Estimation of some heavy metals in different types of leafy vegetables grown and displayed in the markets of Al-Zawiya city

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***Abstract*—This study was conducted to determine the content of some leafy vegetables of some heavy elements presented and cultivated in the city of Zawiya. This study was conducted during the period from 6 to 8 months for the year 2019. The samples were collected from areas that are more prone to pollution, as they are located in places exposed to car exhausts or crowded with people. The samples were selected from the vegetables most consumed by the Libyan citizen. The samples were collected before they were irrigated. They were examined without washing to know the extent of their contamination naturally and without intervention to remove one of the causes and reduce pollution. 108 samples of leafy vegetables were identified, which included four crops (parsley, dill, coriander, chard).Which was collected on three different periods June, July and August (the month of Ramadan is the month between the holidays, the month of Eid al-Adha). It was collected from three different places (Al-Haql, Al-Ajailat Market, Al-Zawiya Market).Its content was studied for the most polluting heavy elements, namely lead, cadmium, copper, nickel and chromium. Use of a microwave device to digest samples and an atomic absorption device (AAS). To analyze and determine the level of heavy metals, the results of the statistical analysis showed that there were significant differences among most of the analyzed samples in terms of their content of the five elements under study. The results showed that there was a rise in the values of the heavy elements, and lead, cadmium and chromium were the highest in the arithmetic mean values, with high significant differences (P = 0>005). Where the chromium element recorded the highest average (15.91 mg / g) for dill, which exceeded the internationally permissible values, while the nickel and copper elements were within the internationally permitted range .The element lead, cadmium and chromium in the three periods in which samples were collected were higher than the permissible limit, as the element chromium recorded the highest value (10.44 mg / g), then the elements lead and cadmium, respectively, and the elements copper and nickel, they were within the permissible limits globally. And through the results of the different regions, the significant increase of all the elements studied was in Al-Ajailat market, and the highest element was chromium (9.75 mg / g) with a significant level (P = 0.000).Followed by lead and cadmium, where all values exceeded the internationally permitted percentages, except for copper and nickel, which were within the internationally permitted limits at a significant level (P = 0.013).**

Introduction:

The issue of contamination of agricultural and food products by various pollutants, such as pesticides, fungal toxins, bacterial contaminants, heavy metals, and others, is of great significance at both local and global levels. Consequently, food safety and human health have received significant attention from global opinions. In recent decades, the risk of contamination with pesticides, heavy metals, and toxins has been associated with the consumption of food products (Chitmanat and Traichaiyaporn, 2010; Vutukuru, 2005). Heavy metals are considered among the most critical primary contaminants of food and one of the most significant environmental issues (Dural, 2007; Zaidi et al., 2005). This problem has become increasingly important globally, especially in developing countries (Sathawara et al., 2004).

Most countries worldwide today (Nnorom et al., 2007) can be regarded as being at risk due to the negative impacts of heavy metal contamination on various aspects of human life, with these impacts becoming evident in biological systems (water, soil, and air) (Naithan et al., 2010; Lokeshwari and Chandrappa, 2006). Consequently, it affects the entire food production process (Itanna, 2002). Industrial processes and their emissions, along with the treatment of mineral compounds, are the primary sources of heavy metal contamination of the ecosystem (Calta and Canpolat, 2006). Moreover, environmental contamination with heavy metals can generally be traced back to oil pollution in water (Nduka and Orisakwe, 2007; Nduka et al., 2006).

The content of vegetables and fruits in manufactured products varies in heavy metal concentration, not only due to accumulation during growth but also due to contamination during harvesting processes (Chojracha et al., 2005). Furthermore, the technical processes used to bring food (vegetables, fruits, and meats) and distribute products (transportation, marketing) to selling points or factories significantly increase the metal content in food due to the unsanitary tools and equipment used for gathering food (Lokeshwari and Chandrappa, 2006), in addition to the poor sanitary conditions in markets and a lack of attention to food safety instructions during selling.

Heavy metals are chemical elements characterized by a relatively high density and are toxic and harmful to humans at both high and low concentrations. Among heavy metals are chromium, iron, nickel, cadmium, mercury, arsenic, zinc, and lead (see Figure 1.1). Heavy metals are natural components of the Earth's crust (like stones and the solid layer covering the Earth's surface), and these metals cannot be removed or recycled. Heavy metals enter our bodies through food, drinks, and the air we breathe, although a small percentage of these elements, such as copper, selenium, and zinc, are considered essential for maintaining metabolic processes in the human body. However, at high concentrations, they can lead to poisoning.

Lead, cadmium, mercury, nickel, and chromium are considered heavy metals and are among the most significant environmental pollutants. Exposure to them can cause temporary harm, such as poisoning, or long-term damage, such as cancer, kidney failure, mental retardation, abortion, birth defects, and mutations (Duruibe et al., 2007). Additionally, it may lead to reduced growth rates and intelligence in children. For adults, exposure to these elements can cause memory impairment, general weakness, and high blood pressure. Exposure to lead compounds is harmful to the motor nervous system. Cadmium has a negative impact on kidney function, while the presence of mercury leads to significant physiological disturbances in tissues (Ghuzali, 1996; Orescanin et al., 2006).

Agricultural soil is considered one of the most significant sources of food contamination with heavy metals, which can occur through contaminated irrigation water or the use of pesticides.

These metals can travel through the plant vascular system, causing vegetables, grains, and fruits to become contaminated. They are then termed systemic toxins. Additionally, fruits and field crops watered with agricultural drainage water that is contaminated with heavy metals are the most critical and dangerous source of toxic heavy metals entering the human body.

Heavy metal poisoning can result from drinking contaminated water (such as using lead pipes for fresh water supply), inhaling air containing high concentrations near emission sources, or through the food chain. The danger of heavy metals lies in their tendency to bioaccumulate, meaning the accumulation of these chemicals in an animal's body over time exceeds their concentration in the environment. The toxicity of heavy metals is due to two primary reasons:

Materials and Methods

Samples were collected from vegetable selling shops located between the Zawiya and Ajilat regions along the coastal road, passing through the areas of Sorman, Abu Aisa, and Sabratha, over a period of three months (May, June, and July) in the years 2019-2020. The samples were taken during their natural harvest time and randomly selected. The samples included four types of vegetables: parsley, coriander, dill, and Swiss chard, in addition to field samples that were grown conventionally using organic fertilizers. The main source of irrigation was groundwater.

A total of 118 samples from each of the four vegetable types under study (parsley, dill, coriander, and Swiss chard) were randomly selected. They were then transported to the laboratory, wrapped in perforated absorbent paper labeled with the type and variety of the sample, the site's name, and the time of sampling. The samples were stored in freezers at -80°C until digestion was performed before use.

Sample Digestion

Before starting the digestion process, the microwave instrument tubes were washed and soaked in a diluted concentration of 10% nitric acid. Then, 0.5 grams of the vegetable sample was placed in the microwave tubes, to which 7 mL of concentrated nitric acid ($HNO3$) and 1 mL of hydrogen peroxide ($H2O2$) were added. The sample was placed in the device for 30 minutes until it was digested.

The samples were cooled and filtered using Whatman 1 filter paper, and the final volume was adjusted to 25 mL using double-distilled water. The heavy metal content of the samples was analyzed in the laboratories of the Brega Oil Marketing Company using atomic absorption spectrometry (Model AAS Nova).

Results:

Heavy Metal Content in (Parsley - Coriander - Dill - Swiss Chard).
The lead content in the dill variety recorded the highest arithmetic mean of (27 mg/g), while the coriander variety recorded the lowest arithmetic mean of (0.27 mg/g).

Table (1): Comparison of lead (Pb) concentrations in parsley coriander, dill, and Swiss chard.

Plant	Parsley	Coriander	Dill	| Swiss Chard
Lead (mg/L)	| 1.89 ± 1.84	0.27 ± 0.17	|0. 27 ± 9.04	0.43 ± 21.28
Significance Level	0.000			

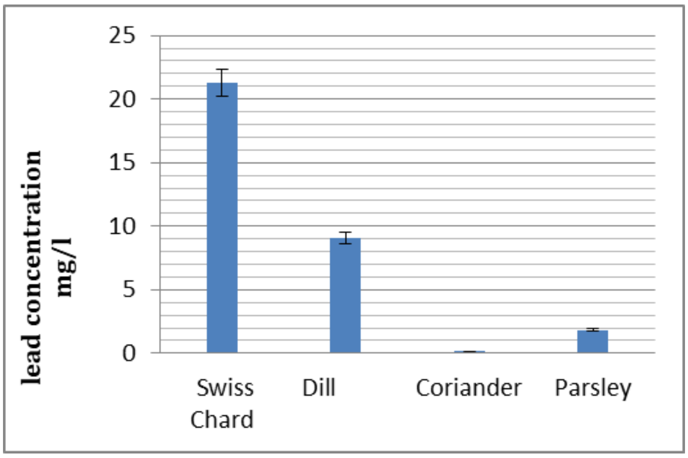

Figure (1) shows the comparison between lead concentrations in (parsley - coriander - dill - Swiss chard).

The arithmetic mean for the coriander variety is the highest (8.81 mg/g), while the Swiss chard recorded the lowest mean (3.81 mg/g).

Table (2): Comparison of cadmium (Cd) concentrations in parsley, coriander, dill, and Swiss chard.

Plant	Parsley	Coriander	Dill	| Swiss Chard
Cadmium (mg/L)	5.24 ± 9.34	8.81 ± 1.87	| 0.000 ± 0.000	3.81 ± 3.62
Significance Level	0.000			

International Multilingual Journal of Science and Technology (IMJST)
ISSN: 2528-9810
Vol. 10 Issue 7, July - 2025

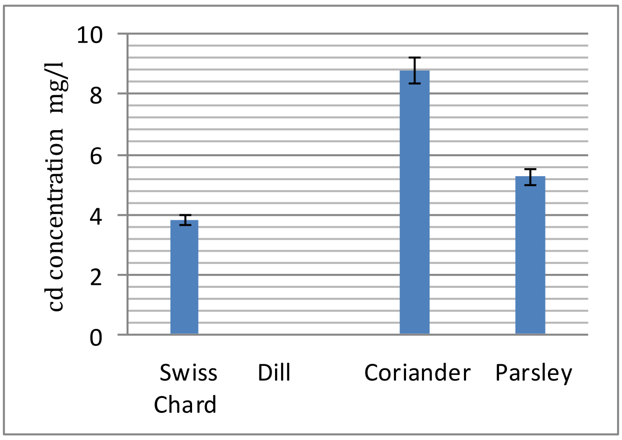

Figure (2): Comparison of cadmium (Cd) concentrations in parsley, coriander, dill, and Swiss chard.

The parsley variety recorded the highest arithmetic mean for copper content at (3.84 mg/g), while dill recorded the lowest arithmetic mean for copper levels at (0.02 mg/g).

Table (3): Comparison of copper (Cu) concentrations in parsley, coriander, dill, and Swiss chard.

Plant	Parsley	Coriander	Dill	| Swiss Chard
Copper (mg/L)	| 3.84 ± 9.34	0.25 ± 0.65	0.12 ± 0.08	1.35 ± 1.14
Significance Level	0.000			

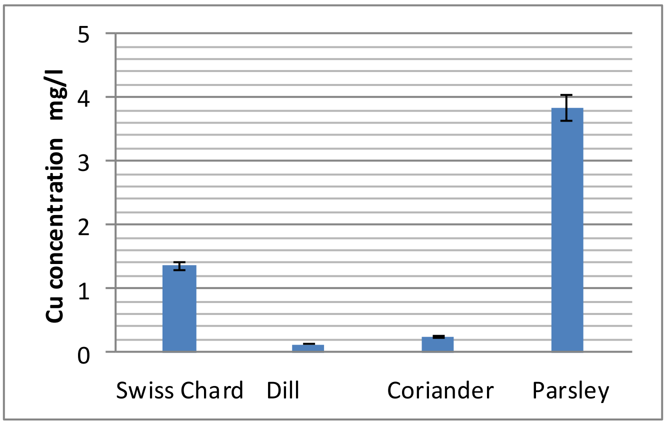

Figure (3): Comparison of copper (Cu) concentrations in parsley, coriander, dill, and Swiss chard.

The parsley variety recorded the highest arithmetic mean (16.79 mg/g) for nickel, while Swiss chard recorded the lowest mean for nickel content at (1.32 mg/g).

Table (4): Comparison of nickel (Ni) concentrations in parsley, coriander, dill, and Swiss chard.

Plant	Parsley	Coriander	Dill	| Swiss Chard
Nickel (mg/L)	16.79 ± 9.44	13.78 ± 6.36	16.60 ± 9.38	1.32 ± 0.63
Significance Level	0.000			

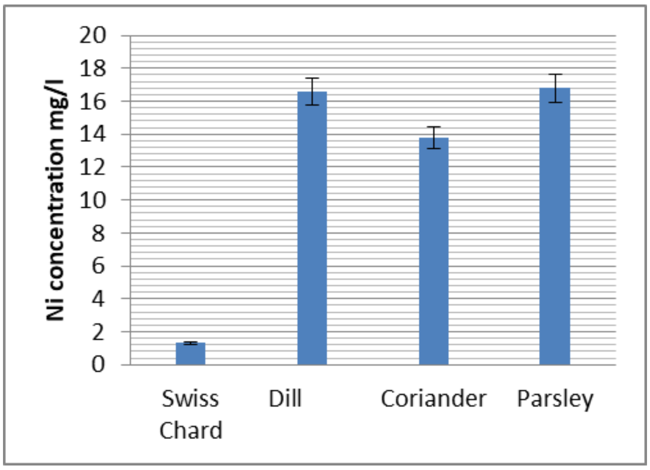

Figure (4): Comparison of nickel (Ni) concentrations in parsley, coriander, dill, and Swiss chard.

The chromium level was highest in the dill variety, with an arithmetic mean of (15.91 mg/g), while coriander recorded the lowest arithmetic mean at (1.82 mg/g).

Table (5): Comparison of chromium (Cr) concentrations in parsley, coriander, dill, and Swiss chard.

Plant	Parsley	Coriander	Dill	| Swiss Chard
Chromium (mg/L)	7.46 ± 0.95	1.82 ± 0.51	15.91 ± 6.16	14.07 ± 4.33
| Significance Level	0.000			

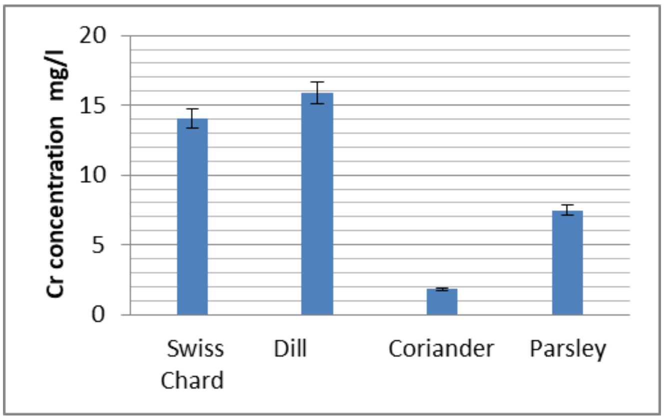

Figure (5): Comparison of chromium (Cr) concentrations in parsley, coriander, dill, and Swiss chard.

Comparison of Element Levels Over Different Time Periods:

It is observed from Table (6) that the level of lead fluctuated between the three periods during which samples were collected. Despite the differences in time intervals, there is a significant closeness between the average values of lead across these periods. This suggests that all samples under study were treated with the same measures despite the varying time periods. The level of lead during Ramadan recorded the highest average at (8.10 mg/g), while the average during the Eid al-Adha period was (8.08 mg/g). The period between the holidays recorded the lowest average level of lead at (7.58 mg/g). There are no significant differences (P = 0.96) among the three periods

Table (6): Comparison of Lead (Pb) Concentration Over Different Time Periods

Time Period	Ramadan	Between Holidays	Eid al-Adha
Lead (mg/L)	10.92 ± 8.10	8.49± 7.58	9.9 ±8.08
Significance Level	0.96		

It is noted from Table (6) that the level of cadmium was similar across the three periods in which samples were collected. The average cadmium level during the period between the holidays was the highest at (5.44 mg/g), followed by the Eid al-Adha period with an average of (4.68 mg/g), and finally the Ramadan period with an average of (3.41 mg/g). There are no significant differences among the three periods (P = 0.35).

Table (7): Comparison of Cadmium (Cd) Concentration (mg/L) Over Different Time Periods

Time Period	Ramadan	Between Holidays	Eid al-Adha
Cadmium (mg/L)	3.08 ± 3.80	5.44 ± 8.63	4.68±4.11
Significance Level	0.347		

It is noted from Table (7) that there are differences in the average values of copper concentration. The Ramadan period recorded the highest average for copper at (2.36 mg/g), followed by the Eid al-Adha period in second place with an average of (0.99 mg/g). The period between the holidays recorded the lowest average at (0.70 mg/g). There were no significant differences among the three periods (P = 0.34).

Time Period	Ramadan	Between Holidays	Eid al-Adha
Copper (mg/L)	1. 4± 2.36	0. 1± 0.70	0.1±0.99
Significance Level	0.34		

It is noted from Table (7) that the nickel content during the three study periods showed a close alignment between the arithmetic mean values, with the highest nickel value recorded during the month of Ramadan at an arithmetic mean of (13.10 mg/g), followed by the The Eid al-Adha period recorded an arithmetic mean of (11.99 mg/g), while the period between holidays recorded the lowest arithmetic mean of (11.62 mg/g) with a significance level of (P = 0.80).

Table (8): Comparison of chromium (Cr) concentrations over different time periods.

Time Period	Ramadan	Between Holidays	Eid al-Adha
Nickel (mg/L)	13.10 ± 10.71	11.62 ± 8.81	11.99 ± 9.5
Significance Level	0.80		

The chromium content showed close values during the three periods, with the highest arithmetic mean recorded during the Eid al-Adha period at (10.44 mg/g), followed by the period between holidays at (9.74 mg/g), while the Ramadan period recorded the lowest value with an arithmetic mean of (8.92 mg/g), where no significant differences were recorded (Table 8).

Time Period	Ramadan	Between Holidays	Eid al-Adha
Chromium (mg/L)	8.92 ± 6.62	| 9.74 ± 6.72	10.44 ± 7.06
Significance Level	0.640		

Comparison of Lead, Cadmium, Copper, Nickel, and Chromium Concentrations Found in Zawiya and Ajilat Markets Compared to the Field

From Table and Figure (5), it is observed that the arithmetic mean and standard deviation of the five elements (lead, cadmium, nickel, chromium, copper) in the three study areas (Field, Zawiya Market, Ajilat Market) show that the lead level was highest in Ajilat Market with an arithmetic mean of (767 mg/g), followed by Zawiya Market with an arithmetic mean of (6.09 mg/g) compared to the field, which recorded an arithmetic mean of (9.9 mg/g), with high significant differences (P = 0.000). As for cadmium, the highest value was recorded in the field with an arithmetic mean of (7.14 mg/g), followed by Ajilat Market with an arithmetic mean of (4.05 mg/g), while Zawiya Market recorded the lowest value with an arithmetic mean of (2.29 mg/g) and high significant differences (P = 0.002).

Table (8): Comparison of Lead, Cadmium, Copper, Nickel, and Chromium Concentrations in the Zawiya and Ajilat Markets Compared to the Field

Study Area	Elements				
	Lead (Pd)	Cadmium (Cd)	Copper (Cu)	Nickel Ni)	Chromium (Cr)
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Field	5.09	2.00	1.04	8.34	5.70
Souk Al-Zawiya	6.09	2.32	1.20	9.16	6.50
Souk Al-Ajilat	7.76	4.05	1.79	13.23	9.75
Level of Significance	0.000	0.002	0.013	0.004	0.000

Copper recorded the highest arithmetic mean at (3.04 mg/g) in the field, while Ajilat Market recorded an arithmetic mean of (1.79 mg/g), and Zawiya Market had the lowest mean at (1.23 mg/g), with significant differences (P = 0.013). Nickel had the highest value in the field with an arithmetic mean of (14.34 mg/g), followed by Ajilat Market at (13.23 mg/g), while Zawiya Market had the lowest value at (9.16 mg/g), with significant differences (P = 0.004). Lastly, chromium recorded the highest value in the field with an arithmetic mean of (12.07 mg/g), followed by Ajilat Market with an arithmetic mean of (9.75 mg/g), while Zawiya Market recorded the lowest mean at (6.5 mg/g), with significant differences (P = 0.000).

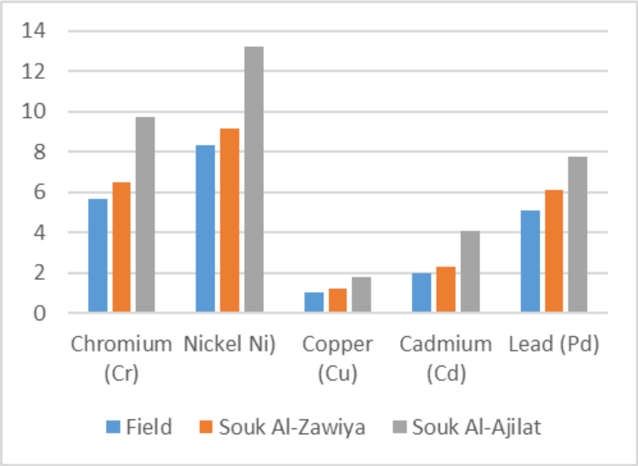

Figure 6 Comparison of the concentrations of lead, cadmium, copper, nickel, and chromium found in Souk Al-Zawiya and Al-Ajilat compared to the field.

Discussion

The results of this study indicated that the levels of lead and cadmium in leafy vegetables (dill and coriander varieties) shown in Tables and Figures (1.4, 2.4) exhibited high cumulative concentration levels and exceeded the permissible limits set by the World Health Organization (WHO) (0.3 mg/L, 0.2 mg/L) (Mensah et al., 2009), with significant differences. When comparing the current study with other studies, we find that it was higher than the results reported by (Anil Gunaratne et al., 2014), while being lower than those recorded in the study by (Abdul-Aziz, 2014). The results also showed elevated concentrations of nickel and chromium, as illustrated in Tables and Figures (4.4, 5.4). The parsley and dill varieties recorded the highest cumulative chromium levels, exceeding the permissible limit set by WHO (1.30 mg/L) (Mensah et al., 2009), and when compared with the study by (Anil Gunaratne et al., 2014), significant differences were also noted. The current study's results indicated that the highest cumulative levels of copper and nickel were found in the parsley variety, and these levels were within the permissible limits (73.3 mg/L, 1.30 mg/L) (Mensah et al., 2009) when compared to the study by (Abdul-Aziz, 2014), where the study recorded clear significant differences.

Regarding the comparison of element levels over different time periods, the results showed no significant differences in element concentrations, attributed to the proximity of the sampling periods. The values of the five elements were closely related among the four varieties, with lead recording the highest value during the month of Ramadan compared to the Eid al-Adha period and the period between the holidays. In contrast, cadmium recorded its highest value during the period between the holidays, while copper peaked during the blessed month of Ramadan. Nickel and chromium recorded their highest rates during Ramadan and Eid al-Adha, respectively. When comparing these results with other studies (Abdul-Aziz, 2014), this study reported elevated values for all elements above the permissible limits set by the health and food organization, except for copper and nickel, which remained within acceptable limits.

In comparing the concentrations of lead, cadmium, copper, nickel, and chromium in the Zawiya and Ajilat markets compared to the field, the results shown in Figure (6.4) revealed no significant differences in the mean values of these elements in the four varieties under study. The highest rates for lead were recorded in the market and Ajilat, while cadmium, copper, nickel, and chromium recorded their highest proportions in the field. This noticeable increase in element levels in the aforementioned leafy crops can be attributed to several reasons, including the nature of leafy crops, their leaf area, and the vegetable marketing systems, which play a crucial role in raising heavy metal levels in vegetables due to heightened pollution levels in the markets.

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