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Evaluation of Heavy Metal Presence in Agricultural Samples of *Lactuca sativa* and *Trifolium alexandrinum* Using Picosecond Laser-Induced Breakdown Spectroscopy and Flame Atomic Absorption Spectroscopy in Banha and Giza Governorates, Egypt

Noura Fayek¹, Walid Tawfik^{2,*}, Ahmed Khalafallah³, Sawsan Hamed¹, Wafaa Mousa¹ and Mohamed Fikry^{4,5}

- ¹ Department of Physics, Faculty of Women for Arts, Science, and Education, Ain Shams University, Cairo 11566, Egypt
- ² National Institute of Laser Enhanced Sciences (NILES), Cairo University, Giza 12613, Egypt
- ³ Department of Botany, Faculty of Women for Arts, Science, and Education, Ain Shams University, Cairo 11566, Egypt
- ⁴ Ultrafast Picosecond Laser Lab, Physics Department, Faculty of Science, Cairo University, Giza 12613, Egypt; mfikry@sci.cu.edu.eg
- ⁵ Egypt Nanotechnology Center (EGNC), Faculty of Nanotechnology for Postgraduate Studies, Cairo University, Sheikh Zayed 41516, Egypt
- * Correspondence: walid_tawfik@niles.edu.eg

Abstract: This pioneering study utilizes Flame Atomic Absorption Spectroscopy (FAAS) and Picosecond Laser-Induced Breakdown Spectroscopy (Ps-LIBS) to quantify heavy metal contents in samples of *Lactuca sativa* L. and *Trifolium alexandrinum* L. collected from Banha and Giza, Egypt for the first time. In order to enhance the performance of Ps-LIBS, laser parameters were carefully optimized. Expressly, laser energy was set to $100 \pm 5\%$ J/cm², pulse duration was calibrated to 170 picoseconds, and 1064 nm Nd: YAG pulses were employed. This optimization facilitated the creation of linear LIBS calibration curves, a crucial element in ensuring precise elemental quantification and bolstering the overall analytical reliability. The assessment of pollution indices revealed concerningly high levels of copper, nickel, and cadmium consistently across all study sites. *Lactuca sativa* L. and *Trifolium alexandrinum* L. also demonstrated multiple metals' bioaccumulation factors (>1), further underscoring the potential health risks associated with copper, nickel, and cadmium contents. Given these findings, it is imperative to recommend constructing a dedicated wastewater treatment facility to address Al Mansouria village's environmental challenges in the Giza governorate.

Keywords: heavy metal contamination; *Lactuca sativa* and *Trifolium alexandrinum*; Banha and Giza Governorates; Flame Atomic Absorption Spectroscopy (FAAS); Picosecond Laser-Induced Breakdown Spectroscopy (Ps-LIBS); bioaccumulation factor

1. Introduction

The increasing challenges posed by population growth and industrial activities are leading to elevated levels of environmental contamination. Such contamination frequently includes trace elements in soil and water, some can be beneficial for biological systems, while others can be hazardous [1–3]. Specifically, heavy metal contamination arises from diverse sources such as industrial effluents, metal-based insecticides and fertilizers, and contaminated irrigation water [4]. These factors collectively contribute to a worrying surge in heavy metal contamination, particularly in soil and environmental matrices, as a direct result of rampant industrialization, urbanization, and the escalated use of irrigation water [5–7].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Analytical techniques like FAAS and Ps-LIBS have been instrumental in quantifying and characterizing these heavy metal contaminants. FAAS specializes in detecting the contents of heavy and trace elements by analyzing the radiation absorption of specific elements [8,9]. FAAS, in particular, has been instrumental in assessing the presence of toxic metals such as copper, manganese, and cadmium in various vegetable samples, including cabbage, mallow, and turnip, as well as their corresponding soils. For example, a study conducted in Qaliubia, Egypt, employed FAAS to measure varying Cu, Mn, and Cd contents in these vegetables and soils, providing critical data on PI values for these metals [10]. Flame Atomic Absorption Spectrometry (FAAS) has played a pivotal role in the evaluation of the presence of toxic trace elements, notably copper (Cu) and cadmium (Cd), in diverse environmental samples [8,9]. In a research investigation conducted at a location situated in northern Egypt, FAAS was employed as the analytical technique of choice to quantify the diverse content levels of Cu and Cd within agricultural samples. The analytical approach provided crucial data regarding PI values associated with trace metals, which can potentially raise health-related concerns [7–9].

Ps-LIBS, offers a range of applications in optical coherence tomography, advanced optical communications, and ultrashort pulse control. This technique employs a picosecond laser that minimizes heat-affected zones and expedites material vaporization through efficient electron–phonon interactions [11,12].

The choice of *Trifolium alexandrinum* and *Lactuca sativa* as test subjects is deliberate and significant. *Trifolium alexandrinum*, commonly known as Egyptian clover, is a key forage crop, and *Lactuca sativa*, or lettuce, is widely consumed as a leafy vegetable. Both are integral to human and animal diets and often serve as bioindicators for environmental health [13]. Their widespread cultivation and consumption make them pivotal in studies focusing on trace metal accumulation and its subsequent impact on human and animal health [14].

LIBS is an analytical technique primarily used for the qualitative and semi-quantitative analysis of the elemental composition of a sample [15,16]. LIBS operates through a highenergy laser pulse to ablate a minute portion of a sample, producing a plasma. Indeed, it is imperative to underscore that preceding phases involving the determination of elemental contents, employing established methodologies such as FAAS, as shown in the above sections, are of utmost significance in establishing LIBS calibration curves [17]. Establishing LIBS calibration curves is essential for converting spectral intensity into accurate elemental contents and mitigating inherent variations due to sample matrices, laser energy, and measurement conditions [18]. This comprehensive reference underscores the critical role of calibration in LIBS analysis. Calibration ensures precise quantification, enhancing the reliability of LIBS analysis across industries such as materials science, environmental monitoring, and archaeology [19–21].

During the last decade, LIBS has been deployed for a variety of applications. For instance, Naeem et al. used a 532 nm Nd: YAG pulsed laser to delve into the properties of copper plasma [22], while Walid Tawfik et al. employed LIBS to assess contamination by heavy elements in environmental samples under ambient air conditions [23–26].

Laser-induced breakdown spectroscopy is a powerful technique for detecting trace heavy elements in environmental samples. Tawfik et al. (2015) demonstrated the utility of LIBS in monitoring inorganic elements in challenging environmental conditions [27]. Farooq et al. (2013) further explored the plasma characteristics of samples, contributing to a deeper understanding of LIBS analysis [28].

Moreover, Tawfik and colleagues (2015) extended the application of LIBS to trace heavy metal analysis in various environmental matrices, showcasing its versatility and sensitivity in environmental monitoring [29]. These studies collectively highlight LIBS as a valuable tool for rapid and non-invasive detection of trace heavy elements, aiding in environmental assessment and analysis.

In this context, the current study employs FAAS and Ps-LIBS to assess the contents of trace heavy metals, such as zinc, manganese, copper, nickel, cadmium, lead, and chromium,

in agricultural samples from *Trifolium alexandrinum* and *Lactuca sativa* plants as well as in their associated soils. The ultimate goal is to comprehensively analyze heavy metal contamination in critical agricultural plants, thereby aiding in developing guidelines for environmental remediation and public health policy.

2. Material and Methods

2.1. Samples Collection

This research selected five sites across two critical governorates in Egypt to analyze the contents of heavy metals in soil and the roots and shoots of local plant life. Within the Banha governorate, three sites were examined: Kafr Al-Arab village (30.4078° N, 31.2253° E), irrigated with groundwater; Sindenhour village (30.4757° N, 31.5024° E), irrigated by a Nile River tributary; Mit Asem village (30.4246° N, 31.1782° E), irrigated directly from the El-Felfla canal. Two additional sites were located in the Giza governorate: Al Mansouria village (30.1375° N, 31.0712° E), irrigated with sewage water, and Nikla (30.9112° N, 30.7583° E), irrigated by the Nile River, Rasheed Branch (27.5833° N, 31.5667° E). Soil samples were collected from each site, extending to a 0–30 cm depth. Geographical data for these sites are presented in Figure 1.



Figure 1. The studied sites where the samples were collected.

2.2. Samples Preparation

The soil samples were brought to the laboratory in plastic bags shortly after collection, air-dried, and then packed in paper bags ready for chemical analysis. The plant samples were collected (*Trifollium alexandrinum* and *Lactuca sativa*). The shoots and roots of each plant were taken from each site, washed with deionized water, left to air-dry, and then oven-

dried at 70 °C for three days [30]. One gram of each sample was taken and placed in the digestion tube of the Kieldahl apparatus. Seven milliliters of nitric acid and one milliliter of perchloric acid were added to each sample for digestion for three hours, then diluted with one hundred milliliters of distilled water [31]. The metal contents were determined using a filament atomic absorption spectrometer system model Thermo Solaar S4 (Thermo Fisher Scientific, Waltham, MA, USA) [32]. The samples (soil and plants) were grounded into powders utilizing a mortar and pestle for Ps-LIBS measurements. A 0.2 mm nylon sieve was used to sift the ground-up samples to produce homogenous sample powder. In this investigation, pellets of the produced sample powder with a 1 cm diameter and 3 mm thickness were formed using a hydraulic press at 15 tons of pressure for 15 min without adding any binders [11].

2.3. Theoretical Background

2.3.1. Pollution Index (PI)

The calculation of the (PI) is given as:

$$PI = \frac{C_c}{C_r} \tag{1}$$

where C_c and C_r represent the estimated heavy metal content and its permissible content in soil and were used to determine the extent of each heavy metal's soil contamination [33].

2.3.2. Bioaccumulation Factor (BF) and Translocation Factor (TF)

A plant's suitability for phytoremediation can be determined using the bioaccumulation and translocation factors. These factors will enable phytoremediation technology, which depends on the possibility of heavy metal bioaccumulation and plant exclusion to clean up regions contaminated by heavy metals [34,35]. According to Fitz and Wenzel, the bioaccumulation factor (*BF*) of the heavy metals in various plant species was estimated by dividing the amount of metal in the root by the amount in the soil as follows [36]:

$$BF = \frac{Metal \ level \ in \ the \ root \ (mg \ kg^{-1})}{Metal \ level \ in \ the \ soil \ (mg \ kg^{-1})}$$
(2)

Using the translocation factor (TF) proposed by some scientists [37,38], the translocation factors of Zn, Mn, Cu, Ni, Cd, Pb, and Cr from shoot to root were evaluated in the current study.

$$F = \frac{Metal \ level \ in \ the \ shoot \ (mg \ kg^{-1})}{Metal \ level \ in \ the \ root \ (mg \ kg^{-1})}$$
(3)

2.4. Statistical Analysis

The Statistical Package for the Social Sciences (SPSS) for Windows Release 20.0 was used to conduct the statistical analysis between the amounts of major and trace heavy metals ((Mg, K, Fe), (Zn, Mn, Cu, Ni, Cd, Pb, Cr)) in the collected samples at various sites. For the examined parameters, means and standard deviations were determined. One-way analysis of variance (ANOVA 1) was used to treat differences between study sites statistically, and the Tukey test was used to compare means (SPSS) [39].

2.5. Instrumentations and Sample Analysis

2.5.1. FAAS System

FAAS measurements are typically performed using an air–acetylene flame. Flame composition and oxidant choice depend on the analyzed elements and the desired flame temperature. The parameter conditions of the instrument are shown in Table 1. The standard solutions used to calibrate the FAAS were obtained from Scharlau Chemie SA (Barcelona, Spain) [40], with a content of 1000 μ g/mL and purity 99.99% for each of the

Element	Wavelength (nm)	Lamp Current (mA)	Fuel Flow (L/min)	Band Pass (nm)	Flame Type	RSD %
Mg	285.2	4	1.1	0.5	Air/acetylene	0.2
K	766.5	8	1.2	0.5	Air/acetylene	2.41
Fe	248.3	15	0.9	0.2	Air/acetylene	1.2
Zn	213.9	10	1.1	0.5	Air/acetylene	0.2
Mn	279.5	12	1.1	0.2	Air/acetylene	0.4
Cu	324.8	5	1.0	0.5	Air/acetylene	3.1
Ni	232.0	15	0.9	0.2	Air/acetylene	2.3
Cd	228.8	8	1.2	0.5	Air/acetylene	3.58
Pb	217.0	10	1.1	0.5	Air/acetylene	2.94
Cr	357.9	12	4.2	0.5	Nitrous oxide/acetylene	1.94

 Table 1. Operating conditions for elements and the values of precision measured by FAAS.

different contents ranging from 0.25 to 8 μ g/mL for the different elements.

studied elements. These standard solutions were diluted with bi-distilled water to give

In the present work, precision is determined as the relative standard deviation (RSD %) with values for different working FAAS conditions for each studied element in Table 1.

2.5.2. LIBS System

The experimental setup of the used Ps-LIBS system has already been demonstrated in detail elsewhere by our group [41]. The brief description is given as the following: the laser system used in the experiment is an ultrafast high-power picosecond Nd: YAG Q-switched laser (Standa LTD, Vilnius, Lithuania) with a wavelength of 1064 nm, a pulse duration of 170 ps, and a repetition rate of 5 Hz. The laser is controlled by Sophi nXt software, and the laser Q-switch delay times range from 400 to 3200 ns. The laser pulses have an energy of $100 \pm 4\%$ mJ and are focused onto the samples' pellets using a plano-convex quartz lens with a 150 mm focal length. The spot size is approximately 0.8 ± 0.1 mm. The energy of the laser pulses is measured using a high-accuracy laser power meter (model 11 Maestro, Standa Ltd., Vilnius, Lithuania).

The plasma plume emission was detected utilizing a high-accuracy picometer spectrometer (ARYELLE 200) that operates in the UV to Vis wavelength range (192–750 nm) with a spectral resolution of 13.8–37.5 pm and a spectral resolving power of 75,000–150,000 [41]. The dispersed spectra from the ARYELLE 200 are then captured and recorded by an adjustable amplification gain (1000), gate (2 μ s), and delay times intensified charge-coupled detector ICCD (Andor, Belfast, UK).

3. Results

3.1. Major and Trace Heavy Metals Content in Lactuca sativa (Lettuce) and Trifollium alexandrinum (Clover) parts (Roots, Shoots) and Their Associated Soil

This study focuses on the most probable trace heavy elements in agricultural samples, Zn, Mn, Cu, Ni, Cd, Pb, and Cr, rather than the major elements such as Mg, K, and Fe, which are essential in the studied samples of trace heavy elements [42]. Tables 2–4 show the contents of heavy metals measured by the FAAS of soil, roots, and shoots of the lettuce and clover plants resulting from irrigation with different water resources in the lettuce and clover-associated soils, roots, and shoots, respectively. In the statistical analysis, the symbols a, b, c, d, and e indicate that the values with different superscript letters in a column are significantly different (p < 0.05). This result means there was a significant variation between the values obtained by the Tukey test.

Major and Trace Heavy Metals		Lettuce (mg/kg)					Clover (mg/kg)				
		S 1	S2	S 3	S 4	S 5	S 1	S2	S 3	S 4	S 5
	Mg	182.3 ± 5.91 a	$183.6\pm2.83~\mathrm{a}$	$204\pm30.9~\mathrm{a}$	$199.3\pm13.9~\mathrm{a}$	180.2 ± 6.77 a	197.1 ± 2.22 a	$200.4\pm4.8~\mathrm{a}$	$205\pm0.00~a$	$196.4\pm20.1~\mathrm{a}$	$192\pm10.9~\mathrm{a}$
Major elements	К	12,050 \pm 831 а	$6441\pm208~cd$	$9976\pm121\mathrm{b}$	$5713\pm311~\mathrm{d}$	$7396\pm82~{\rm c}$	12,819 \pm 477 а	$6025\pm623~{\rm c}$	$9349\pm623b$	$4778\pm207~\mathrm{c}$	$5402\pm415~{\rm c}$
	Fe	$829\pm13.4~\mathrm{d}$	$981\pm44.1~{\rm c}$	$2373\pm37.5~\mathrm{a}$	$2031\pm110.5~\text{b}$	$640\pm0.75~\mathrm{e}$	$37.80\pm1.65~\mathrm{c}$	$24.04\pm0.34~c$	$26.05\pm3.54~\mathrm{c}$	$3832\pm96~\mathrm{a}$	$879\pm30.5~\mathrm{b}$
Trace heavy metals	Zn	$33.58\pm1.21~\text{b}$	$40.42\pm3.49~\text{a}$	$35.18\pm1.31~\text{b}$	$20.46\pm0.79~\mathrm{c}$	$21.69\pm1.32~c$	$17.15\pm3.45~\mathrm{c}$	$22.15\pm0.16~\mathrm{c}$	$21.49\pm1.71~\mathrm{c}$	$244\pm15.3~\mathrm{a}$	$49.69\pm1.68~\text{b}$
	Mn	$47.09\pm2.03~\mathrm{a}$	$45.58\pm1.10~\mathrm{a}$	$22.41\pm1.81~\text{b}$	$23.05\pm0.02b$	$21.45\pm0.63b$	$9.07\pm0.10~\text{d}$	$23.21\pm0.04~c$	$22.66\pm0.13~\mathrm{c}$	$758\pm9.23~a$	$37.77\pm1.75~\mathrm{b}$
	Cu	$19.75\pm1.05~\mathrm{c}$	$24.58\pm0.30~\text{a}$	$22.78\pm2.15~ab$	$19.82\pm0.49bc$	$25.41\pm0.57~\mathrm{a}$	$18.49\pm0.92~\mathrm{c}$	$23.55\pm0.73b$	$27.90\pm1.92~\mathrm{a}$	$23.11\pm1.17b$	$22.55\pm2.16~b$
	Ni	$12.92\pm0.86~\mathrm{c}$	$226\pm12.92~\mathrm{a}$	$33.04\pm0.57~b$	$13.84\pm0.43~\mathrm{c}$	$24.21\pm1.69~bc$	$27.25\pm3.45bc$	$26.45\pm5.29~\mathrm{c}$	$36.35\pm2.77~ab$	$42.07\pm3.44~\mathrm{a}$	$25.83\pm2.09~c$
	Cd	$11.56\pm1.23~\mathrm{a}$	$8.98\pm0.86b$	$8.85\pm0.38~b$	11.44 ± 0.37 a	$10.09\pm0.25~ab$	$10.64\pm1.05~\mathrm{a}$	$7.87\pm0.00~\mathrm{c}$	9.96 ± 0.37 ab	$11.13\pm0.68~\mathrm{a}$	$8.38\pm0.23bc$
	Pb	$4.44\pm0.24~\mathrm{c}$	$6.77\pm0.12\mathrm{b}$	$6.31\pm0.16~\text{b}$	$6.64\pm0.25\mathrm{b}$	$8.00\pm0.86~\mathrm{a}$	$5.90\pm0.49~bc$	$7.63\pm0.00~\mathrm{a}$	$6.77\pm0.37~ab$	$5.66\pm0.00~\mathrm{c}$	$6.27\pm0.37bc$
	Cr	$5.12\pm0.73~\text{ab}$	$6.30\pm0.30~\text{a}$	$6.46\pm0.20~\mathrm{a}$	$4.92\pm0.65b$	$6.34\pm0.43~\mathrm{a}$	$4.29\pm0.32~\mathrm{c}$	$4.34\pm0.00~\mathrm{c}$	7.07 ± 0.27 a	$6.97\pm0.36~\mathrm{a}$	$5.74\pm0.24\mathrm{b}$

Table 2. Major and trace heavy metals content in the lettuce and clover-associated soils irrigated with different water resources using the FAAS technique.

The symbols a, b, c, and d indicate that the values with different superscript letters in a column are significantly different (p < 0.05).

Table 3. Major and trace nearly metals content in the roots of lettuce and clover irrigated with different resources of water using the FAAS technique
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Major and Trace Heavy Metals		Lettuce (mg/kg)					Clover (mg/kg)				
		S1	S2	S3	S4	S 5	S1	S2	S 3	S4	S 5
	Mg	$298\pm9.6b$	$291\pm1.1b$	$286\pm4.2b$	$336\pm19.2~\mathrm{a}$	$327\pm3.5~\mathrm{a}$	$351\pm18~\mathrm{a}$	$336\pm4.8~\mathrm{a}$	$337\pm5.1~\mathrm{a}$	$353\pm8.5~\mathrm{a}$	$324\pm12.2~\mathrm{a}$
Major elements	К	$2239\pm0.45~\mathrm{a}$	$2251\pm0.40~\mathrm{a}$	$2248\pm1.00~\mathrm{a}$	$2064\pm83.1~\mathrm{a}$	$2174\pm430~\mathrm{a}$	$2246\pm1.7~\mathrm{a}$	$2244\pm7.1~\mathrm{a}$	$2247\pm3.2~\mathrm{a}$	$2292\pm187~\mathrm{a}$	$1898\pm83.2~\mathrm{b}$
	Fe	$480\pm7.2~\mathrm{a}$	$421\pm41.9\text{b}$	$485\pm10.5~\mathrm{a}$	$419\pm19.7~\mathrm{b}$	$349\pm5.9~\mathrm{c}$	$1122\pm22.2~\text{b}$	$551\pm21.6~\mathrm{c}$	$517\pm20.9~\mathrm{c}$	$1872\pm4.9~\mathrm{a}$	$429\pm12.6~d$
- Trace heavy - metals _ -	Zn	$31.49\pm0.79~\mathrm{c}$	$42.92\pm0.67\mathrm{b}$	$46.47\pm0.39~\text{b}$	58.85 ± 3.95 a	$33.45\pm1.56~\mathrm{c}$	$43.27\pm0.39~\text{d}$	$58.72\pm0.20~\mathrm{c}$	$77.08\pm2.03~b$	139.8 ± 7.90 a	$43.39\pm2.65~d$
	Mn	$64.00\pm0.96~\mathrm{c}$	$59.55\pm2.94~c$	$64.68\pm1.40~\mathrm{c}$	119.9 ± 4.74 a	$91.57\pm0.72b$	$74.79\pm1.51~\mathrm{c}$	$73.48\pm2.88~c$	$103.4\pm4.18b$	118.1 ± 1.77 a	$58.64\pm3.65~d$
	Cu	$37.27\pm2.01~\mathrm{c}$	$25.28\pm0.30~d$	$40.82\pm0.20bc$	$54.53\pm1.31~\mathrm{a}$	$45.16\pm2.75\mathrm{b}$	$35.75\pm0.99\mathrm{b}$	$48.17\pm1.85~\mathrm{a}$	$37.44\pm1.26~\mathrm{b}$	50.76 ± 0.99 a	$50.80\pm1.15~\mathrm{a}$
	Ni	$238\pm10~b$	266 ± 22 ab	$150.5\pm24.5~\mathrm{c}$	$229\pm1.6b$	$307\pm31.7~\mathrm{a}$	$269\pm49b$	$273\pm29~b$	$494\pm14~\mathrm{a}$	$226\pm14.3b$	$240\pm16.6~b$
	Cd	$0.02\pm0.00~b$	$0.02\pm0.00b$	$0.02\pm0.00~b$	$0.23\pm0.02~\text{a}$	$0.23\pm0.03~\mathrm{a}$	$0.05\pm0.01~\text{b}$	$0.05\pm0.01~\text{b}$	$0.05\pm0.01~\text{b}$	$0.17\pm0.02~\mathrm{a}$	$0.20\pm0.00~\mathrm{a}$
	Pb	$1.59\pm0.03~bc$	$1.56\pm0.12~c$	$2.12\pm0.08~\mathrm{a}$	$2.13\pm0.14~\text{a}$	$1.95\pm0.25~ab$	$3.07\pm0.17~\mathrm{a}$	$2.00\pm0.13~bc$	$2.16\pm0.29b$	$2.03\pm0.04~bc$	$1.60\pm0.17~\mathrm{c}$
	Cr	$0.17\pm0.01~\mathrm{b}$	$0.19\pm0.01~\mathrm{a}$	$0.18\pm0.00~\mathrm{ab}$	$0.13\pm0.00~\mathrm{c}$	$0.14\pm0.01~{\rm c}$	$0.11\pm0.00~{\rm c}$	0.17 ± 0.01 a	$0.17\pm0.00~\mathrm{a}$	$0.14\pm0.00~\text{b}$	$0.13\pm0.01~\text{b}$

The symbols a, b, c, and d indicate that the values with different superscript letters in a column are significantly different (p < 0.05).

				Lettuce (mg/kg)					Clover (mg/kg)		
Major and Trace Heavy Metals			\$2	S3	S 4	\$5	S 1	S 2	S3	S 4	\$5
		200 15.0 -	210 2 -	212 1 5 -	282 4 6 2 -	242 \ 0.001	220 + E 4 h	224 + 271	212 0.001	410 \ 0.00 -	200 + 4.4 h
	Mg	300 ± 15.9 c	310 ± 3 c	313 ± 1.5 c	$383 \pm 6.2 \text{ a}$	343 ± 0.00 b	339 ± 5.4 b	324 ± 27 b	312 ± 0.00 b	410 ± 0.00 a	$309 \pm 4.4 \text{ b}$
Major elements	K	$2247\pm5.9~\mathrm{a}$	$2244\pm6.7~\mathrm{a}$	$2246\pm4.1~\text{a}$	$1731\pm166.3~\text{b}$	$2209\pm145.5~\text{a}$	$2247\pm5.5~\text{a}$	$2241\pm1.9~\mathrm{a}$	$2242\pm0.15~a$	$2002\pm62.3b$	$2345\pm84.4~\text{a}$
	Fe	$548\pm13.7~\mathrm{c}$	$545\pm17.1~{\rm c}$	$1430\pm16.1~\mathrm{a}$	$300\pm7.5~d$	$816\pm14.2b$	$529\pm26.6~\mathrm{c}$	$559\pm0.15~{\rm c}$	$2106\pm3.8~b$	$453\pm2.5~c$	$2259\pm88.6~\mathrm{a}$
- Trace heavy - metals _ -	Zn	$57.88\pm1.64~\mathrm{bc}$	$60.54\pm3.78b$	$74.06\pm0.46~\mathrm{a}$	$53.34\pm1.47~\mathrm{c}$	$35.07\pm0.68~d$	$31.49\pm1.67~d$	$49.75\pm11.6~\text{bc}$	$56.29\pm0.41~b$	$112.8\pm6.5~\mathrm{a}$	$36.12\pm0.13~cd$
	Mn	$135.3\pm0.29\mathrm{b}$	$114.4\pm1.87~\mathrm{c}$	$212\pm2.6~\mathrm{a}$	$93.18\pm2.85d$	$99.03 \pm 6.93 \text{ d}$	$72.22\pm1.87\mathrm{b}$	$74.54\pm0.02b$	$148.2\pm8.1~\mathrm{a}$	$36.01\pm0.90~\mathrm{c}$	$81.35\pm5.34~\text{b}$
	Cu	$37.57\pm1.91~\mathrm{b}$	$36.64\pm2.30~\text{b}$	$40.91\pm1.53~\text{b}$	$47.36\pm1.20~\mathrm{a}$	$36.84\pm1.71~\text{b}$	$41.39\pm0.85~\text{b}$	$36.45\pm1.97~\mathrm{c}$	$38.33\pm2.11\text{bc}$	$53.79\pm1.84~\mathrm{a}$	57.91 ± 0.94 a
	Ni	$342\pm28~ab$	$342\pm10~ab$	$299\pm17~\mathrm{b}$	$370\pm16~\mathrm{a}$	$348\pm9.4~\mathrm{a}$	$246\pm18~{\rm c}$	$500\pm52~\mathrm{a}$	$534\pm30~\mathrm{a}$	$329\pm16.4bc$	$335\pm35.7~\text{b}$
	Cd	$0.07\pm0.00~\text{b}$	$0.06\pm0.00~\text{b}$	$0.06\pm0.00~b$	$0.23\pm0.01~\text{a}$	$0.22\pm0.03~\mathrm{a}$	$0.06\pm0.00~b$	$0.05\pm0.01~b$	$0.02\pm0.00\ c$	$0.20\pm0.01~\text{a}$	$0.21\pm0.01~\mathrm{a}$
	Pb	$0.92\pm0.00~\text{b}$	$1.22\pm0.04b$	$1.16\pm0.02~\text{b}$	$1.92\pm0.34~\mathrm{a}$	1.76 ± 0.21 a	$1.66\pm0.10~\text{b}$	2.11 ± 0.19 a	1.97 ± 0.09 ab	$2.03\pm0.11~\text{a}$	2.21 ± 0.15 a
	Cr	$0.18\pm0.01~ab$	$0.18\pm0.01~\mathrm{a}$	$0.17\pm0.01~\text{ab}$	$0.15\pm0.01~bc$	$0.14\pm0.01~{\rm c}$	$0.16\pm0.01~\text{ab}$	$0.15\pm0.00~\text{abc}$	$0.16\pm0.01~\mathrm{a}$	$0.14\pm0.01~bc$	$0.14\pm0.01~{\rm c}$

Table 4. Major and trace heavy metals content in the shoots of lettuce and clover irrigated with different resources of water using the FAAS technique.

The symbols a, b, c, and d indicate that the values with different superscript letters in a column are significantly different (*p* < 0.05).

3.2. Pollution Index (PI) of the Soils

Table 5 lists the exact values of permissible contents in soils and plants for those elements according to Cal/EPA [43] for soil and FAO/WHO [44] for vegetables. At the same time, Figure 2a represents a histogram of the PI values of Zn, Mn, Cu, Ni, Cd, Pb, and Cr for *Lactuca sativa* in the five sites. The mean value of Cu, Ni, and Cd for *L. sativa* soils is higher than one by one order or two orders of magnitude in all sites, while that for Mn, Pb, and Cr is very far away from one by one order of magnitude in all sites. In Al Mansouria and Nikla, the PI of Zn is less than one, whereas it is significantly higher than one in Kafr Al-Arab, Sindenhour, and Mit Asem. Figure 2b also shows a histogram of the PI values of Pb and Cr pollution indices for *T. alexandrinum* soils are less than one by one order of magnitude. In Kafr Al-Arab, Sindenhour, and Mit Asem for Cu, Ni, and Cd are higher than one by one order of magnitude. In Kafr Al-Arab, Sindenhour, and Nikla. In Al Mansouria and Nikla, the PI of Zn is less than one by two orders of magnitude in Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla. In Al Mansouria and Nikla, the PI of Zn is less than one by two orders of magnitude in Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla. In Al Mansouria and Nikla, the PI of Zn is less than one in Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla. In Al Mansouria and Nikla, the PI of Zn is less than one in Kafr Al-Arab, Sindenhour, and Mit Asem.

Table 5. Permissible content in agricultural systems (soil and plant), according to the World Health Organization (WHO) and the Food and Agriculture Organization (FAO).

Heavy Metals	Permissible Levels in Soil (mg/kg)	Permissible Levels in a Plant (mg/kg)
Zn	23 [43]	60 [44]
Mn	437 [43]	100 [44]
Cu	3 [43]	2 [44]
Ni	1.6 [43]	0.5 [44]
Cd	1.7 [43]	0.5 [44]
Pb	80 [43]	2 [44]
Cr	100 [43]	1 [44]



Heavy Metals

(b)

Figure 2. The pollution index (PI) of the studied heavy metals in the soils associated with (**a**) lettuce and (**b**) clover in all studied sites.

3.3. Bioaccumulation and Translocation Factors of Metals by Plants

Figure 3a shows that lettuce plants have a high potential to accumulate Zn, Mn, Ni, and Cu in all areas where their BF is more significant than one. However, at all sites, the Cd, Pb, and Cr BF are less than one. Figure 3b shows that clover plants irrigated with various water sources have a high potential to accumulate Cu and Ni in all sites, Zn in Kafr Al-Arab, Sindenhour, and Mit Asem, and Mn in Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla. The figure also shows that these sites have different potentials for Zn accumulation. However, the BF of Cd, Pb, and Cr are all lower than one, as are the BFs of Zn in Al Mansouria and Nikla, and Mn in Al Mansouria only.



Figure 3. Bioaccumulation factor (BF) of heavy metals in (**a**) lettuce and (**b**) clover plants irrigated with different water resources in different sites using the FAAS technique.

In Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla, the translocation factor (TF) of Zn and Mn from roots to shoots was more significant than one, according to Figure 4a. Additionally, there was a transfer of Cu and Cd in Kafr Al-Arab, Sindenhour, and Mit Asem; Ni in all locations; and Cr in Kafr Al-Arab, Al Mansouria, and Nikla. Figure 4b shows that Sindenhour, Mit Asem, and Nikla have a translocation factor (TF) of Mn from roots to shoots that are more than one. Also, the TF is more than one for Cu in Kafr Al-Arab, Mit Asem, Al Mansouria, and Nikla; Ni in Sindenhour, Mit Asem, Al Mansouria, and Nikla; Cd in Kafr Al-Arab, Sindenhour, Al Mansouria, and Nikla; Pb in Sindehour, Al Mansouria, and Nikla; Cr in Kafr Al-Arab, Al Mansouria, and Nikla.

3.4. Ps-LIBS Spectrum Studies

In the current study, by intruding the ultrafast laser into LIBS, the present Ps-LIBS, as a qualitative and semi-quantitative compositional analysis developed method for the ambient samples, was carried out using the optical emission spectrum of the generated plasma emission [45]. The high-resolution Ps-LIBS emission spectra of the plant parts (roots, branches, and accompanying soil) are shown in Figure 5. This study was focused only on the emission lines for the studied heavy elements (Zn, Mn, Cu, Ni, Cd, Pb, and Cr), so the spectral region from 210–390 nm is selected because it gathers the essential characteristic

emission lines with high resolution for these elements as shown in Figure 5. These spectral lines have been recognized with the help of the NIST database [46], as shown in Table 6.



Figure 4. Translocation factor (TF) of heavy metals in (**a**) lettuce and (**b**) clover plants irrigated with different water resources in different sites using FAAS technique.



Figure 5. Ps-LIBS emission spectra using NIR laser 1064 nm at pulse energies of 100 mJ of the plant parts (roots and shoots) and their associated soil (**a**) lettuce and (**b**) clover.

Hoory Motols	Selected Wavelengths					
Heavy Metals	λ (nm)	Transition Configuration				
Zn	213.85	$3d^{10}4s^2 ightarrow 3d^{10}4s4p(^1P^\circ)$				
Mn	279.48 280.11	$\begin{array}{l} 3d^54s^2 \to 3d^5({}^6\mathrm{S})4s4p({}^1\mathrm{P^\circ}) \\ 3d^54s^2 \to 3d^5({}^6\mathrm{S})4s4p({}^1\mathrm{P^\circ}) \end{array}$				
Cu	324.75 327.39	$\begin{array}{c} 3d^{10}4s \rightarrow 3d^{10}4p \\ 3d^{10}4s \rightarrow 3d^{10}4p \end{array}$				
Ni	234.55	$3d^8(^3F)4s^2 ightarrow 3d^8(^1D)4s4p(^3P^\circ)$				
Cd	228.8	$4d^{10}5s^2 \rightarrow 4d^{10}5s5p$				
Pb	283.31	$6s^26p^2 ightarrow 6s^26p7s$				
Cr	236.47	$3d^5(^6S)4s \rightarrow 3d^5(^6S)5p$				

Table 6. The heavy metals' spectral selected wavelengths [46].

3.5. Content Calibration Studies

The calibration curves between the contents measured by FAAS and the Ps-LIBS signal intensity for the chosen spectral lines for the plant-associated soil and the plant sample parts (root and shoots) are shown in Figures 6–8, respectively. Tables 7–9 show the examined metals' fitting equation and standard error for the plant-associated soil and the plant sample parts (root and shoots), respectively.

Table 7. The standard error of the calibration curves experimental fitting equation between the Ps-LIBS relative intensity and the studied trace heavy metals content in the lettuce and clover-associated soils.

Metals	Standa	rd error	Fitting Equation			
	Lettuce	Clover	Lettuce	Clover		
Zn	$\pm 0.01\%$	$\pm 0.05\%$	$I_{Ze} = 5.7 \times 10^{-3} C_{Zn} - 0.08$	$I_{Ze} = 1 \times 10^{-3} C_{Zn} + 0.21$		
Mn	$\pm 0.02\%$	$\pm 0.80\%$	$I_{Mn} = 0.09C_{Mn} - 0.29$	$I_{Mn} = 0.016C_{Mn} + 8.73$		
Cu	$\pm 0.03\%$	$\pm 0.10\%$	$I_{Cu} = 0.04C_{Cu} - 0.54$	$I_{Cu} = 0.06C_{Cu} - 0.97$		
Ni	$\pm 0.03\%$	$\pm 0.02\%$	$I_{Ni} = 7 \times 10^{-3} C_{Ni} - 0.05$	$I_{Ni} = 0.017 C_{Ni} - 0.34$		
Cd	$\pm 0.001\%$	$\pm 0.006\%$	$I_{Cd} = 1 \times 10^{-3} C_{Cd} - 0.006$	$I_{Cd} = 0.017C_{Cd} - 0.12$		
Pb	$\pm 0.05\%$	$\pm 0.02\%$	$I_{Pb} = 0.16C_{Pb} - 0.64$	$I_{Pb} = 0.12C_{Pb} - 0.52$		
Cr	$\pm 0.03\%$	$\pm 0.05\%$	$I_{Cr} = 0.14C_{Cr} - 0.57$	$I_{Cr} = 0.11C_{Cr} + 0.12$		

Table 8. The standard error of the calibration curves experimental fitting equation between the Ps-LIBS relative intensity and the content of the studied trace heavy metals in the roots of lettuce and clover.

Metals	Standa	rd error	Fitting Equation			
	Lettuce	Clover	Lettuce	Clover		
Zn	$\pm 0.02\%$	$\pm 0.02\%$	$I_{Ze} = 0.011 C_{Zn} - 0.34$	$I_{Ze} = 1 \times 10^{-3} C_{Zn} - 0.06$		
Mn	$\pm 0.20\%$	±0.15%	$I_{Mn} = 0.049 C_{Mn} - 1.38$	$I_{Mn} = 0.038C_{Mn} - 1.87$		
Cu	$\pm 0.01\%$	$\pm 0.01\%$	$I_{Cu} = 2 \times 10^{-3} C_{Cu} - 0.034$	$I_{Cu} = 4 \times 10^{-3} C_{Cu} - 0.14$		
Ni	$\pm 0.005\%$	$\pm 0.008\%$	$I_{Ni} = 4 \times 10^{-4} C_{Ni} - 0.045$	$I_{Ni} = 2 \times 10^{-4} C_{Ni} - 0.04$		
Cd	$\pm 0.001\%$	$\pm 0.005\%$	$I_{Cd} = 0.049C_{Cd} + 0.003$	$I_{Cd} = 0.19C_{Cd} - 0.006$		
Pb	$\pm 0.008\%$	$\pm 0.01\%$	$I_{Pb} = 0.15C_{Pb} - 0.23$	$I_{Pb} = 0.028C_{Pb} - 0.03$		
Cr	±0.02%	±0.01%	$I_{Cr} = 3.79C_{Cr} - 0.48$	$I_{Cr} = 1.82C_{Cr} - 0.2$		



Figure 6. Calibration curves between the Ps-LIBS relative intensity and the studied trace heavy metals content in the associated soil for (**a**) lettuce and (**b**) clover in all studied sites.



Figure 7. Calibration curves between the Ps-LIBS relative intensity and the content of the studied trace heavy metals in the roots of (**a**) lettuce and (**b**) clover in all studied sites.



Figure 8. Calibration curves between the Ps-LIBS relative intensity and the content of the studied trace heavy metals in the shoots of (**a**) lettuce and (**b**) clover in all studied sites.

Table 9. The standard error of the calibration curves experimental fitting equation between the Ps-LIBS relative intensity and the content of the studied trace heavy metals in the shoots of lettuce and clover.

Metals	Standa	rd Error	Fitting Equation			
	Lettuce	Clover	Lettuce	Clover		
Zn	$\pm 0.005\%$	$\pm 0.01\%$	$I_{Ze} = 1 \times 10^{-3} C_{Zn} - 0.03$	$I_{Ze} = 8 \times 10^{-4} C_{Zn} - 0.02$		
Mn	$\pm 0.08\%$	±0.15%	$I_{Mn} = 0.01 C_{Mn} - 0.34$	$I_{Mn} = 0.025C_{Mn} - 0.46$		
Cu	$\pm 0.002\%$	$\pm 0.005\%$	$I_{Cu} = 2 \times 10^{-3} C_{Cu} - 0.06$	$I_{Cu} = 3 \times 10^{-3} C_{Cu} - 0.13$		
Ni	$\pm 0.001\%$	$\pm 0.005\%$	$I_{Ni} = 9 \times 10^{-5} C_{Ni} - 0.02$	$I_{Ni} = 2 \times 10^{-4} C_{Ni} - 0.04$		
Cd	$\pm 0.001\%$	$\pm 0.002\%$	$I_{Cd} = 0.063C_{Cd} - 0.003$	$I_{Cd} = 0.15C_{Cd} - 0.002$		
Pb	±0.007%	$\pm 0.005\%$	$I_{Pb} = 0.047 C_{Pb} - 0.018$	$I_{Pb} = 0.09C_{Pb} - 0.15$		
Cr	$\pm 0.005\%$	$\pm 0.005\%$	$I_{Cr} = 1.93C_{Cr} - 0.27$	$I_{Cr} = 1.99C_{Cr} - 0.27$		

4. Discussion

4.1. Heavy Metals Content in Lactuca sativa (Lettuce) and Trifollium alexandrinum (Clover) Parts (Roots and Shoots) and Their Associated Soil

The observed results from Table 2 indicate that for the soils associated with both types of plants, major elements (Mg, K, and Fe) were in the range of the permissible levels according to FAO/WHO [47]. For Zn, the measured values showed a high content (240 mg/kg) in site four for clover only, but on average, the mean values for Zn in both lettuce and clover soils varied between 15 mg/kg and about 40 mg/kg in the other sites. For Mn, the high content values were found in site four for clover, while the average mean values for Mn varied between 9 mg/kg and about 47 mg/kg for both plants' soils in the other sites. We did not find a recognizable change in Cu abundance for both plants' soils; the mean values vary between 18 mg/kg and 25 mg/kg in all sites for both plants' soils. For Ni, unexpectedly high contents have been found in site two for lettuce, while the mean values varied between 12 mg/kg and 42 mg/kg for both soils in all other sites. There are no elevated values for Cd; the mean values varied between 7 mg/kg and 12 mg/kg for both plant soils in all sites. Also, elevated values were not found for both plants' soils for Pb, while the average mean values varied between 4 mg/kg and 8 mg/kg in all sites. Similar behavior was found for Cr for both plants' soils in the five sites, with mean values varying between 4 mg/kg and 7 mg/kg. This study shows that the soil in site four showed high contamination with most of these heavy elements. Site four is Al Mansouria village irrigated with sewage water, which may explain the high contents, especially for zinc and manganese.

The results in Table 3 indicate that major elements (Mg, K, and Fe) fall within permissible levels by FAO/WHO [44]. Clover showed high Zn (135 mg/kg), while average Zn in lettuce and clover roots ranged from 31 mg/kg to 77 mg/kg. Both clover (108 mg/kg) and lettuce (119 mg/kg) had the highest Mn contents at site four, while typical mean Mn values ranged from 58 mg/kg to around 103 mg/kg for roots in other sites.

Cu contents in the roots of both plants ranged from 25 mg/kg to 54 mg/kg across all sites, with no distinct changes. Ni was elevated in site three for clover and site five for lettuce; mean values in other locations ranged from 150 mg/kg to 273 mg/kg for both plants' roots. Cd showed no high values, with mean values from 0.02 mg/kg to 0.23 mg/kg across sites. Pb measurements were not high; its mean values ranged from 1.5 mg/kg to 3 mg/kg. For Cr, levels in the roots of both plants ranged from 0.11 mg/kg to 0.19 mg/kg across sites.

Root samples revealed that site four (Al Mansouria village) had notable contamination, particularly zinc and manganese. Site five (Nikla village) had elevated nickel in clover roots, and site three (Mit Asem village) had elevated nickel in lettuce roots. Contamination sources in these sites may be linked to irrigation water contamination, high contents of fertilizers, and industry emissions [48].

Table 4 data reveal major elements (Mg, K, Fe) fall within FAO/WHO permissible levels [44]. Clover showed high Zn (112 mg/kg) at site four, while Zn in lettuce and clover shoots ranged from 31 mg/kg to 74 mg/kg at other sites. The highest Mn contents were at site three, clover (148 mg/kg), and lettuce (212 mg/kg); average Mn ranged from 36 mg/kg to 135 mg/kg in other sites. Cu contributions ranged from 36 mg/kg to 57 mg/kg in all sites for both plants' shoots. Ni contents peaked at sites two and three (500 mg/kg and 534 mg/kg) for clover; other sites had 246 mg/kg to 370 mg/kg for shoots. Cd had no high values; mean Cd ranged from 0.05 mg/kg to 0.23 mg/kg. Pb contents ranged from 0.92 mg/kg to 2.21 mg/kg. Cr showed similar behavior across sites (0.14 mg/kg to 0.18 mg/kg).

This study's shoot research highlights significant heavy metal contamination at site three, Mit Asem village, irrigated by the Nile from the Felfla canal. Plant metal contents vary due to soil, water, nutrition, permissibility, selectivity, and absorption capabilities [49]. Major and trace heavy elements content across the five sites (S1: Kafr Al-Arab, S2: Sindenhour, S3: Mit Asem, S4: Al Mansouria, S5: Nikla) are displayed in Tables 2–4, utilizing statistical analysis (ANOVA 1) [50]. Notably, the contents of heavy metals vary significantly in the lettuce and clover-associated soils', roots, and shoots of lettuce and clover among different locations.

4.2. Pollution Index (PI) of the Soils

As shown in Table 5 and Figure 2, the proposed reasons for such high pollution indices may be the continuous irrigation of the investigated sites with contaminated water. The contaminated water may be polluted wastewater, sewage water, and industrial wastewater, as found during the current investigations in these sites, which may result in a high accumulation of heavy elements. The observed results agree with previous studies where the total heavy metal contents in soils were increased by contaminated water irrigation [51].

The current study revealed that the PI of Zn at the studied sites for both plants' soils averaged 0.75 in Kafr Al-Arab and 10.61 in Al Mansouria. By calculating the PI on the previous results, we can conclude that the average value of PI in the agricultural soils along the highway between Damietta and Cairo in the Nile Delta, Egypt, was about 0.4 to 3.41 [52]. The more recent results demonstrated that the expected PI for Zn is consistent with the findings of the current investigation. In the current study, the PI of Mn in both plants' soils in all sites ranged from 0.02 in Kafr Al-Arab to 1.74 in Al Mansouria, which was nearly in agreement with the PI obtained by El-Bady and Metwally [52]. For Cu, the average values of PI for both plants' soils in all sites were about 6.16 in Kafr Al-Arab and 9.3 in Mit Asem, which was lower than those obtained by Mohamed S.M. EL-Bady [53]. Nickel's PI in the investigated soils was found between 8.08 in Kafr Al-Arab and 141.84 in Sindenhour, which was in the range of the PI reported by Osman et al. [54], which was nearly 45.94. The PI of Cd for both plants' soils in all sites was about 4.63 in Sindenhour and 6.8 in Kafr Al-Arab, while that of Pb at all sites was about 0.06 in Kafr Al-Arab and 0.1 in Sindenhour and Nikla. These results were higher than those found by El-Bady [53], which were predicted in the range of 0.06 to 0.59 for Cd, but lower than those predicted for Pb in the range of 1.58 to 3.49. The mean PI values for both plants' soils in all sites of Cr were in the range of 0.04 in Kafr Al-Arab and Sindenhour to 0.07 in Mit Asem and Al Mansouria, which were lower than those found by Osman et al. [54], which were assumed to be about 1.07.

Zinc contents are rising unnaturally due to anthropogenic additions. Most Zn is added during industrial activities, such as mining, coal and waste combustion, and steel processing [55–57]. Elevated Mn content in the soil may primarily result from burning wastes, oil, and the metallurgical industry [58]. High contamination of the soil environment with Cu is strongly correlated with car traffic intensity [59]. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulfate) and copper oxychloride [60]. The primary sources of Ni contamination in the soil are metal plating industries, the combustion of fossil fuels, and nickel mining and electroplating [61]. Applying agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes, or the deposition of atmospheric contaminants increases the total content of Cd in soils [62]. The lower values of Cr suggest less traffic in this sampling area compared to larger cities with heavy traffic. The soil type affected Cr accumulation in the soil [63].

The most recent findings showed that most of the sites' studied soil samples were contaminated with Zn, Cu, Ni, and Cd at higher levels than those permitted by Cal/EPA [43].

4.3. Bioaccumulation and Translocation Factors of Metals by Plants

Figures 3 and 4 show that vegetables absorb heavy metals from contaminated soil, air, and water, especially leafy vegetables, which accumulate higher amounts of heavy metals in their leaves [64–66].

The bioaccumulation factor (BF) of metals in the plant roots and their translocation factor (TF) to the shoot were used to demonstrate the potential of the plant as a metal bio-accumulator in the phytoremediation process [67]. The investigated metals (Zn, Mn, Cu, and Ni) for *L. sativa* were accumulated in roots with BF > 1 in all sites, whereas for

T. alexandrinum, (Zn) was accumulated in Kafr Al-Arab, Sindenour, and Mit Asem, and (Mn) was accumulated in Kafr Al-Arab, Sindenour, Mit Asem, and Nikla. The hyperaccumulation of certain metals varies with the examined plant species, as is evident from these results, which are consistent with those of other researchers [68,69]. The BF of the investigated metals for *L. sativa* fell in the order Ni > Mn > Cu > Zn > Pb > Cr > Cd, and that of *T. alexandrinum* was Ni > Mn > Cu > Zn > Pb > Cr > Cd. In the present study, most of the investigated heavy metals in the two plants had TF > 1 in all sites, as previously found by Zoufan et al. [70]. Like rootstalk and fruit vegetables, leafy vegetables had relatively higher TF of heavy metals, suggesting that leafy vegetables have higher transportation rates than other vegetable types [71]. TF and BC values > 1 can be considered hyper-accumulators for the respective metals [68,69,72,73]. Lactuca sativa had BF and TF > 1 for Zn, Mn, Cu, and Ni, while those of *T. alexandrinum* were > 1 for Cu and Ni. For the soils associated with *T.* alexandrinum, the locations Kafr Al-Arab, Sindenhour, Mit Asem, and Nikla are suitable for Zn and Mn accumulation and unsuitable in Al Mansouria. The latter result is consistent with Sabir et al. [74]. However, the two plants can be considered an excluder for Cd, Pb, and Cr, where they have BF and TF < 1.

4.4. Ps-LIBS Spectrum Studies

The observations of Figure 5 and Table 6 indicate that the appearance of the Ps-LIBS element spectral lines proved the presence of the metal in the sample matrix [41,75].

The observed results show characteristic emission lines for the studied elements as follows: two lines (324.75 nm and 327.39 nm) for Cu and only one line for Pb (283.31 nm) was detected. Also, two lines (279.48 nm and 280.11 nm) for Mn, as well as the lines (236.47 nm, 234.55 nm, 228.8 nm, and 213.85 nm) for Cr, Ni, Cd, and Zn, respectively, were analyzed. The signal intensities of the elemental characteristic spectral lines depend on the content of the element in the sample matrix [76].

4.5. Content Calibration Studies

As mentioned in Section 3.4, calibration curves within LIBS are pivotal for generating reliable quantitative analyses [77]. Fundamental tools, such as spectral line or peak intensity, are plotted against known element contents [78]. Through calibration, the accuracy and precision of measurements are markedly enhanced, establishing a correlation between spectral signals and actual element contents [79–81]. Knowledge of the dynamic range of the LIBS system aids in deciding potential sample dilution or content adjustments. Calibration elucidates linear or polynomial-logarithmic content-intensity relationships. Regular calibrations compensate for system drift caused by laser degradation, detector aging, or environmental shifts. Generating calibration curves for diverse matrices enhances cross-matrix analysis, highlighting plasma condition disparities [81]. In the current work, the analysis of Figures 6-8 and Tables 7-9 indicate that the association between a rise in the metal content as determined by FAAS and a linear increase in the Ps-LIBS signal for the wavelength of the various metals in both plants' soils, shoots, and roots shows a high correlation coefficient of 0.975 ± 0.05 . A rise in the metal content in the target ablated volume causes an increase in the absorbed laser pulse energy due to an increase in the ablated mass. This performance, in turn, causes an increase in the Ps-LIBS signal intensity due to an increase in the target plasma electron temperature and density [82–85].

4.6. Factors Influencing Heavy Metal Content

The presence of high levels of heavy metals such as copper, nickel, and cadmium in soil and their bioaccumulation in *Lactuca sativa* and *Trifolium alexandrinum* is mentioned in the above sections to be related to different water irrigation sources which may be contaminated. However, different factors, including contaminated water irrigation concerns, may also be attributed to various factors. These potential factors can be discussed as follows:

4.6.1. Contaminated Water Irrigation

Utilizing contaminated water for irrigation is another prominent factor influencing heavy metal content in soil and plants. Water contaminated with heavy metals, either from industrial effluents, sewage, or natural deposits, can lead to the accumulation of these toxic elements in the soil. Consequently, plants irrigated with such water absorb and accumulate heavy metals, impacting their growth quality, and these heavy metals potentially enter the food chain [86].

4.6.2. Environmental Conditions

Heavy metals in the environment often stem from industrial processes and wastewater disposal, with both natural and anthropogenic activities contributing to the contamination of ecosystems [87].

4.6.3. Soil Characteristics

The chemical and physical properties of soil, such as pH, texture, and composition, are pivotal in heavy metals' retention, mobility, and bioavailability [88].

4.6.4. Plant Species Attributes

Different plant species exhibit varied capacities for the bioaccumulation and translocation of heavy metals, influencing the potential health risks associated with these metals [89].

4.6.5. Climatic Influences

Weather patterns, including rainfall and temperature, can impact heavy metals' distribution and concentration levels in soil and plants [90].

4.6.6. Human Activities

Activities such as agricultural practices involving chemical use and urban expansion significantly contribute to increasing soil heavy metal levels [91].

The above discourse represents a preliminary overview of the potential factors influencing heavy metal content in soil and plants. A more detailed, exhaustive, and nuanced discussion and analysis, incorporating a more comprehensive range of variables and contextual factors, may be undertaken in future research endeavors to deepen our understanding and develop targeted mitigation strategies.

Given the discerned elevated contamination levels evident in the sites under the current study, it is prudent to institute an adequate contamination remediation facility within areas exhibiting substantial contamination to ameliorate prevailing public health apprehensions.

5. Conclusions

This study employed FAAS and Ps-LIBS as advanced analytical techniques to assess heavy metal contents in lettuce and clover and their associated soil samples from some sites in Egypt. Both plant species exhibited high bioaccumulation factors for multiple metals, notably copper, nickel, and cadmium. These contents exceeded permissible safety limits, posing significant health risks. The results revealed elevated copper, nickel, and cadmium pollution indices across all sites. These findings underscore the urgent need for wastewater treatment solutions, particularly in identified high-risk areas. The study emphasizes the efficacy of the developed spectroscopic method in identifying contamination in the studied sites. Based on the results, it is advisable to establish an efficient contamination treatment facility in high content regions to address public health concerns.

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