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Estimation of Some Heavy Metal Concentrations in Selected Dried Fruit Amples Available in Local Markets and Assessment of Their Health Risks

Bashar Abdulazeez Mahmood[1*], Sami Awad Alkubaisy[2], Esraa Abd AL-Karim Marouf[3], Enas H. Mohammed[4]

[1] Department of Chemistry, College of Education for Pure Science, University of Anbar, 31001 Anbar, Iraq
[2] Desert Studies Center, University of Anbar, 31001 Anbar, Iraq
[3] Nano-Materials Research Center, University of Anbar, 31001 Anbar, Iraq
[4] Department of Science, College of Basic Education, University of Mosul, 41001 Mosul, Iraq

[*] Correspondence: Bashar Abdulazeez Mahmood (esp.bashar.abdulaziz@uoanbar.edu.iq)

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Abstract: Dried fruits are a popular and widely consumed food due to their high nutritional value and long shelf life. However, their contamination with heavy metals poses a health and environmental concern. This study aims to estimate the levels of some heavy metals (copper, nickel, manganese, iron, lead, and chromium) in selected dried fruit samples available in local markets and assess their compliance with international standards approved by the World Health Organization (WHO) and the Codex Alimentarius (CAC). Samples were collected from multiple sources and analyzed using advanced techniques (Atomic Absorption Spectroscopy (AAS)). The results showed that some samples contained concentrations exceeding permissible limits, indicating potential health risks, especially in cases of long-term consumption. The sources of this contamination are often attributed to the use of chemical pesticides and fertilizers, and unsafe drying and packaging methods. The research suggests implementing stricter surveillance of food products and increasing consumer awareness on selecting safe dried fruits. Research for different area basis needs to be pursued for better apprehension of menace.

Keywords: Dried fruits; Heavy metals; Local markets; Health risks

1 Introduction

Dried fruits are a popular foodstuff because of their nutritive value and because they do not require refrigeration for storage. They provide a high content of dietary fiber, vitamins, minerals and other health-promoting plant compounds and therefore they are consumers' preferable option for snacks or an ingredient in food products [1].

In addition, dried fruits have various health benefits, but they can become exposed to heavy metals from planting, processing, drying, packaging, and storage. They are regarded as a serious environmental pollutant because of their toxicity and bio-concentration in the tissues of organisms alive and thereby endangering human health [2]. These heavy metals that can be found in food can be copper, lead, chromium, nickel, manganese and iron, among others [3].

Some of these are required by your body in trace amounts to do essential things like make energy, form blood, and build up the nervous and immune systems. Nevertheless, when the limits are exceeded, damages could range from liver lesions, nerve injury, respiratory complaints, and even have the potential to promote chronic and severe diseases, like kidney failure and cancer [4, 5]. Heavy metal sources are many. These may be caused by pesticides, chemical fertilizers with a high heavy metal content, and by plants absorbing them from polluted soil or water. Post-harvest processes such as unhygienic drying and storage in contaminated containers may also lead to high content of these elements in finished products [6].

It emphasizes the significance of guidelines provided by regulatory agencies and health bodies, especially World Health Organization (WHO) and Codex Alimentarius (CAC), for maximum safe limit of these metals in different foods. It is designed to protect human health and avoid dangers which may result from chronic intake [3, 7]. This study aims to assess the extent of contamination of local fruits dried fruits in local market with the above-mentioned

heavy metal. The atomic absorption spectrometry (AAS) is the most sensitive technique to low concentration detection, particularly AAS because of its high sensitivity toward heavy metals [6].

Heavy metal contamination has been detected in the most commonly consumed dried fruit including, fig, quince, oranges, apples, bananas, kiwi, gooseberries and mangoes and several studies have concentrated on their monitoring levels. A 2018 report from the European Environmental Science Institute found that imported raisins from a few industrialised countries have high lead levels that are above the maximum limits according to the European Union standards [8]. Likewise, another research article published in the Journal of Food Science and Nutrition in 2022 revealed that the content of cadmium in dried apricots prepared in some agricultural fields close to factories was higher than the accepted value according to the WHO standards, suggesting that the long-term exposure to these heavy metals might be posing a risk [9].

Several research papers confirmed that, health risks of heavy metals in dried fruits if taken more than recommended amounts. According to a WHO report in 2019, long-term exposure to lead and cadmium can lead to neurological conditions, kidney challenges and immune system disorders and, consequently to chronic diseases, such as cancer [10].

In addition, a study published in 2021 in the Journal of Environmental Medicine, found undercooked fish can cause permanent brain and nervous system damage in children who eat mercury-contaminated dried fruit. Furthermore, the study suggested that long-term exposure to low doses of mercury can cause delayed neurodevelopment and cognitive dysfunction in children [11]. There are also studies detailing methods to reduce the amount of heavy metals in dried fruits. A 2020 study from the International Center for Food Safety demonstrated that good agricultural practices (GAPs) including the use of organic fertilizers, the selection of clean irrigation water sources, and the monitoring of soil quality can alleviate heavy metal uptake by plants [12]. The heavy metal contamination of the surface of dried fruits could be reduced by between 10 and 30% as well through proper washing of these dried fruits before consumption and that they can have modern food processing methods such as fermentation and filtration to thank for lowering the levels still further [13].

A survey of earlier studies indicates that heavy metal contamination of dried fruits presents a universal problem and call for a multi-pronged approach, such as improved application of food quality control standards, use of sensitive methods for detecting contamination, and creation of awareness about the potential health risks of consuming contaminated products [14]. Recently, research has shown new methods that can be used in detecting heavy metals (electrodes, pre-treatment methods, and prediction models), in addition to the traditional methods used in detecting heavy metals, such as the atomic absorption technique and other familiar methods [15–20].

Results of the study indicated that a high proportion of all measured concentrations of the metals were below the maximum allowable concentrations established by the Food and Agriculture Organization (FAO) and the WHO. So, these metals should be safe to ingest. In addition, the concentrations of certain metals in chosen citrus fruits available in the markets of Anbar Governorate, also, exceeded the standard limits [21]. The samples used in the study were sourced from different origins and storage methodologies to demonstrate diversity in provenance. The samples were also prepared carefully in the lab and were also investigated in the laboratory. Techniques in order to validate the results. This research adds to an important pool of scientific knowledge which may be employed by decision-makers, regulators, as well as consumers. It also points to further future research that targets a more in-depth and thorough understanding of the magnitude of such problems in different areas.

2 Materials and Methods

2.1 Practical Part

Methods: The current research adopted a descriptive analytical method to determine the concentrations of some heavy metals in different samples of dried fruits which were collected from local markets and to evaluate the compliance of these items with acceptable health standards. Care was taken to sample from various sources to allow for diversity of production and storage conditions.

2.2 Sample Collection

A set of dried fruit samples was collected from various local outlets, including public markets, shops, and shopping centers in Anbar Governorate. Various types of commonly consumed dried fruits were selected (e.g., kiwifruit, bananas, oranges, mango, quince, apples, and figs). Care was taken to avoid duplication at source and ensure that samples were in their original condition, unopened or damaged. The samples were transported to the laboratory in clean, sealed containers and stored in a cool, dry environment until analysis began.

2.3 Sample Preparation and Grinding

The samples were washed with distilled water to remove any surface impurities, and then dried in an oven at an appropriate temperature to prevent loss of mineral elements. After drying, the samples were ground using a clean

stainless steel grinder to obtain a fine, homogeneous powder. Specific quantities of powder were weighed for each sample and placed in sterile analysis vessels.

2.4 Sample Digestion

The digestion was performed at College of Education for Pure Sciences/University of Anbar, and concentrated hydrochloric acid (HCl) and concentrated nitric acid (HNO_3) were mixed to form aqua regia ($30HNO_3$: 70HCl). The sample was weighed (1 g) in a precision balance and diluted with 10ml aqua regia. The sample and acid were added to a glass beaker and heated on a heater at 100℃ until the reaction was completed and the organic compounds decomposed. The mixture was cooled, then filtered, and the filtrate was diluted with distilled water to the mark. The clear solution was then collected and stored in plastic containers in a dark room for analysis.

2.5 Analytical Techniques

These metals were assayed using flame Atomic Absorption Spectroscopy (AAS), as this method is highly sensitive and accurate for detecting such metals. The analyzer was calibrated using standard solutions appropriate for each element to determine the concentrations of heavy metals in the samples. Six metals were analyzed: copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), manganese (Mn), and iron (Fe). The instruments were calibrated using standard solutions of known concentrations in accordance with the manufacturer's instructions to ensure the accuracy of the results [22].

A series of standard solutions with concentrations of 0.1 ppm, 0.5 ppm, 1 ppm, 1.5 ppm, and 2 ppm were prepared by diluting a 100 ppm intermediate solution, which was itself prepared from a certified 1000 ppm stock solution. For each of the studied elements, absorbance measurements were conducted using the atomic absorption device shown in Figure 1, and calibration curves were generated accordingly [23].

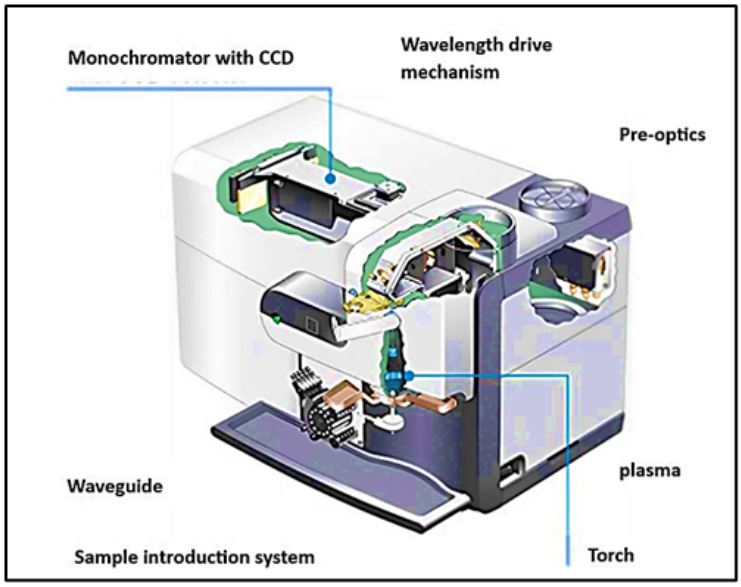

Figure 1. Atomic absorption system employed in the current study

For the purpose of using the atomic absorption device for measurement, the best conditions for measurement have been fixed before the start of work and according to the following:

• Choosing the optimal current of the cathode lamp for each element with a constant standard concentration from it.

• Choosing the optimal height of the acetylene-air burner with a fixed standard concentration for each element.

• Finding the linear calibration curve for each element using a series of dilute standard solutions and measure them under optimal conditions of the device and draw the direct calibration curve.

In the laboratory, the samples were filtered by a Behner filter to ensure that the ablation tube in the atomic absorption system is not clogged.

Since atomic vapor absorbs light from the light source (hollow cathode lamp), the flame transforms the sample mist into atomic vapor. This apparatus was used to analyze every sample for every element [24], and a hollow cathode lamp served as the radiation source.

A high concentration standard solution (1000 ppm) of the prepared element salt was used to create a number of standard solutions, one for each element. Using distilled water, the necessary volume was first diluted after being

pipetted into a 500 mL volumetric flask. The dilution procedure was then used to extract a number of standard solutions from the diluted standard solution [25].

$$C1\ V1 = C2\ V2$$

where, C1 is the first standard solution's concentration. The first standard solution's volume is denoted by V1. The second standard solution's concentration is denoted by C2. The volume of the second standard solution is denoted by V2. The wavelength of each element was used to estimate it. In addition to a chelate solution (blank) made entirely of the acid mixture, a standard solution of each element was made from a 1000 ppm stock solution. Using a flame atomic absorption spectrophotometer to estimate elements:

• Establish the atomic absorption spectrophotometer's ideal operating parameters.

• The kind of flame utilized to estimate each measured element and the equipment's detection limit.

• The standard stock solution is used to create a number of standard solutions with a concentration of 1000 mg/l. Both lower and higher concentrations of the element to be assessed in the sample fall within this range.

• The pH value of the sample solution is acidic and ranges from 4 to 6.5, which affects the flow rate of the solution in the nebulizer. Therefore, the standard solution must be acidified by adding (4–5) drops of concentrated nitric acid.

• Fuel is made from acetylene.

• Using an atomic absorption spectrophotometer, we begin the measuring procedure after finishing the aforementioned stages [7]. The digested samples are appropriately noted and examined. The metal concentration is ascertained using the observed absorbance. To guarantee quality control and assurance, the samples are examined several times. Every sample needs to be examined several times in order to determine the average concentration that is used to demonstrate accuracy. To evaluate precision, the standard deviation of the average is also calculated. The standard solution and the procedural blank are included in the analytical quality control procedure.

3 Results and Discussion

Reference standard samples were used to verify the accuracy of the analyses. Table 1 shows the codes for the samples under study. At least three repeat analyses were performed for each sample to ensure consistency. Laboratory precautions were taken to reduce the possibility of cross-contamination between samples during all stages of preparation and analysis. Table 1 shows the concentration of heavy metals in selected dried fruit samples (mg/kg).

Table 1. Concentration of heavy metals in selected dried fruit samples (mg/kg)

Symbol Element	Plum	Banana	Orange	Kiwi	Mango	Quince	Apple	Fig	$LSD_{0.05}$
	W1	Z1	B1	Q1	M1	S1	H1	T1	
Cu Copper	0	0.166	0.11	0	0.355	0.259	0.295	0.309	0.0161*
Pb Lead	0	0	0	0	0.002	0	0.063	0.191	0.0101*
Cr Chromium	11.483	2.19	2.934	0	1.406	3.225	0.257	0	0.0142*
Ni Nickel	0	0	0	11.412	1.765	0.336	0	0	0.0091*
Mn Manganese	0.084	0.164	0.014	0	0.168	0.105	0.121	0.11	0.0144*
Fe Iron	4.887	3.626	4.654	5.329	1.91	4.337	4.419	3.055	0.1022*

There is a significant difference between groups (p-value < 0.05).

3.1 Copper (Cu)

Concentrations of copper ranged between 0.000 mg/kg in samples W1 and Q1, and 0.355 mg/kg in sample M1. The remaining samples recorded varying concentrations: Z1 (0.166), B1 (0.110), S1 (0.259), H1 (0.295), T1 (0.309). The least significant difference (LSD) for copper was 0.0161 mg/kg, and the differences between samples were statistically significant at p-value < 0.05, indicating a real difference in copper contamination levels between samples. Figure 2 shows the concentrations of Cu in the samples under study.

3.2 Lead (Pb)

Most samples recorded a concentration of 0.000 mg/kg, with the exception of three samples that showed varying concentrations: M1 (0.002), H1 (0.063), and T1 (0.191). The calculated LSD value indicates 0.0101 mg/kg. However, the differences between these samples are statistically significant (p-value < 0.05), suggesting the presence of local contamination in some samples, perhaps due to packaging or storage conditions. Figure 3 shows the Pb concentrations in the samples under study.

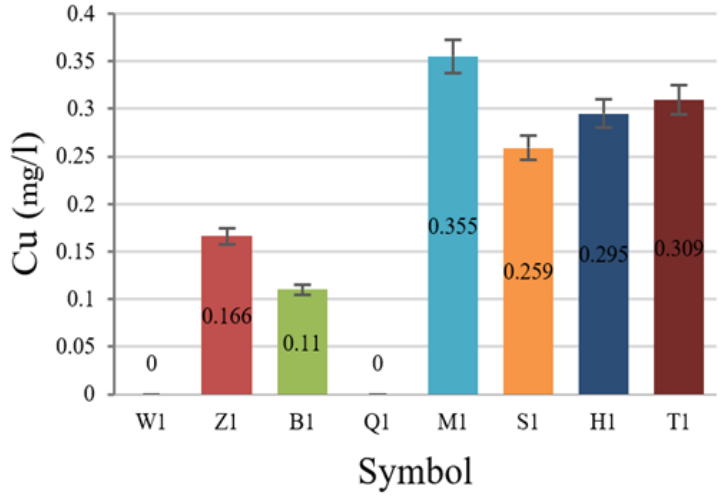

Figure 2. Cu concentrations in the samples under study

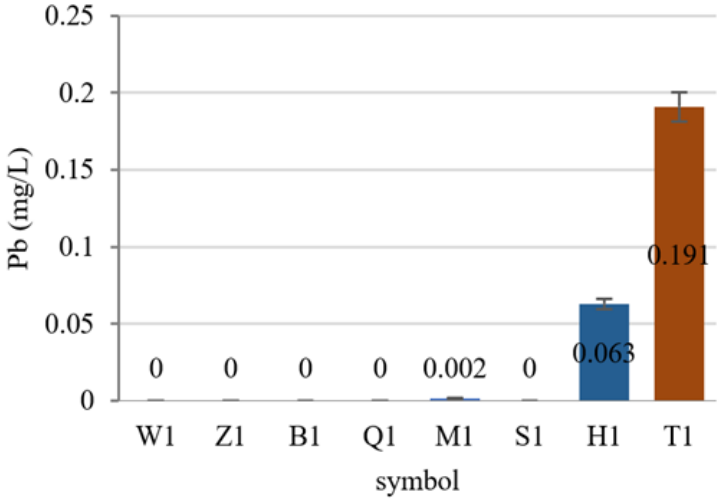

Figure 3. Pb concentrations in the samples under study

3.3 Chromium (Cr)

Samples B1 (2.934), S1 (3.225), Z1 (2.190), M1 (1.406), W1 (1.483), and H1 (0.257) recorded varying concentrations of chromium, while no concentration was recorded in samples Q1 and T1. The LSD value was 0.0142 mg/kg, and significant differences (p-value < 0.05) were evident between the samples, reflecting significant variations in pollution sources or production conditions. Figure 4 shows the Cr concentrations in the samples under study.

3.4 Nickel (Ni)

Samples W1, Z1, B1, H1, and T1 were free of nickel, while concentrations were recorded in samples Q1 (1.412), M1 (1.765), and S1 (0.336). The calculated LSD value of 0.0091 mg/kg indicates statistically significant differences (p-value < 0.05), indicating the possibility of contamination from industrial sources or fertilizers. Figure 5, shows the Ni concentrations in the studied samples.

3.5 Manganese (Mn)

Manganese concentrations varied as follows: W1 (0.084), Z1 (0.164), B1 (0.014), Q1 (0.000), M1 (0.168), S1 (0.105), H1 (0.121), T1 (0.110). The LSD value was 0.0144 mg/kg, confirming the presence of statistically significant differences (p-value < 0.05) in the levels of this element between samples. Figure 6 shows the Mn concentrations in the studied samples.

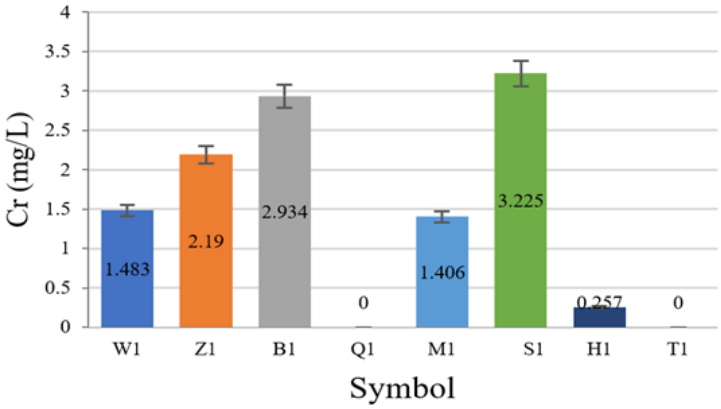

Figure 4. Cr concentrations in the studied samples

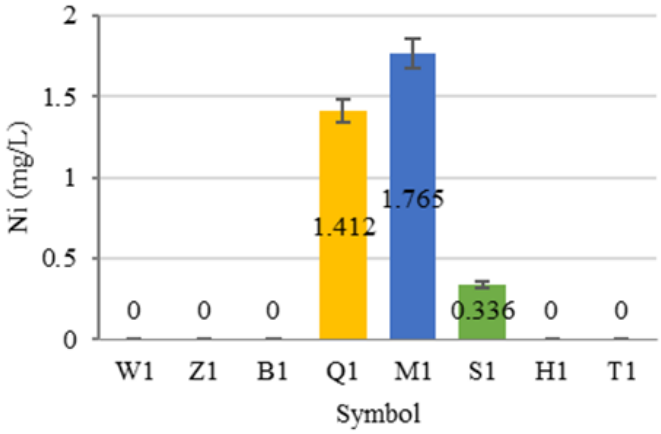

Figure 5. Ni concentrations in the studied samples

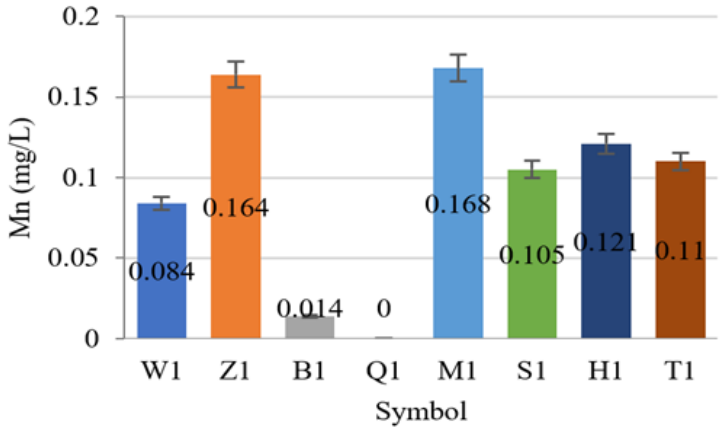

Figure 6. Mn concentrations in the studied samples

3.6 Iron (Fe)

The highest iron concentrations were recorded in samples Q1 (5.329), W1 (4.887), B1 (4.654), H1 (4.419), and S1 (4.337), while the lowest concentrations were found in M1 (1.910) and T1 (3.055). Z1 recorded a concentration of 3.626. The LSD value for iron was 0.1022 mg/kg, and the differences between samples were clearly significant (p-value < 0.05), reflecting differences in the growing conditions, treatment, or quality of the soil and water use. Figure 7 shows the Fe concentrations in the studied samples.

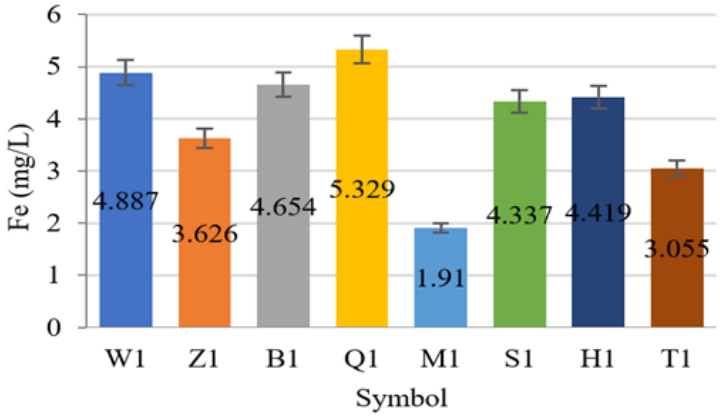

Figure 7. Fe concentrations in the studied samples

3.7 Statistical Analysis and Software Utilized

Statistical analyses in this study were performed using SPSS software, version 27 (IBM Corp., Armonk, NY, USA). The primary statistical test applied was the Least Significant Difference (LSD) post-hoc analysis, which was used to determine whether the observed differences in heavy metal concentrations across the dried fruit samples were statistically significant. Prior to conducting LSD, analysis of variance (ANOVA) was used to assess the overall significance of group differences at the 0.05 level. The LSD method then allowed pairwise comparison of sample means to identify which specific fruit types exhibited significantly different concentrations of each heavy metal. To ensure the validity of the inferential procedures, assumptions related to normal distribution and homogeneity of variances were examined. The validity of applying ANOVA followed by LSD tests in food contamination studies has been well documented in previous research [26]. In line with this approach, the LSD value in the present study was computed based on the pooled standard error and the critical t-value from the student's t-distribution, using the formula [27, 28]:

$$LSD = t_{a,df} \times \sqrt{\frac{2 \cdot MSE}{n}}$$

where, $t_{\alpha,df}$ is the critical value at the 0.05 significance level, MSE is the mean square error from ANOVA, and n is the number of replicates per group. The LSD values provided in Table 1 of the study confirm that differences in metal concentrations between many samples are statistically significant ($p < 0.05$), thereby supporting the interpretation of meaningful variation in contamination levels among the examined fruit types.

4 Conclusions

(1) Significant differences between samples: The study showed significant statistical differences (p-value < 0.05) in the concentrations of all studied heavy metals (copper, lead, chromium, nickel, manganese, and iron) between samples. This is confirmed by the calculated LSD values for each element, reflecting a clear variation in pollution sources or production conditions.

(2) Variation in pollution sources: The results indicate that some samples contain high concentrations of specific elements, such as chromium and nickel, while other samples are devoid of these elements. This suggests that contamination likely results from local sources associated with the use of contaminated water or fertilizers and pesticides rich in heavy metals.

(3) The risk of toxic element accumulation: Some samples recorded elevated levels of hazardous elements such as lead and chromium, which are known to be highly toxic even at low concentrations, potentially posing a potential health risk to consumers, especially with continuous, long-term consumption.

(4) Essential elements may become contaminants: Although elements such as copper, manganese, and iron are essential for the body, their significantly elevated concentrations in some samples indicate a potential exceedance of safe health limits, changing their role from a nutrient to a contaminant requiring monitoring.

(5) The Importance of Using Statistical Analysis in Nutrition Studies: The study demonstrated the importance of using statistical analysis tools such as LSD and significance tests to interpret variance in data. These tools help distinguish between random differences and true, statistically significant differences, which is essential when assessing the safety of food products. The Need for Stricter Oversight: The study results call for intensified oversight of the production and storage stages of dried fruit, and ensuring that products on the market comply with the limits permitted by international health authorities such as the WHO and CAC.

5 Suggestions

(1) Work to introduce modern technologies in the fields of plant nutrition and agricultural pest control, particularly biological control, which has become widespread in most countries around the world.

(2) In this study, we emphasize the need to monitor the concentration of other general heavy metals, not only in fruits, but also in all foods, to determine the extent of individual exposure to these heavy metals.

(3) Urge the Food and Drug Control Center, the Agricultural Research Center, and relevant authorities to conduct numerous studies and analyses on all agricultural products, including vegetables, fruits, grains, legumes, and fodder, to ensure their safety for human, animal, and environmental health.

(4) Conduct extensive studies, including a larger number of samples from various geographic regions, and link the results of chemical analyses to agricultural production conditions and processing methods, to gain a deeper understanding of the causes of pollution and identify prevention and treatment methods.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

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Conflicts of Interest

The authors declare that they have no conflicts of interest.

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