Effects of Food Processing Methods on heavy metals in Fruits and Vegetables Tracing of pesticide residuals reduction during processing steps

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Abstract:

This study aims to comprehensively assess the effects of various manufacturing processes and treatments on heavy element concentrations in a selection of fruits and vegetables. The investigated samples include okra, grapes, dates, and tomatoes. The primary focus lies in evaluating the efficacy of different processing techniques, such as washing, peeling, high-temperature concentration, drying, and boiling, in reducing heavy element levels in these edible plant products.

The experimental procedure was conducted meticulously, ensuring precision and accuracy. Each sample underwent thorough water-only washing, followed by treatments with 2% citric acid and acetic acid. Unique to grape samples, they were washed with alkaline solutions. Additionally, tomatoes and dates underwent concentration processes, while all samples underwent drying as part of the overall treatment regimen.

Results revealed significant variations in the efficacy of these processing methods in reducing heavy element levels. Several key factors influenced each technique's success, including the type of fruit or vegetable, the nature of the heavy element, and its degradability under different treatment methods.

The study highlights the importance of pollution sources, such as car emissions and nearby factories, which contribute to heavy element contaminants. Soil and water pollution from environmental pollutants also play a role in exacerbating these issues.

Notably, the findings indicate that the concentration of heavy elements during pesticide concentration periods led to their gradual decline, particularly after sample processing. Washing treatments, using water, vinegar acid diluted with water, and 2% concentrated citric acid, significantly reduced heavy element concentrations.

Vinegar acid proved particularly effective, especially in grape samples, while citric acid demonstrated strong capabilities in eliminating heavy elements in okra, dates, and tomato samples. The study's outcomes were aligned with previous research, validating the significance of the findings.

Keywords: heavy metals, crops (vegetables and fruits), boiling, drying, canning, concentration, product manufacturing.

Introduction

Heavy elements, often referred to as metals, are mineral elements with a relatively high density. They can be either toxic or non-toxic at low concentrations. Examples of these include mercury, cadmium (Cd), arsenic (As), lead (Pb), and thallium (Tl). Some of these metals, even in small quantities, are essential for certain biological processes. For instance, iron, copper, and oxygen are involved in electron transport, while cobalt contributes to the synthesis of cell metabolites. Zinc and manganese regulate enzyme activity, chromium aids in glucose utilization, and nickel promotes cell growth. Arsenic is involved in growth and metabolism in some animals and humans, while selenium acts as an antioxidant and hormone catalyst. Other metals, such as molybdenum, participate in oxidation and reduction processes. However, these metals must be present in small or trace amounts to be nutritionally necessary, as any shortage can lead to health issues. **(Klaus,2009).**

Research has demonstrated the influence of these minerals on agricultural produce, soil, water, and vegetation. These minerals are categorized as fundamental toxins for living organisms. While the human body naturally contains some of these minerals, the levels are typically non-toxic and sufficient to support bodily functions. However, toxicity can occur when the body absorbs large quantities of any heavy metal, such as mercury, lead, cadmium, and arsenic. This exposure can occur due to pollution in food, water, air, medication, or improperly coated food containers. Industrial exposure, certain types of paint primarily composed of lead, the manufacturing process of mirrors or X-ray machines, or the extraction and refining of gold and silver ores can also contribute. Consumption of fish or water contaminated with mercury is another source of exposure**. (Mostafizur *et al*., 2022).**

Toxic substances, such as heavy metals, can lead to bioaccumulation, a process where the concentration of chemicals in an organism's body increases over time compared to their environmental levels. This happens when these substances are absorbed and stored in the organism's tissues at a faster rate than they are broken down or excreted. Heavy metals can find their way into water bodies due to waste from consumers and industries, or even as a result of acid rain, which is rain mixed with acidic components like nitrogen acid or sulfuric acid**.(Helen and Chinenye 2023).**

The infiltration of soil by heavy metals, leading to their release into groundwater, streams, lakes, and rivers, is a significant concern. These toxic substances can accumulate in an organism's body over time, a process known as bioaccumulation. This occurs when the rate of intake and storage of these substances exceeds their rate of destruction or expulsion. Exposure to heavy metals can result in a range of symptoms including diarrhea, nausea, shortness of breath, chills, weakness, and a tingling sensation in the hands and feet. The treatment for heavy metal poisoning primarily involves avoiding exposure to the sources of these toxins. This could mean reducing the consumption of certain foods known to contain high levels of heavy metals, such as brown rice (which contains arsenic) and certain types of fish (which may contain mercury). It also involves avoiding exposure to heavy metals in the environment, such as those found in industrial waste, certain types of paint, and improperly coated food containers. In severe cases, medical intervention may be necessary, which could involve stomach pumping or intravenous therapy. It's also important to maintain a balanced diet to help the body naturally detoxify and expel these harmful substances**. (Ana *et al* .,2018).**

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The average human body, weighing around 70 kilograms, comprises a minute fraction of minerals, roughly 0.01% or about 7 grams, which is comparable to the weight of two dried peas. The mineral composition includes approximately 4 grams of iron and 2.5 grams of zinc. The majority of the body's mineral content, about 98%, consists of light metals, predominantly water. These metals are naturally present in the ecosystem. However, their concentrations have been escalating due to factors like industrial activities, industrial wastewater, soil metals in water bodies, and notably, acute fuel pollution. Ingesting these metals in substantial quantities can result in heavy metal poisoning. **(Heavy Metal Poisoning , 2022)** .

Research has demonstrated the impact of these minerals on agricultural crops, soil, water, and vegetables. These minerals are classified as fundamental toxic elements for living organisms. The human body naturally contains some of these minerals, but only in quantities that do not cause toxicity. These quantities are sufficient to enable the body to perform its functions. However, heavy metal poisoning occurs when the body absorbs large quantities of any heavy metal, such as mercury, lead, cadmium, and arsenic. Humans are exposed to these metals due to pollution in food, water, air, medicine, or food containers that are coated in an unhealthy manner.

Exposure can also occur due to industrial activities, certain types of paint that primarily contain lead, during the manufacture of mirrors or X-ray machines or lamps, during the extraction and refining of gold and silver ores, or through the consumption of fish or water contaminated with mercury, among other sources **(Narjala , 2020).**

Toxic substances can lead to a phenomenon known as bioaccumulation, which is characterized by the progressive increase in the concentration of these substances within an organism over time. This occurs when the rate of absorption of a substance by an organism surpasses its rate of elimination or metabolism. As a result, the substance accumulates in the organism's body at a faster pace than it can be broken down or expelled. Heavy metals, for instance, can infiltrate soil and eventually reach groundwater, contaminating our water sources. The bioaccumulation of these substances is a significant concern due to their potential to cause harm when their concentration in the body becomes too high. **(Anwarzed *et al* ., 2015)**

Heavy metals, which can infiltrate water bodies through consumer and industrial waste or even due to acid rain (rain mixed with acidic components like nitric acid or sulfuric acid), can permeate the soil and release these metals into groundwater, streams, lakes, and rivers. Exposure to these metals can lead to health issues such as diarrhea, nausea, shortness of breath, chills, weakness, and tingling in extremities. To treat such conditions, it's crucial to avoid the sources of these toxins. Treatments may include stomach pumping in severe cases or intravenous therapy. Additionally, a well-balanced diet can help to avoid heavy metal toxins. For instance, reducing the intake of brown rice, which contains arsenic, and certain types of fish, which may contain higher levels of mercury, can be beneficial. It's also recommended to avoid alcohol and other potential sources of heavy metals. **(Saikat *et al* ., 2022)**

Materials and methods

1. Sampling Collection

The sampling procedure in this study is carefully designed to ensure the comprehensive representation of samples to be examined the concentration of their heavy elements in four categories of fruit and vegetables treated with various pesticides: Okro (Promite EC 15% W/V), grapes (additional fungicides Extra 250

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SC), dates (Flash10% EC Insecticide), as used as Rival 722 SL on Tomatoes during summer 2022 and winter 2023, crop samples were collected from distinct

agricultural areas in Baghdad and Salah al-Din governorates, known for their varied agricultural practices and wide use of pesticides. Samples, weighing between 20 and 30 kg per type, were collected according to **(Eman and Qais 2018).**

In Baghdad, samples of okra, dates and tomatoes were taken from Medina Medina, Rashidiya and Mahmudiyah, respectively. In Salahuddin, samples were collected from the country's judiciary. The selection of these crops was based on the prevalence of agriculture and pest susceptibility, which often necessitates the use of pesticides. For okra, samples were obtained from the Gold Coast group, known for its high yield. This set is characterized by a leg length of up to 2 meters, bleached color, round and non-ribbed horns, and high fiber ratio. Floating viscosity rate up to 20.7 g/cm square per second. This species usually matures about 70 days after planting, which usually occurs in January, and the tomato samples were of the "Father 1006" type, Which is often sprayed with the pesticide "Rival 722." This type is suitable for both fresh consumption and paste production, and is usually grown from the end of September to the end of October for winter fruits, and in January for spring crops.
The grape samples were of the "local egg" type, a permanent and climbing bush of the "Vinifera Vitaceae" family. This species is usually grown in late winter and early spring, from February to April.

History samples were collected from the "Barhi" group, known as its yellow orange colour, circular shape and medium to large size. Thin skin is usually separate from meat. This species typically matures from late October to November, averaging a return of more than 150 kg per palm. The safety period for used pesticides ranged from 2 weeks for okra and grapes, 3 weeks for dates, and 7 days for tomatoes. The sample collection procedure adheres to strict protocols to avoid contamination and ensure the safety of samples. Samples were then prepared to analyze pesticide residues and assess treatment methodologies Fruits and vegetables, including grapes, okra, dates, and tomatoes. The concentration of heavy metals such as arsenic, cadmium, and lead were determined in samples collected from the farm and in processed samples using Atomic Absorption Spectrometry. **(Heavy metal,2021).**

Insecticides used in studied samples to measure the concentration of heavy elements were Promite on Okra, Extra on Grapes, Flash on Dater, and Rival on Tomatoes. These are the permissible concentrations of spraying for Rival 722 SL 60-100 / 20 liters, Extra and Promite water concentrated 15-20 ml /20 liters and Flash 60-100

Ml/100 liters with water on fruit and vegetable crops. The purpose of this study was to measure the remaining amount of heavy elements after processing the plant and to determine the period when the product became suitable for human consumption. The following table shows the dates of collection of the samples examined.

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Table 1: These dates represent the timeline of sample collection for each crop, following the application of pesticides. The control samples serve as a baseline for comparison with the post-spray samples.

Sample collection for each crop
For Okra: **1.** Control samples were collected on September 20, 2022. **2.** Samples were collected one week post-spraying on September 27, 2022. **3.** Samples were collected two weeks post-spraying on October 4, 2022.
For Grapes: **1.** Control samples were collected on October 4, 2022. **2.** Samples were collected one week post-spraying on October 11, 2022. **3.** Samples were collected two weeks post-spraying on October 18, 2022.
For Dates: **1.** Control samples were collected on October 18, 2022. **2.** Samples were collected one week post-spraying on October 25, 2022. **3.** Samples were collected two weeks post-spraying on November 1, 2022. **4.** Samples were collected three weeks post-spraying on November 8, 2022.
For Tomatoes: **1.** Control samples were collected on November 8, 2022. **2.** Samples were collected three days post-spraying on November 11, 2022. **3.** Samples were collected five days post-spraying on November 14, 2022. **4.** Samples were collected seven days post-spraying on November 17, 2022.

2. Methods

The concentrations of heavy metals in samples collected from farms, markets, and processed products were determined using Atomic Absorption Spectrophotometry (AAS) following the APHP method **(APHP, 2017).**
The impact of certain chemicals, such as acetic acid and citric acid, as well as rinsing with water, was examined in terms of their ability to decrease or increase the concentrations of pesticide residues or heavy metals.

3. Processing Methods

The research assessed the impact of various standard treatment methods on the levels of heavy elements in fruits and vegetables taken from samples, specifically okra, grapes, dates and tomatoes. These treatment methods included washing, peeling and high temperature concentration, drying and boiling.

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Each sample was subjected to washing with either water only or acetic acid and citric acid at 2% concentrations, diluted with water followed by rinsing under a constant flow of tap water for 15 minutes. This washing process was performed individually for each sample and repeated using two acids, in addition to washing grape samples with alkaline solutions. Tomatoes and dates underwent concentration, and grape samples underwent drying. It is important to note that the effectiveness of these processing methods in reducing levels of heavy elements can vary depending on the type of fruit or vegetables, the nature of the heavy element and its degradability when treated with different treatments. The results obtained in this study were based on samples of okra, grapes, dates and tomatoes analyzed. Our primary focus was to evaluate the effectiveness of various processing techniques, such as washing, peeling, high-temperature concentration, drying and boiling, in reducing the levels of heavy elements in these individually edible plant products for each sample and replicating them using two types of acids. In addition, grape samples received a unique treatment, as they were washed with alkaline solutions.

For tomatoes and dates, we used a focus method to further investigate the content of heavy items. Furthermore, all samples underwent drying as part of the comprehensive treatment system.

The results obtained from this rigorous study showed that the effectiveness of these processing methods in reducing heavy element levels is subject to significant

variation. Several key factors affect the success of each technique, including the type of fruit or vegetables, and the nature and composition of the heavy ingredien It is imperative to emphasize that the findings presented in this study are based on thorough analyses of okra, grapes, dates, tomatoes, and insecticide samples. We employed the most advanced analytical techniques to ensure the accuracy and reliability of our data.

4. Results

In this detailed study, we employed cutting-edge technology, the atomic absorption spectrum analyzer (AAS), to investigate the effects of various manufacturing processes and treatments on samples of okra, grapes, dates, and tomatoes. Our main objective was to assess the extent to which these processes could reduce or concentrate heavy elements present in the studied samples to initiate the investigation, we subjected the samples to two different washing methods: water-only washing and washing with 2% citric acid solution. Additionally, we tested the effects of diluted 2% citric acid on the samples. Subsequently, we examined the samples after subjecting them to processes such as manufacturing boiling at temperatures exceeding 100°C, solar and industrial drying, as well as the concentration of tomatoes and passage through heavy materials.

The use of the AAS proved invaluable in reading the transaction results on the studied samples, revealing significant reductions in the remaining percentage of heavy elements after the processing and manufacturing procedures. Throughout the course of the examination, we observed a gradual decrease in the concentration of heavy elements in the grape, okra, date, and tomato samples over specific time intervals. The ban period for okra crops extended two weeks, while grapes were examined over three weeks, and dates and tomatoes were studied for seven days.

It is worth noting that these heavy element contaminants are often a consequence of pollution from sources like car emissions and factories situated near farms. Moreover, soil and water pollution resulting from environmental pollutants can contribute to these issues.

Our findings indicated that the concentration of heavy elements during the pesticide concentration period led to the corrosion of these elements. Specifically, cadmium, arsenic,

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and lead elements exhibited dramatic and gradual declines during all stages of pesticide decomposition, particularly after sample processing. Notably, the washing

Treatments using water, vinegar acid diluted with water, and 2% concentrated citric acid played a significant role in reducing heavy element concentrations.

The effectiveness of vinegar acid was particularly prominent, followed by grape samples. Meanwhile, citric acid demonstrated its strong capability in eliminating heavy elements in okra, dates, and tomato samples. We discovered that the efficacy of heavy metal removal was influenced by various factors, including the concentration of acids used in processing (vinegar acid and steric), as well as the pH levels and duration of material processing.

Our study's results align with previous research conducted by **Food and Agriculture 2021).**further supporting the validity and significance of our findings.

Table 2: shows the low concentrations of heavy elements in the Okra and grape samples with all the manufacturing processes and treatments carried out on the samples:

NO	Samples / Okra				Samples / Grapes			
	Samples	**Pb**	**Cd**	**As**	**Samples**	**Pb**	**Cd**	**As**
1	Control: Without any treatment	4.58	2.74	3.58	Control: Without any treatment	0.29	0.69	0.86
2	Sample washed with water before cutting	1.29	2.16	1.29	Sample washed with water	0.27	0.65	0.25
3	Sample washed with water after cutting	0.39	0.45	0.36	Sample washed with water after being treated with NaOH (0.5%) solution	0.26	0.62	0.22
4	Sample washed with citric acid solution2% before cutting	1.22	3.02	1.01	Sample washed with water after being treated with NaOH (0.5%) and sodium metabisulfite solutions	0.24	0.47	0.18
5	Sample washed with citric acid solution2% after	0.32	0.34	0.11	Sample washed with citric acid solution2%	0.57	0.48	0.20

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	cutting							
6	Sample washed with acetic acid solution 2% before cutting	3.06	2.22	3.26	Sample washed with citric acid solution2% after being treated with Noah (0.5%) solution	0.33	0.71	0.17
7	Sample washed with acetic acid solution 2% after cutting	1.28	0.63	0.97	Sample washed with citric acid solution2% after being treated with NaOH (0.5%) and sodium metabisulfite solutions	0.26	0.39	0.14
8	After blanching for 3 min at 100℃, cooling and packaging	ND	ND	ND	Sample washed with acetic acid solution 2%	0.27	0.64	0.25
9	---------	--------	--------	--------	Sample washed with acetic acid solution 2% after being treated with NaOH (0.5%) solution	0.16	0.44	0.12
10	---------	--------	--------	--------	Sample washed with acetic acid solution 2% after being treated with NaOH (0.5%) and sodium metabisulfite solutions	0.08	0.37	0.08
11	--------	--------	-------	-------	Sample after conventional drying or sun drying	ND	ND	ND

ND/Not detectable

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Conclusion

This comprehensive study delved into the impact of diverse manufacturing processes and treatments on the levels of heavy elements found in fruits and vegetables. Our examination focused on the samples of okra, grapes, dates, and tomatoes, aiming to evaluate the effectiveness of different processing techniques, including washing, peeling and high-temperature concentration, drying, and boiling, in reducing heavy element concentrations.

The experimental methodology adhered to strict protocols, ensuring precise and accurate results. Each sample underwent meticulous water-only washing and subsequent treatments with 2% citric acid and acetic acid. The grape samples were uniquely treated with alkaline solutions. Additionally, tomatoes and dates underwent concentration processes, while all samples underwent drying as part of the overall treatment regimen.

The findings unveiled that the efficiency of these processing methods in reducing heavy element levels varies significantly, influenced by factors like the fruit or vegetable type, heavy element nature, and its degradal under different treatments. Notably, the re obtained in this study were based on thorough analyses of okra, grapes, dates, tomatoes, and insecticide samples, employing state-of-the-art analytical techniques for reliability.

Furthermore, we explored the effects of manufacturing processes and treatments on the samples using atomic absorption spectrum analysis (AAS). The outcomes demonstrated substantial reductions in heavy element concentrations after processing and manufacturing procedures. Over time, the concentrations of heavy elements gradually decreased in the grape, okra, date, and tomato samples.

Importantly, the presence of heavy element contaminants is often linked to pollution from sources such as vehicle emissions, nearby factories, and environmental pollutants in soil and water. The study confirmed that pesticide concentration periods led to the corrosion of heavy elements, with cadmium, arsenic, and lead showing significant declines during pesticide decomposition, especially after sample processing.

Moreover, the effectiveness of various washing treatments played a vital role in reducing heavy element concentrations. Vinegar acid exhibited noteworthy

efficiency, followed by grape samples, while citric acid proved highly effective in eliminating heavy elements in okra, dates, and tomato samples.

The success of heavy metal removal was influenced by multiple factors, including acid concentration, pH levels, and processing duration. These findings align with previous research, corroborating the significance of our study.

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