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Assessment of Heavy Metals Content in The Agricultural Soils of Kafr El-Zayat Egypt Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Optical Emission Spectroscopy

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Abstract
Recent years have witnessed a tremendous increase in contamination levels of heavy metals in the agricultural soils due to the uncontrolled release of chemicals and toxic substances from various human activities. The transfer of heavy metals to the groundwater and humans through the various food chains may cause serious health problems. Therefore, continuous evaluation of heavy metals content in the agricultural soil is important to control the spread of pollution, to preserve the soil quality, and to protect human health. In this study, we determined the content of heavy metals (V, Cr, Mn, Co, Ni, Cu, Zn, and Pb) in the agricultural soils of Kafr El-Zayat city, Egypt using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES). In ICP-OES, the soil samples were digested using a mixture of concentrated nitric and hydrochloric acids at a ratio of 1: 3 and heating on a hot plate at a temperature of 120 ℃ for few hours. This method of sample preparation was not efficient in extracting the total metal content in the soils and the results had to be corrected for using reference materials. In LA-ICP-MS, the soil samples were prepared in a form of rigid pellets using a hydraulic press. The accuracy of the analyses was examined by analyzing reference materials and comparing the observed results to the published concentration values. The concentrations of heavy metals determined by the ICP-OES were found to be 90.14 ppm for Zn, 57.90 ppm for Cu, 75.3 ppm for Ni, 115.18 ppm for Cr, 32.75 ppm for Co, and 11.49 ppm for Pb. Meanwhile, the concentrations of heavy metals as measured by LA-ICP-MS were found to be 100.60 ppm for Zn, 69.78 ppm for Cu, 90.8 ppm for Ni, 116.42 ppm for Cr, 41.38 ppm for Co, and 18.24 ppm for Pb. The concentrations of V, Cr, and Ni exceeded the concentration levels of the Canadian soil quality guidelines, which indicate the contamination of the examined agricultural soils with these elements.

Keywords: Thermal parameters Agricultural Soils; Heavy Metal; Kafr El-Zayat; LA-ICP-MS; ICP-OES.

1. Introduction

Human life is closely linked to the quality of agricultural soils. However, in recent years, the uncontrolled release of chemicals and toxic substances due to various human activities has caused heavy metal pollution to become a serious concern in all developed and developing countries. In particular, agricultural soils can be a long-term container for heavy metals [1]. Heavy metals (HMs) are natural elements in the earth's crust, they are persistent and can exist for long periods in aqueous and terrestrial environments [2, 3]. Heavy metals are important environmental pollutants, which can be introduced into the environment through various industrial and agricultural activities such as solid waste disposal, fertilizers, pesticides, sludge application, irrigation with wastewater, and automobile exhausts [4, 5]. The accumulation of heavy metals in the agricultural soils can be harmful to the soil, plants, animals, people, and can lead to the contamination of groundwater [2, 6-10]. Exceeding the background concentration levels of heavy metals in soils is an indicator of the presence of contamination. According to numerous studies, the sources of heavy metals pollution in the environment are derived from human activities such as pollution caused by chemical fertilizers, pesticides, air pollution from cars and factories exhaust, sewage, combustion of oil, coal, tires and wood, lead mines, and the plastics

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industry, dyeing materials, burning of medical and solid waste, petroleum refining industry and others [11-17]. HMs can enter the body in various ways, including smelling, digestion, and absorption through the skin [5, 18]. It can accumulate in the body to reach a risk level causing severe health issues such as cancer, kidney and lung diseases, Digestive system, liver and intestinal diseases [2, 9, 19].

Many advanced techniques that have been commonly used for the analysis of heavy metals in soils and sediments include laser-induced breakdown spectroscopy (LIBS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) [20-31]. LA-ICP-MS is a rapid multi-element analytical technique that needs no or minimal sample preparation and has the capability of high spatial resolution analysis with high accuracy and low detection limits. The preparation procedures of solid samples for analysis by LA-ICP-MS include pressing into pellets, embedding in a high purity polymer resin, and fusion with borate [26, 28, 29]. Binders such as polyvinyl alcohol, metallic powders, and microcrystalline cellulose are sometimes used to improves the cohesion and mechanical strength of the prepared pellets [31, 32]. The ICP-OES technique requires long-time preparation steps to digest solid samples using a mixture of acids to form solutions. Some elements can be lost or added during sample preparation due to heating or the use of contaminated glassware. Therefore, strict measures should be followed during sample preparation to avoid element loss or contamination. It is vital to recognize the polluted soils and the potential contamination sources in Kafr El-Zayat to arrange administration methodologies for achieving way better natural quality in comparable areas of Egypt. This study is the nitty-gritty report on metal accumulation in agricultural soils of Kafr El-Zayat city, and comes about will advance the care for the environment by monitoring heavy metal levels in getting soils and controlling the toxin sources [1].

In this work, we measured the concentrations of heavy metals (V, Cr, Co, Ni, Mn, Cu, Zn, and Pb) in some agricultural soil samples, collected from farm fields close to chemical factories in Kafr El-Zayat city in Egypt using LA-ICP-MS and ICP-OES. We also evaluated the analytical performance of the two techniques in terms of accuracy and precision.

2. Materials and Methods

2.1 Study Area

The study area was located in Kafr El-Zayat city, Egypt. Kafr El-Zayat is an important city that belongs to Gharbia Governorate in Egypt. It is located between Cairo and Alexandria in the middle of the road. The city of Kafr El-Zayat has a large number of factories and companies such as chemical plants, pesticides, fertilizers, paper, oils, and soaps [33]. Kafr El-Zayat is famous for cultivating many types of crops such as wheat, cotton, rice, potatoes, bananas, corn, beans, and others.

2.2. Sample Collection and Sample Preparation

Five agricultural soil samples were collected in winter 2019 from 5 different locations in a region close to many industrial facilities in Kafr El-Zayat city, Figure 1. At each site, four sub-samples were collected using a shovel and an axe from four positions making a square of a 1 m side-length at a depth of 0-25 cm. The samples were manually mixed, placed in clean plastic zip-lock bags, and transported to the laboratory. Samples were left to dry under the sun for about 3 days, cleaned manually by removing plant residues and any strange objects, ground using a mortar and pestle, and finally sieved using meshes of different sizes (0.25-0.212-0.16 mm) to obtain powders of small particle sizes. The obtained homogenized powders were prepared for analysis by LA-ICP-MS by pressing into pellets of 1 cm diameter and 0.3 cm thickness using a hydraulic at a pressure of 5 TNS.

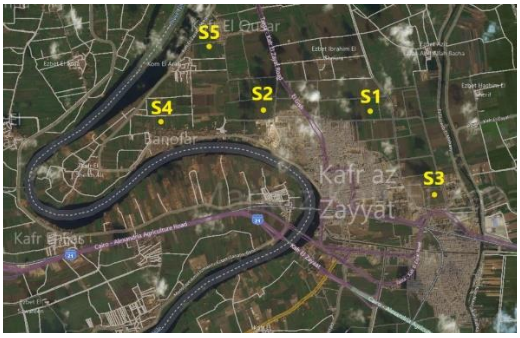


Fig.1. A map showing locations of the collected soil samples in Kafr El-Zayat city, Egypt. Sampling Sites (points in yellow)

The powdered soil samples were prepared for ICP-OES analysis by using the wet digestion method developed at the Great Lakes Institute for Environmental Research, University of Windsor, Canada. This method uses aqua-regia (i.e., a mixture of concentrated nitric and hydrochloric acid at a ratio of 1: 3) for sample digestion. About 1 gram of each dry powdered soil sample was accurately weighed and mixed with 7 ml concentrated nitric acid and 21 ml concentrated hydrochloric acid (Fisher brand® ACS-Pure analytical grade) in a 100 ml glass flask. The mixture was left on a hot plate for about 5 hours at a temperature of 120 ℃. After cooling down, the digested soil samples were filtered using a filter paper (Whatman^{TM}, Kent, UK), diluted to about 100 ml, and analyzed for using ICP-OES. All glassware including sample bottles and pipettes were washed cleaned and rinsed with diluted HNO3 followed by distilled water to avoid contamination. All reagents used were of analytical grade.

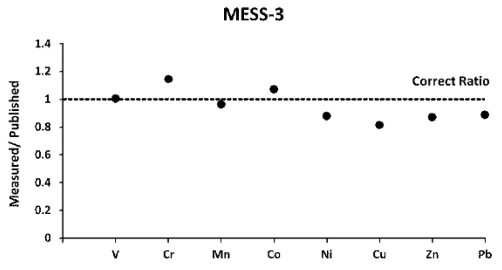
2.3. Instrumentation

LA-ICP-MS and ICP-OES analyses were conducted at the University of Windsor, Canada. The LA-ICP-MS system consists of an ArF excimer laser operating at a wavelength of 193 nm coupled to an Agilent Technologies 7900 ICP-MS. The description of the laser system can be found in Shaheen et al. [34]. Soil samples in a form of pellets were analyzed by scanning a laser beam of 25 µm spot size on the sample surface at a speed of 5 µm/ s for 90 s. The laser energy and repetition rate were fixed to 2.9 mJ and 20 Hz, respectively. Digested soil samples were analyzed using Agilent Technologies 700 ICP-OES.

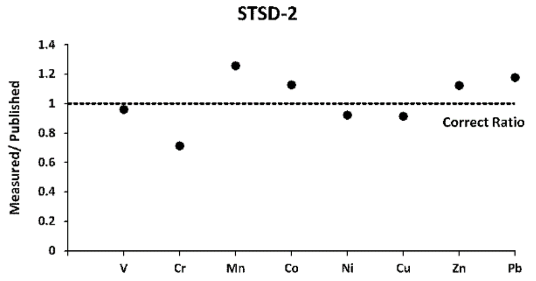
3. Results and Discussion

3.1. LA-ICP-MS versus ICP-OES Analysis of Reference Materials

Analyses of reference materials were performed to verify the accuracy and precision of the analyses by LA-ICP-MS and ICP-OES. Marine (MESS-3) and stream (STSD-2) sediment reference materials were used in this study to evaluate the accuracy and precision of the measurements. Table 1 shows the average concentrations of heavy metals in marine (MESS-3) and stream (STSD-2) sediment reference materials as determined by LA-ICP-MS and ICP-OES. The published concentrations of elements in MESS-3 and STSD-2 are also listed. The concentrations of heavy elements determined by LA-ICP-MS in sediment reference materials are very close (better than 15 % for most elements) to the published values. The situation is different in the case of analysis by ICP-OES, where most elements were found to have concentration much lower than the published values. This large deviation can be attributed to the sample preparation method which was inadequate for extracting the total metal content from the sediment samples. Other methods that use more aggressive acids such as Hf combined with microwave digestion are recommended for the dissolution of sediment and soil samples.

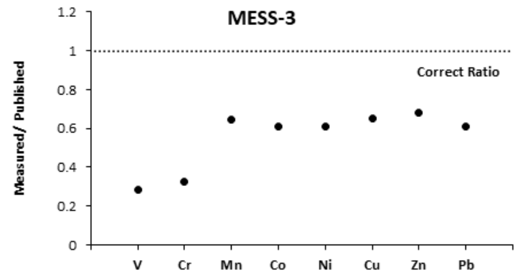


(A)

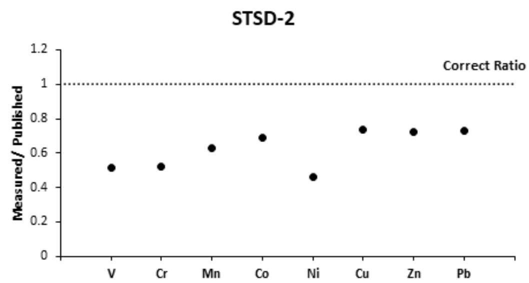


(B)

Fig.2. The ratio of the measured/published values of elements in A) MESS-3 and B) STSD-2 as determined by LA-ICP-MS



(A)



(B)

Fig.3. The ratio of the measured/published values of elements in A) MESS-3 and B) STSD-2 as determined by ICP-OES

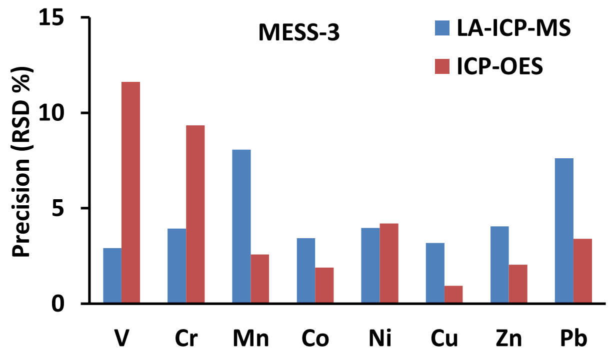


Fig.4. The precision of measurements of elements determined by LA-ICP-MS and ICP-OES in marine sediment reference material MESS-3.

Figure 2 shows the measured/published ratio of the elements in MESS-3 and STSD-2 as determined by LA-ICP-MS to indicate the accuracy of the measurements. Accurate concentrations are those for elements that lie on or close to the value one.

Figure 3 shows the measured/published ratio of the elements in MESS-3 and STSD-2 as determined by ICP-OES. The precision of the measurements of elements determined in MESS-3 by LA-ICP-MS and ICP-OES is shown in Figure 4.

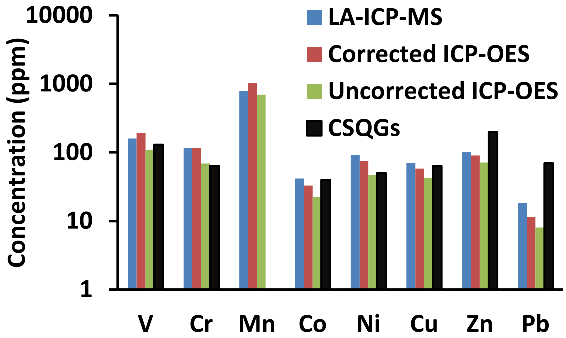


Fig.5. The average concentration of heavy metals in the agricultural soils as measured by LA-ICP-MS and ICP-OES. Corrected ICP-OES represent the concentrations obtained from the ICP-OES after being corrected for the inappropriate digestion using reference materials. CSQGs is the Canadian soil quality guidelines

The precision (agreement between different replicate measurements), shown as relative standard deviation (RSD %), is better for solution ICP-OES than LA-ICP-MS except for V and Cr. The high RSD values of V and Cr indicates that these elements are either not homogeneously distributed in the soil or are not equally extracted from the soil during the digestion process. In general, the precision was better than 5 % for most elements determined by the two techniques. We conclude from the analysis of the sediment reference materials (which have properties similar to those of the soils) that LA-ICP-MS is more accurate than ICP-OES under the digestion procedure applied in this study. A correction has to be made or another robust preparation procedure should be applied for the accurate analysis of soils and sediments.

Table 1. The average concentrations of heavy metals in marine (MESS-3) and stream (STSD-2) sediment reference materials as determined by LA-ICP-MS and ICP-OES. The published concentrations of elements in MESS-3 and STSD-2 are also listed.

	MESS-3			STSD-2		
Element	**Published** [35] **(ppm)**	**LA-ICP-MS (ppm)**	**ICP-OES (ppm)**	**Published** [35] **(ppm)**	**LA-ICP-MS (ppm)**	**ICP-OES (ppm)**
V	243	244.5±7.1	68.8 ± 8	104	96.7 ± 4.4	53.5 ± 1.01
Cr	105	120.1± 4.7	34.1 ± 3.2	106.64	82.6 ± 6.9	55.8 ± 1.1
Mn	324	311.7± 25.2	209.4 ± 5.4	934	904.4 ± 112	590 ± 9.1
Co	14.4	15.5± 0.53	8.6 ± 0.12	20	21.4 ± 2.8	13.7 ± 0.13
Ni	46.9	41.2± 4.6	28.7 ± 1.2	84.6	48.8 ± 6.2	38.8 ± 0.14
Cu	33.9	27.6± 0.84	22.1 ± 0.21	45.7	42.9 ± 5.8	33.7 ± 0.27
Zn	159	138.7± 5.6	108 ± 2.2	246	275.9 ± 29.4	177.7 ± 1.01
Pb	21.1	18.8± 1.17	12.9 ± 0.44	66	77.6 ± 13.8	48 ±0.16

3.2. Analysis of Agricultural Soils

Table 2 shows the concentrations of heavy metals in the agricultural soil samples as determined by the LA-ICP-MS. The average concentrations of the upper earth crust and the Canadian soil quality guidelines (CSQGs) of the agricultural soils are also listed in Table 2. The levels of heavy metals in the agricultural soil investigated in this study were highest for Mn followed by V, Cr, Zn, Ni, Cu, Co, and Pb. The average concentrations were found to be 792.7 ppm for Mn, 158.5 ppm for V, 116.4 ppm for Cr, 100.6 ppm for Zn, 90.8 ppm for Ni, 69.8 ppm for Cu, 41.4 ppm for Co, and 18.2 ppm for Pb. The average concentrations of all investigated heavy metals are higher than their corresponding concentrations in the upper crust of the Earth [36]. This indicates the contamination of the agricultural soils by heavy metals. The concentration of V, Cr, Mn, Co, and Ni exceeds the Canadian quality guidelines concentration. Zinc and Pb are exceptions, where their concentrations are lower than the CSQGs. The results obtained from the LA-ICP-MS analysis indicate that there is large contamination of most investigated heavy elements in the agricultural soils. The contamination of the agricultural soils with heavy metals can be attributed to the use of chemical and organic fertilizers, pesticides, irrigation with contaminated wastewater, and deposition of particulates from various industrial activities [1].

Table 2. The concentrations of heavy elements in the agricultural soil samples as determined by LA-ICP-MS. The average concentrations of heavy elements in the upper earth crust [36] and the Canadian soil quality guidelines(CSQGs) are shown [37].

Sample	V	Cr	Mn	Co	Ni	Cu	Zn	Pb
S1	175.1	158.1	968.8	51.5	113.3	89.8	132.4	25.8
S2	141.8	81.5	793.6	40.0	89.1	53.9	85.9	13.9
S3	162.5	128.8	686.6	43.5	92.0	83.2	105.4	18.7
S4	157.5	102.9	795.4	36.7	79.4	62.8	94.1	20.4
S5	155.7	115.7	719.1	35.2	79.9	59.2	85.1	12.5
Average	158.5	116.4	792.7	41.4	90.8	69.8	100.0	18.2
SD	12.0	28.8	109.2	6.5	13.8	15.8	19.6	5.3
Average upper earth crust (ppm)	53	35	527	11.6	18.6	14.3	52	17
CSQGs of agricultural soils (ppm)	130	64	……	40	50	63	200	70

Table 3. The concentrations of heavy elements in the agricultural soil samples as determined by ICP-OES. The average concentrations of heavy elements in the upper earth crust [36] and the Canadian soil quality guidelines(CSQGs) are shown [37].

Sample	V	Cr	Mn	Co	Ni	Cu	Zn	Pb
S1	105.1	68.7	718.8	21.9	46.2	43.8	74.3	10.8
S2	113.0	64.7	573.1	22.7	43.8	35.6	65.9	5.5
S3	106.8	70.8	710.4	22.4	46.8	44.0	71.1	9.8
S4	112.1	68.2	708.4	22.9	46.4	43.5	72.6	8.8
S5	109.6	73.6	774.2	23.2	50.0	42.1	72.2	5.4
Average	109.3	69.2	697.0	22.6	46.7	41.8	71.2	8.0
SD	3.4	3.3	74.3	0.5	2.2	3.6	3.2	2.5
Average upper earth crust (ppm)	53	35	527	11.6	18.6	14.3	52	17
CSQGs of agricultural soils (ppm)	130	64	……	40	50	63	200	70

Table 3 lists the concentrations of heavy metals in the agricultural soil samples as measured by ICP-OES. The concentration values were lower than the corresponding concentrations determined by LA-I CP-MS. Therefore, the concentrations of heavy metals determined by the ICP-OES were corrected for using the true values of the reference materials. The correction of the measured ICP-OES concentrations using reference material, however, was not perfect for all elements due to the variation of total element extraction among individual elements and samples. The ICP-OES corrected concentration values, shown in Table 4, lie within 20% of the LA-ICP-MS values. The approach followed in this study to correct for the ICP-OES data is not perfect and it is much better to apply the optimum methods for sample digestion to get accurate data. Figure 5 shows the concentration of heavy metals in the agricultural soils as determined by LA-ICP- MS and ICP-OES (corrected and uncorrected). Canadian soil quality guidelines are also shown in Figure 5. Based on the analysis of reference materials, ICP-OES yields concentrations lower than the true values due to the inappropriate sample preparation method used in this study. In the next section, we will stick to the LA-ICP-MS data to evaluate the quality of the agricultural soils.

Table 4. The corrected concentrations of heavy elements in the agricultural soil samples as determined by ICP-OES. The average concentrations of heavy elements in the upper earth crust [36] and the Canadian soil quality guidelines(CSQGs) are shown [37].

Sample	V	Cr	Mn	Co	Ni	Cu	Zn	Pb
S1	183.7	114.4	1059.0	31.7	74.6	60.7	94.0	15.4
S2	197.5	107.7	844.3	32.9	70.8	49.3	83.5	7.8
S3	186.6	117.9	1046.6	32.4	75.6	61.0	90.0	14.0
S4	195.9	113.5	1043.6	33.1	74.9	60.3	91.9	12.6
S5	191.6	122.5	1140.5	33.6	80.7	58.3	91.4	7.7
Average	191.1	115.2	1026.8	32.7	75.3	57.9	90.2	11.5
SD	5.9	5.5	109.5	0.7	3.5	4.9	4.0	3.6
Average upper earth crust (ppm)	53	35	527	11.6	18.6	14.3	52	17
CSQGs of agricultural soils (ppm)	130	64	……	40	50	63	200	70

3.3. *Assessment of Soil Pollution (Pollution Indices)*

Pollution indices were calculated in this study to assess the contamination levels of the agricultural soils in Kafr El-Zayat city. Many geochemical indices such as enrichment factor (*EI*), geo-accumulation index (I_{geo}), and contamination factor (*FF*) are commonly used to evaluate the quality of the environment [38, 39]. These indices compare the concentration of the element measured in the environment to its original concentration before contamination. The average concentration of the upper Earth crust or the worldwide average soil concentration is usually used as the background concentration for comparison [40-42]. The data obtained from LA-ICP-MS analysis was used in the calculation of pollution indices.

4.3.1 Enrichment Factor (EF)

To estimate critical inputs over natural levels and the anthropogenic commitment of heavy metals within the Kafr El-Zayat soils, the enrichment factor (*EF*) was calculated as follow [43] :

$$EF = (M/Al)_{sample}/(M/Al)_{UEC} \qquad (1)$$

Where $(M/Al)_{sample}$ and $(M/Al)_{UEC}$ refer to the ratio of the concentration of the target metal *M* and *Al* in the soil samples and the upper earth crust by [36]. Aluminum was utilized as a reference metal since it is accepted to be overpoweringly inferred from a single source [44]. The categories for evaluating *EFs* were considered as follows: $EF < 2$ indicates deficiently to minimal enrichment, $2 \leq EF < 5$ indicates moderate enrichment, $5 \leq EF < 20$ indicates a significant enrichment, $20 \leq EF < 40$ indicates very high enrichment, and $EF \geq 40$ indicates extremely high enrichment [13, 45]. Enrichment factor values between 0 and 1.5 indicate the metal is entirely from crustal materials of natural origin, while an $EF > 1.5$ suggests that the sources are more likely to be anthropogenic. Enrichment factors greater than 10 are considered to be non-crusted source [46].

Table.5. Enrichment factor (*EF*), geo-accumulation index (I_{geo}), contamination factor (*CF*) for heavy metals in agricultural soils of Kafr El-Zayat city. LA-ICP-MS data was used in calculations.

Pollution indices	V	Cr	Mn	Co	Ni	Cu	Zn	Pb
EF	3.57	3.97	1.798	4.27	5.83	5.83	2.31	1.28
I_{geo}	0.995	1.15	0.004	1.25	1.70	1.70	0.367	-0.49
CF	2.99	3.33	1.50	3.57	4.88	4.88	1.93	1.07

Table 5 shows the *EF* values calculated for heavy metals in the agricultural soils. The mean *EF* of V, Cr, Mn, Co, Ni, Cu, Zn, and Pb are 3.57, 3.97, 1.80, 4.27, 5.83, 5.83, 2.31, and 1.28, respectively. Manganese and Pb have enrichment factor lower than 2, which indicates a deficiency or minimal contamination levels. Vanadium, Cr, Co, Cu, and Zn have enrichment factors between 2 and 5, which indicate a moderate enrichment. The soil is significantly contaminated with Ni and Cu with enrichment factors greater than 5. The relatively high enrichment factors of V, Cr, Co, Cu, and Zn indicate that the source of these elements in the soils is anthropogenic [47]. The values of the geochemical parameters (pollution indices) are determined based on the background concentration of the soils. Therefore, the interpretation of the soil quality and its degree of contamination is relative and may vary from a researcher to another even for the same element concentrations due to the difference in the background element concentration used.

4.3.2 Geo-accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) was utilized to estimate the heavy metal contamination within Kafr El-Zayat area soil samples. It was calculated using the following equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5 \times B_n}\right) \qquad (2)$$

Where C_n denotes the measured concentration of heavy metal n in a soil sample and B_n denotes the concentration of heavy metal n in the upper earth crust by [36]. The geo-accumulation index consists of seven grades or classes [44, 46]. $I_{geo} \leq 0$, class 0) practically unpolluted; ($0 < I_{geo} \leq 1$, class 1) unpolluted to moderately polluted; ($1 < I_{geo} \leq 2$, class 2) moderately polluted; ($2 < I_{geo} \leq 3$, class 3) moderately to heavily polluted; ($3 < I_{geo} \leq 4$, class 4) heavily polluted; ($4 < I_{geo} \leq 5$, class 5) heavily to extremely polluted; ($I_{geo} > 5$, class 6) extremely polluted. Table 5 shows that the mean value of I_{geo} for V, Cr, Mn, Co, Ni, Cu, Zn, and Pb are 0.995, 1.15, 0.004, 1.25, 1.70, 1.70, 0.367, and -0.49, respectively. Lead has a negative geo-accumulation index, which indicates that the soil is unpolluted with Pb. Vanadium, Mn, and Zn have geo-accumulation index between 0 and one, which indicate that the soil is in class 1 (unpolluted to moderately polluted). The soil is moderately polluted with Cr, Co, Ni, and Cu since they have a geo-accumulation index between 1 and 2. The mean value of I_{geo} shows that most agricultural soil samples were practically unpolluted with Pb and unpolluted to moderately polluted with Zn, Mn, and V, while moderately polluted with Ni, Cu, Co, and Cr, showing that the majority of the agricultural soils in the study area were polluted by Ni and Cu. In general, the analytical results of I_{geo} were similar to the analytical results of *EF*.

4.3.3 Contamination Factor (CF)

The Contamination Factor (*CF*) is used to assess contamination by comparing heavy metal concentrations in soils with upper earth crust values. The calculation of *CF* uses the equation:

$$CF = C/C_{UEC} \qquad (3)$$

Where *C* is the measured concentration of the element in soil and C_{UEC} is the upper earth crust concentration of the element. The categories for evaluation *CFs* were considered as follows: $CF<1$ indicates low contamination, $1\leq CF < 3$ indicates moderate contamination, $3 \leq CF < 6$ indicates considerable contamination and $CF \geq 6$ indicates very high contamination [48]. The mean *CF* of V, Cr, Mn, Co, Ni, Cu, Zn, and Pb are 2.99, 3.33, 1.5, 3.57, 4.88, 4.88, 1.93, and 1.07, respectively as shown in Table 5. The average values of the *CF* are higher than one for all elements. Chromium, Co, Ni, and Cu have the highest contamination factors (3-6), which indicate considerable contamination of soils with these elements. The soil is moderately contaminated with V, Mn, Zn, and Pd as they have contamination factors between1-3. The application of pesticides may be a source of Zn pollution in agricultural soils from Kafr El-Zayat. Application of products that contain Cu such as organic or mineral fertilizers, crop protection products, sewage sludge, and plant nutritional supplements might also be the direct route for the higher concentration observed for Cu in agricultural soils from Kafr El-Zayat [49].

4.4 Analysis of Agricultural Soils in this study versus different countries

An endeavor has been carried out which is planning to supply comprehensive up-to-date comparison concerning heavy metals concentrations in agricultural soil of different locales in Egypt and numerous countries over different continents, Table 6. As can be seen, the mean concentrations of Co, Cr, Ni, and Zn were higher than those from Siwa Oasis [50]. Cobalt, Cr, Cu, and Ni were higher than those from Southwestern Nile Delta [44]. Chromium, Cu, and Zn were lower than those from Upper Egypt (Aswan) [51]. Copper and Zn were higher than those from Kafr El-Zayat [52]. Interestingly, the mean concentration of Ni was higher than those from different regions in Egypt while the mean concentration of Pb was lower than those from different regions in Egypt. Compared to other worldwide studies shown in Table 6, the mean concentration of Pb was lower than those from worldwide. Overabundance Pb content of soils above regulatory limits makes serious health risks to both humans and animals due to its capacity to bio-accumulate in soft tissues creating organ and tissue failures [2]. On the other side, Co, Cr, Cu, Ni, and Zn were both higher and lower than those from worldwide. Co was higher than those from Sudan [53]. Chromium and Ni were lower than those from India [54]. Copper was lower than those from India [54] and higher than those from different worldwide regions. Zinc was lower than those from Saudi Arabia [55] and India [54]. A high concentration of Zn in soil nourishment crops does not constitute any genuine toxicity risk to humans or animals expending them but frequently zinc contaminated soils are also contaminated with non-fundamental elements such as Cd and Pb [3].

Table.6. Heavy metal contents (ppm) in the agricultural soil of Kafr El-Zayat compared with other works in Egypt and worldwide.

Location	Analytical technique	Co	Cr	Cu	Ni	Pb	Zn	Reference
Egypt								
Kafr El-Zayat	LA-ICP-MS	41.4	116.4	69.8	90.8	18.2	100.6	This
	ICP-OES	32.8	115.2	57.9	75.3	11.5	90.1	Study
Southwestern Nile Delta	ICP-OES	15.75	93.2	46.5	42.7	63.5	145	[44]
Upper Egypt (Sohag)	AAS	39	167	78	74	32	203	[51]
Kafr El-Zayat	AAS	….	….	23.65	….	44.2	28.5	[52]
Siwa Oasis	INAA	3.9	19.6	….	8.3	….	16.6	[50]
Worldwide								
Sudan (Alhasahisa)	ICP-OES	24	….	34.4	71.2	13	90.3	[53]
India (Singhbhum)	ICP-MS	32.3	149.6	218	94.2	47	210	[54]
Saudi Arabia (Hail)	AAS	….	37	27.2	27.9	24.7	158.2	[55]

AAS is the atomic absorption spectroscopy.
INAA is the instrumental neutron activation analysis.

It is worth noticing that the above comparison isn't fundamentally accurate due to the impacts of numerous variables (such as geographic area, climatic conditions, geology and mineralization, levels of anthropogenic activities, and analytical techniques). These results demonstrate the impact of anthropogenic activities on metal (Co, Cr, Cu, Ni, Pb, and Zn) contamination within the study area [44]. This impact is most likely related to industrial activities near the sampling sites, serious urbanization, and agricultural activity. As the study area is characterized by the presence of large industrial facilities, it is normal to have elevated levels of metals within the soils [56-58]. Agricultural soils can be contaminated with Co, Cr, Ni, and Zn through fertilizers, and organic manure application [48, 59-61]. Also, it can be contaminated with Cr, Cu, Ni, Pb, and Zn from industrial activity via atmospheric deposition [61-64].

Conclusion

Kafr El-Zayat is a densely populated city in Egypt and is the capital of the local pesticides and chemicals industry. This study determined the concentrations of heavy metals in the agricultural soils of Kafr El-Zayat city using LA-ICP-MS and ICP-OES as analytical techniques. Based on the analysis of reference materials, LA-ICP-MS provided more accurate concentrations than ICP-OES which gave low concentration values due to the inappropriate sample preparation method used for digestion of the soils. The method of sample preparation for analysis by ICP-OES followed in this study was not efficient in extracting the total metal content in the soils and the results had to be corrected by using reference materials. The results indicated the contamination of the investigated area with V, Cr, Co, Cu, Ni, Zn, and Pb. The concentrations of all elements were higher than the concentration of the upper Earth crust which indicates soil contamination. All elements except for Zn and Pd had concentrations values higher than the Canadian soil quality guidelines.

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