to the enrichment of V, Cu, Cr, Zn, Ni, and Pb due to possible accumulation in the soils (Mortvedt 1995). The atmospheric deposition from nearby industrial facilities and traffics can also contribute to Pb contamination in the soil at some sites. The low average Ba concentration in this group of elements, compared to the average worldwide soil concentration, may be attributed to its leaching in the form of organic Ba complexes (Lagas et al. 1984).

The second principal component explains 17.74% of the total variance and contains Mn and Fe. Manganese is an abundant element in the Earth’s crust and exists in the soils at concentrations that vary between 20 and 3000 µg/g with an average value of 600 µg/g (Malcolm et al. 2004) (Mousavi et al. 2011). Manganese and Fe belong to the same family of elements and are closely associated with geochemical processes (Kabata-Pendias 2011). The correlation of Mn to Fe suggests a lithogenic nature of Mn in the soils. The contribution of anthropogenic sources to Mn enrichment, however, cannot be neglected when its concentration is higher than the worldwide average. The anthropogenic sources of Mn include municipal wastewater discharges, metal smelting processes, and sewage sludges (Kabata-Pendias 2011) (Malcolm et al. 2004). Vanadium can be considered to have a mixed source of contamination (i.e., anthropogenic and natural) since it has a close loading factor in PC1 and PC2. Figure 4 shows the loading plot obtained from the principal component analysis for PC1 and PC2 components.

The third principal component (PC3) explains 13.64% of the total variance and contains Cr and Mo. Chromium and Mo belong to the same group of elements that have strong

Fig. 4 Principal component analysis loading plots for PC1 and PC2

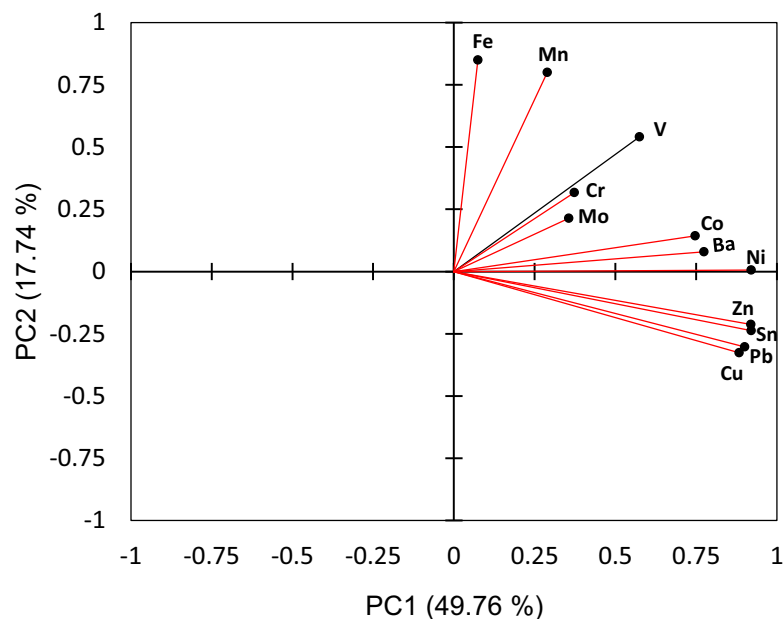
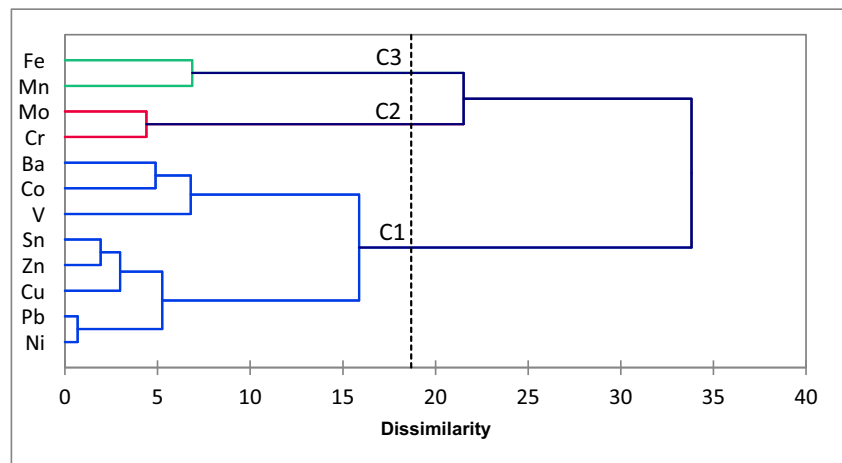


Fig. 5 Dendrogram representing the results of the hierarchical cluster analysis of heavy metals in agricultural soil samples. C1, C2, and C3 are the clusters to which heavy elements are grouped. The first cluster C1 contains V, Co, Ni, Cu, Zn, Sn, Ba, and Pb; the second cluster C2 includes Cr and Mo, while the third cluster C3 includes Fe and Mn. The results of HCA agree with those of PCA



lithophilic tendencies (Kabata-Pendias 2011). The origin of Cr and Mo comes from the parent rocks with a worldwide average content in soils of 60 and 1.1 $\mu\text{g/g}$, respectively (Kabata-Pendias 2011). Contamination from various sources such as municipal (sewage sludge) and industrial wastes has increased the Cr levels in the agricultural soils. The Mo content in soils is similar to that in parent rocks and does not show large differences among different groups of soils (Kabata-Pendias 2011). The application of sewage sludges may increase the content and solubility of Mo content in agricultural soils (Kabata-Pendias 2011).

Hierarchical cluster analysis (HCA) was also applied to estimate the source of similarities between elements. The dendrogram that represents the results of the HCA of the heavy metals is shown in Fig. 5. The measured heavy metals can be grouped into three clusters. The first cluster C1 includes V, Co, Ni, Cu, Zn, Sn, Ba, and Pb. The second cluster C2 includes Cr and Mo. The third cluster C3 includes Fe and Mn. The results of HCA agree with those of PCA.

Conclusions

The content of 16 collected agricultural soil samples from Kafr El-Zayat city, Egypt, was determined using LA-ICP-MS as an analytical technique. The technique was evaluated by analyzing reference materials similar to the agricultural soils. The measured concentrations in reference materials were found to lie within the referenced values with a precision better than 15% for most elements. The degree of agricultural soil contamination was evaluated by calculating several geochemical parameters such as the contamination factor, enrichment factor, and the geo-accumulation index. The concentrations of heavy metals showed medium contamination levels compared to the Canadian soil quality guidelines (CSQGs). The concentration values of V, Cr, Co, Ni, and Cu were found

to be higher than the CSQG values. The elevated levels of these elements can be attributed to anthropogenic sources that can be related to various agricultural practices (e.g., application of fertilizers and organic manures) and industrial activities (e.g., atmospheric depositions from nearby industrial facilities). Hierarchical cluster analysis has shown the clustering of heavy metals into three groups, which agrees with the results of the principal component analysis. The results reported in this study provide useful information about the quality and the content of heavy metals in the agricultural soils of Kafr El-Zayat city, which is essential in the assessment, management, and control of soil contamination. Depending on the observed results, it is recommended that strict measures should be considered to avoid further contamination of the agricultural soils and limit the spread of pollution in the long term.

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Author contribution MES performed the experimental work, interpreted the data, and wrote the manuscript. WT reviewed the manuscript. AFM collected the soil samples and participated in data interpretation. JEG and BJB supported the experimental analysis using LA-ICP-MS and SEM instruments in their labs. FEM reviewed the manuscript.

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Data availability The data sets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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