

ICP-MS Assessment of Heavy Metals in Several Varieties of Raisins (*Vitis vinifera* L.) from Quetta, Pakistan: Food Safety Implications

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Abstract

This study aims to assess heavy metals in dried fruit raisins because safety concerns arise when heavy metals from anthropogenic and geogenic sources enter the agricultural system through soil, water, and atmospheric deposition, bioaccumulate in food crops, and ultimately reach the human body through dietary ingestion. For this purpose, five varieties of raisins were purchased from the local markets in Quetta City, Pakistan, and transported to the laboratory for analysis of the three potentially toxic and three essential metals, lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), and arsenic (As), using advanced ICP-MS technology. *Vitis vinifera* L., commonly called raisins, is referred to in the local language as Black, Artavi, Munakka, Gardak, and Shond khani; these were dried, converted into a fine powder, and subjected to heavy-metal analysis. Results showed the mean concentration ranges of the elements Pb, Cd, Ni, Cu, Zn, and As in raisins were 0.1165-3.673ppm, 0.0080-0.1235ppm, 0.0077-0.0229ppm, 0.0333-0.1722ppm, 0.0989- 0.2623 ppm, and 0.0034- 0.0109 ppm, respectively. In all detected cases, Ni concentrations were below the detection limit in Black, Artavi, Munakka, and Seeds of Munakka raisins. All metal concentrations were in the permissible range recommended by FAO/WHO except Pb, which was detected at a relatively higher concentration in all the analyzed raisins, which may be related to the presence of Pb in soil and atmosphere. The high concentration of lead highlights the importance of regular and scientific measurements by state regulatory authorities that may minimize heavy metal contamination and its transfer into food crops, including electrostatic precipitators, baghouse filters, biofilters, phytoremediation, nano-amendment, and biochar, followed by the latest machine-learning (ML) models for continued monitoring to ensure the quality and safety of dry fruits.

Keywords: raisins (*Vitis vinifera* L.), heavy metals, inductively coupled plasma mass spectrometry

1. Introduction

Raisins (*Vitis vinifera* L.) are dried grapes used as a dry fruit worldwide in large quantities, as different sizes, colors, and varieties of grapes produce different sizes, colors, and varieties of raisins when processed [1]. Thompson seedless grapes produce the most common type of dark raisins. Black Corinth grapes produce smaller raisins, known as Zante currants, currants, or Corinthian raisins. White Muscat grapes produce Muscat or Golden raisins. The sweeter and softer variety of raisins is sultanas, which are produced from the seedless yellow grapes [2]. To avoid grape waste, dehydrating the grapes is an excellent way to preserve the fruit [3]. The top four raisin-producing countries are Turkey, the United States of America, China, and Iran.

In 2021, global raisin production was 1.4 million metric tons [4]. Raisins can be obtained by processing grapes, which generally involves pre-drying, drying, and post-drying phases. Drying processes affect raisin quality and sugar content [5]. They provide macronutrients, micronutrients, fiber, vitamins, minerals, sugars, and bioactive compounds such as polyphenols [6]. Polyphenols in the raisins, including quercetin, kaempferol derivatives, and phenolic acids, contribute to the antioxidant activity. When used as part of a balanced diet, these bioactive compounds and nutrients support overall health and protect cells against oxidative stress [7]. In both healthy and diabetic subjects, consuming raisins decreased glycaemic and insulinemic responses. Adult in vivo studies show that grapes and raisins are most effective at reducing the risk of type 2 diabetes. Grapes and raisins have a high level of anthocyanins; adenosine monophosphate-activated protein kinase is increased by it, and glucose uptake is increased in the adipose tissue and glucose production is reduced in the liver [8]. As raisins are beneficial for health, they reduce appetite and have a low-to-moderate glycemic index; consequently, they are a healthy snack. Their consumption reduces the risk of cardiovascular disorders (CVD), cancer, and Alzheimer's disease, benefits colon functioning, and maintains good oral health and pH due to their antibacterial activity [1].

The human body intakes both essential minerals and heavy metals, which occur in varying quantities in fruits [9]. Heavy metals are found naturally in rocks, water, and soil. Anthropogenic sources of heavy metals are mining, sewage discharge, industrial waste, pesticides, traffic, and combustion of coal-burning plants [10]. Heavy metal levels in fruits depend on environmental pollution from industrial waste. Other factors that influence heavy metal concentrations in fruits, including grapes, include fertilizers, pesticides, soil type, storage, harvesting, and transportation. Because heavy metals are toxic, they can disrupt the functions of the lungs, kidneys, liver, brain, and other organs. Acute or chronic effects depend on the exposure period and the amount of heavy metals consumed in fruits [11]. Pb, As, Cd, and Hg are the most toxic heavy metals because they have no biological role and the human body cannot eliminate or break them down [12].

This study focused on Balochistan province, Pakistan's main grape-producing region. An area of 13.8 thousand hectares is cultivated with an annual production of 46.5 thousand tons. Balochistan contributes 97% of Pakistan's grape production (GoP, 2007). The particular areas are Pishin, Killa Abdullah, Quetta, Killa Saifullah, Mastung, Zhob, and Kalat, where grapes are produced [13]. Pishin and Killa Abdullah contributed 51% of the area, and grape production accounted for about 69%, so they are called the heart of grapes and the leading districts in grape and raisin production [14]. Quetta is the main market for raisins, where local and imported raisins from Afghanistan, Iran, and China are available for commercial sale. This research aimed to determine and compare heavy-metal concentrations among different raisin varieties, compare them with permissible limits, and assess potential implications for food safety. Therefore, five different raisin varieties were sampled from Quetta markets and analyzed for six heavy metals using inductively coupled plasma mass spectrometry. Figure 1 shows the sampling area in Quetta in yellow.

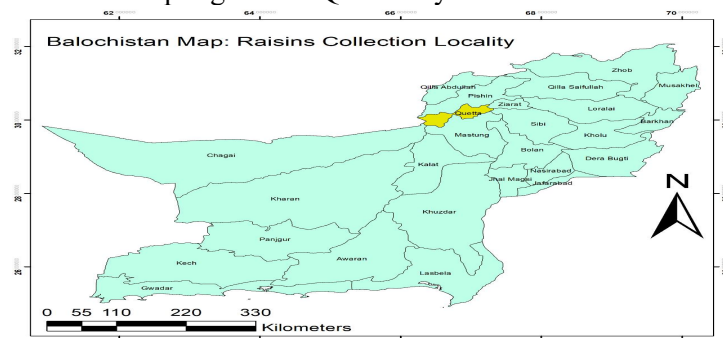


Figure 1: The yellow color shows Quetta city, where five different varieties of raisins were sampled. The map was plotted using QGIS 3.38.2.

2.0. Materials and Methods

2.1. Reagents and Solutions

The reagents consumed in the procedure were nitric acid (65%) and hydrogen peroxide (30%). All the chemicals consumed were of analytical reagent grade (Merck, Germany). We used high-purity deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$; Elgastat Maxima, UK) throughout the process. The glassware and other required materials were soaked in 20% nitric acid for 24 hours, then rinsed with deionized water.

2.2. Sample Collection and Preparation

Five different varieties of raisin samples, 300 g of each, were collected in polyethylene bags by a random selection procedure from the five different local markets of Quetta in March 2026. For each variety, three samples were collected and were not associated with specific brands. The raisins were purchased from the local markets of Quetta and originated from Pakistan, Afghanistan, Iran, and China. These five raisin varieties were brought to the Department of Chemistry laboratory, University of Balochistan, Quetta, Pakistan, and kept at 25°C for further analysis. The samples were then washed and rinsed with deionized water to remove dust, dirt, potential chemicals, and preservatives. All the raisins were seedless except Munakka raisins, which had seeds. The seeds were removed from the flesh part of the raisins, and both were analyzed. The raisin samples were dried in an oven at 80°C until they reached constant weight (almost 14 h) and became crispy. Afterward, the dried samples were ground into a fine powder using a mortar and pestle to obtain homogenized samples. The powdered samples were kept in polythene bags for analysis.

2.3. Acid Digestion and Analysis of Samples

The wet digestion method was used for acid digestion with analytical-grade reagents. 0.5 g of sample was taken in a conical flask. A mixture of 10mL of 65% nitric acid and 30% hydrogen peroxide (2:1) was added to the conical flask and heated on a hot plate under a fume hood to 80°C . When the organic part dissolved, the digestion was stopped. The digest was cooled for 5 minutes, filtered through Whatman No. 42 filter paper, and diluted to 25mL with deionized water [15]. Inductively coupled plasma mass spectrometry (Perkin Elmer, USA, NexION 2000, ICP-MS) was used to determine the concentrations of heavy metals, namely lead, cadmium, nickel, copper, zinc, and arsenic in five different varieties of raisins, viz., Black raisins (*Vitis vinifera* L.), Artavi raisins (*Vitis vinifera* L.), Munakka raisins (*Vitis vinifera* L.), Gardak raisins (*Vitis vinifera* L.) and Shond khani (*Vitis vinifera* L.) raisins collected from Quetta markets. The ICP-MS was equipped with an S20 series autosampler and a High Throughput System (HTF). A certified multi-element standard was used to prepare calibration standards and construct the calibration curve to determine heavy metals in the sample. To correct the background signals, the blank solution was analyzed. The internal standards were added to blanks, calibration standards, and the sample solutions to compensate for instrumental drift, matrix effects, and variations in sample introduction. The heavy metals were determined by using inductively coupled plasma mass spectrometry based on AOAC Official Method 2015.01, with appropriate modifications for the raisin matrix [16]. The operating conditions of the inductively coupled plasma mass spectrometry are shown in Table 1. Each sample was analyzed in triplicate by ICP-MS, and the results were reported as the mean and standard deviation.

Table 1. Operating parameters of the optimized ICP-MS instrument.

Parameters	Operating conditions
Model	Perkin Elmer NexION 2000
RF power	1500 W
Plasma gas flow	15L/min
Auxiliary gas flow	1.1 L/min
Nebulizer gas flow	1 L/min
Sample uptake rate	0.9 mL/min
Scan mode	Peak hopping
Dwell time	40 ms
Detector dead time	60 ns
Detector	Dual-Electron multiplier

2.4. Statistical Analysis

All the samples were examined in triplicate, and the results were expressed as mean and standard deviation. Statistical differences among the raisin varieties were assessed using one-way analysis of variance (ANOVA) in Microsoft Excel (version 16). A p-value of <0.05 was considered statistically significant.

3.0. Results and Discussion

Five different varieties of raisins, namely Black raisins, Artavi raisins, Munakka raisins, Gardak raisins, and Shond khani raisins, were sampled from local markets of Quetta and then studied for six heavy metals, which were Pb, Cd, Ni, Cu, Zn, and As. The raisins are produced locally in the province and also imported from Afghanistan, Iran, and China. Dry fruits, including raisins, are consumed in large quantities as a snack and may be polluted in various ways, including industrial waste, mining, traffic emissions, fertilizers, pesticides, climate effects, and soil characteristics. Inductively coupled plasma mass spectrometry (ICP-MS) was applied to determine the concentrations and calculate mean concentrations and standard deviations of Pb, Cd, Ni, Cu, Zn, and As, as summarized in Table 2. The mean ranges of elements I Pb, Cd, Ni, Cu, Zn, and As are 0.1165-3.673ppm, 0.0080-0.1235ppm, 0.0077-0.0229ppm, 0.0333-0.1722ppm, 0.0989-0.2623ppm and 0.0034- 0.0109 ppm, respectively. Figures 2-7 show the mean metal concentrations (ppm) with standard deviations. Maximum permissible limits recommended by the World Health Organization (WHO) and Food and Agriculture Organization (FAO) in fruits for Pb, Cd, Ni, Cu, Zn, and As are 0.1ppm, 0.1ppm, 0.5ppm, 0.3ppm, 20 ppm and 0.1 ppm, respectively [17].

Table 2. Mean concentration of heavy metals in five different varieties of raisin samples and Seeds of Munakka raisins from Quetta markets.

Samples	Metals (Mean $\pm$ STD*)					
	Pb(ppm)	Cd(ppm)	Ni(ppm)	Cu(ppm)	Zn(ppm)	As(ppm)
FAO/WHO	0.1	0.1	0.5	0.3	20	0.1
Permissible limits						
Black raisins	0.5033 $\pm$ 0.0063	0.0266 $\pm$ 0.0007	ND**	0.0834 $\pm$ 0.0026	0.1084 $\pm$ 0.0053	0.0047 $\pm$ 0.00025
Artavi raisins	0.2093 $\pm$ 0.0039	0.0080 $\pm$ 0.0001	ND**	0.0421 $\pm$ 0.0003	0.1339 $\pm$ 0.0055	ND**
Munakka raisins	0.1165 $\pm$ 0.0079	0.0106 $\pm$ 0.0003	ND**	0.0333 $\pm$ 0.0006	0.1150 $\pm$ 0.0012	0.0034 $\pm$ 0.00035
Gardak raisins	0.3776 $\pm$ 0.0073	0.0171 $\pm$ 0.0003	0.0077 $\pm$ 0.0007	0.0600 $\pm$ 0.0010	0.1485 $\pm$ 0.0057	0.0097 $\pm$ 0.00025
Shond khani raisins	0.3337 $\pm$ 0.0036	0.0126 $\pm$ 0.0006	0.0229 $\pm$ 0.0007	0.0517 $\pm$ 0.0012	0.0989 $\pm$ 0.0129	ND**
Seeds of Munakka	3.673 $\pm$ 0.015	0.1235 $\pm$ 0.0014	ND**	0.1722 $\pm$ 0.0020	0.2623 $\pm$ 0.0072	0.0109 $\pm$ 0.00015

STD*= standard deviation, ND**= not detected

3.1. Concentration of Pb in Different Samples of Raisins

Results showed that the seeds of Munakka had the highest concentration of Pb (3.673 $\pm$ 0.0150ppm) as determined in present study followed by Black raisins (0.5033 $\pm$ 0.0063ppm), Gardak raisins (0.3776 $\pm$ 0.0036ppm), Shond khani raisins (0.3337 $\pm$ 0.0036ppm) and Artavi raisins (0.2093 $\pm$ 0.0039ppm), while the Flesh of Munakka raisins had the lowest concentration of Pb element (0.1165 $\pm$ 0.0073ppm). All the raisins and Seeds of Munakka have a slightly higher concentration of Pb than the permissible limit recommended by FAO/WHO (2011) [17], which is 0.1ppm in the fruits. The mean concentration of Flesh of Munakka (0.1165ppm) and seeds of Munakka (3.673 ppm) is 1.895 ppm, which is above the permissible limit. Pb concentrations differed significantly among the raisin varieties ($p=8.37E-10$).

Pb has toxic effects (reproductive toxicity, mitochondrial dysfunction, oxidative stress, and neurotoxicity), is considered a hazardous element, and is one of the ten most hazardous elements for human health. Data from IHME (Institute for Health Metrics and Evaluation) in 2016 showed 54,000 deaths globally from Pb poisoning. Deaths from lead poisoning mostly occur in poor countries. 3% of ischemic heart disease cases, 3.1% of heart attacks, and 64% of primary idiopathic intellectual disabilities occur due to lead [18]. The high concentration of Pb in resin may be attributed to its persistent presence in the atmosphere, as it is an important part of the oil used in vehicles. Major sources include mining and smelting, battery manufacturing and recycling, industrial activities, electronic-waste processing, contaminated paints, and Pb-containing plumbing materials, which are also disposed of in soil and water used for crop irrigation. [19]. As heavy metal concentrations increase in soil, plants absorb more heavy metals [20]. The current results are similar to those of

McBride [20], who reported the highest concentrations of toxic metals in crops when he used sewage water to irrigate agricultural land. It was also reported that in Saudi Arabia, Pb concentrations exceeded limits in date palm samples due to various industries (china, plastics, wood, and cement) and illegal development in urban areas [15]. Atmospheric lead deposition on the edible portion of vegetables increases Pb concentration in crops, as reported in the current investigation [21].

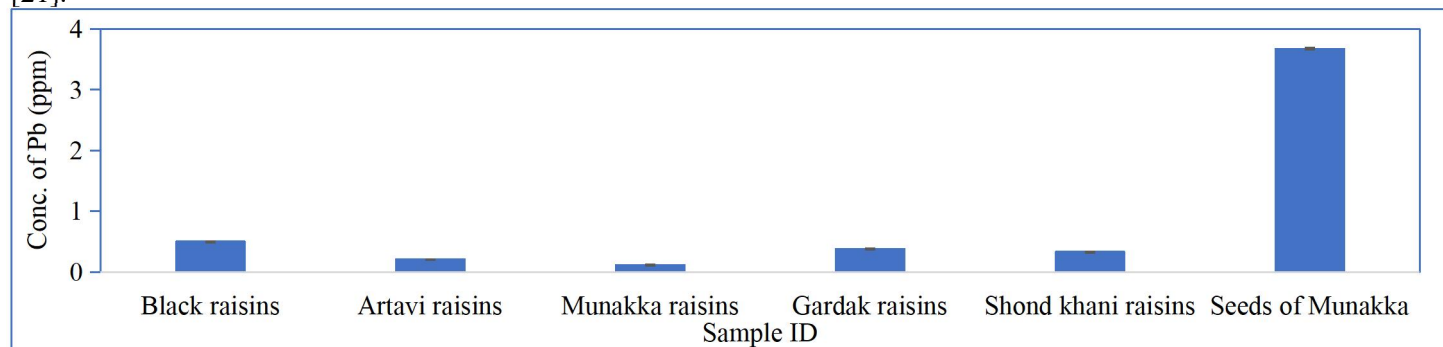


Figure 2: Concentration of Pb in five different varieties of raisins and Seeds of Munakka raisins.

3.2. Concentration of Cd in Different Samples of Raisins

ICPS analysis showed that Cd was present in all five investigated raisin varieties (Table 2). Results present that Munakka seeds accumulated the highest amount of Cd (0.1235 ± 0.0014 ppm), exceeding the FAO/WHO (2011) permissible limit. Still, the average concentration of Seeds of Munakka and Flesh of Munakka raisins had a value lower than the permissible limit followed by Black raisins (0.0266 ± 0.0007 ppm), Gardak raisins (0.0171 ± 0.0003 ppm), Shond khani raisins (0.0126 ± 0.0006 ppm) and Flesh of Munakka raisins (0.0106 ± 0.0003 ppm), while Artavi raisins (0.0080 ± 0.0001 ppm) had the least Cd than other varieties of raisins. The concentration of Cd in the different varieties of raisins was within the permissible limit reported by FAO/WHO (2011) [17], that is, 0.1 ppm in the fruits. No significant difference among raisin varieties was observed for Cd ($p=0.598$). These are safe for health with respect to Cd. The higher Cd concentration is due to plant-growing practices in soil containing sludge, sewage, or both, and the use of Cd-containing fertilizers [24].

Although the analyzed Cd concentration is within permissible limits, continued use may still pose health risks, as Cd is a non-essential trace metal that can accumulate progressively in the body and is widely present in the environment. The kidney is the primary target of Cd; when it accumulates, it damages renal tubular epithelial cells, causing kidney dysfunction and, ultimately, kidney failure. Long-term Cd exposure can cause renal cancer, proteinuria, and chronic kidney disease [22]. Cd can also accumulate in bone, where it disrupts bone metabolism and replaces calcium, causing osteoporosis and bone fractures [23]. Cd can also affect the lungs, central nervous system, and prostate [22].

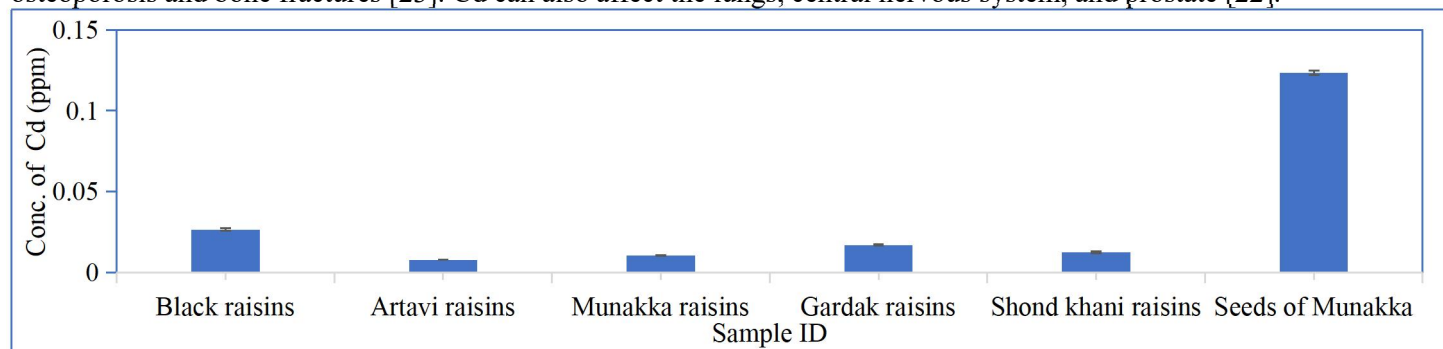


Figure 3: Concentration of Cd in five different varieties of raisins and Seeds of Munakka raisins.

3.3. Concentration of Ni in Different Samples of Raisins

The current study indicated low Ni concentrations in two varieties of raisins, while it was not detected in Black raisins, Artavi raisins, Munakka raisins, and Seeds of Munakka because concentrations were below the detection limit. Shond khani (0.0229 ± 0.0007 ppm) had a higher concentration than Gardak raisins (0.0077 ± 0.0007 ppm). The detected concentration of Ni in the two raisin varieties was below the permissible limit reported by FAO/WHO (2011) [17], which is 0.5 ppm in the fruits. No significant difference was observed among the raisin varieties statistically ($p=0.922$). Detailed research found that Ni concentrations exceeded the permissible limit recommended by FAO/WHO in Malayer, Iran. Ni levels were higher in fruits and vegetables in the North of South Atlantic. Nickel is an essential element that occurs abundantly in the Earth's crust, with an average concentration of approximately 75 $\mu\text{g/g}$.

However, excessive Ni exposure can cause damage to the spleen, kidneys, liver, and brain, as well as skin disorders such as vesicular eczema. Acute nickel exposure may also increase the risk of lung and nasal cancers [25]. Ni exposure has been associated with contact dermatitis, allergic reactions, and embryotoxic and nephrotoxic effects [26]. Nickel compounds are classified as carcinogenic to humans and can enter the cell nucleus. When nickel binds to nuclear proteins,

DNA, and RNA, it can induce DNA strand breaks and other genotoxic effects. It may also cause sister chromatid exchange, inhibit RNA synthesis, and alter mitotic activity [27]. Metal concentrations in vegetables depend on several factors, including the growth medium, soil texture, and soil composition [28]. In vineyard cultivation areas and raisin-production sites located near roads, Ni contamination may originate from diesel exhaust emissions, vehicle corrosion, and brake abrasion [29]. A study conducted in Sakarya, Turkey, reported that Ni concentrations in fruit samples were below the maximum permissible levels recommended by the World Health Organization (WHO). Areas with limited or no traffic generally exhibit lower levels of nickel contamination [30].

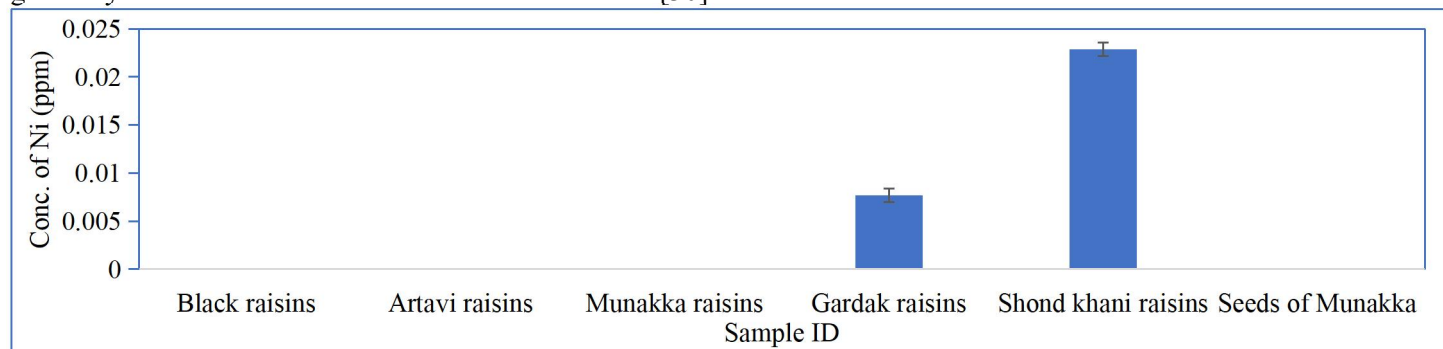


Figure 4: Concentration of Ni in five different varieties of raisins and Seeds of Munakka raisins.

3.4. Concentration of Cu in Different Samples of Raisins

Cu is an essential trace element that plays a vital role in the human body; therefore, it was selected to determine its concentration in raisin studies. The results showed that Munakka seeds had the highest copper concentration (0.1722 ± 0.0020 ppm). Black raisins had the second-highest Cu concentration (0.0834 ± 0.0026 ppm), followed by Gardak raisins (0.0600 ± 0.0010 ppm), Shond Khani raisins (0.0517 ± 0.0012 ppm), and Artavi raisins (0.0421 ± 0.0003 ppm). In contrast, the flesh of Munakka raisins had the lowest Cu concentration (0.0333 ± 0.0006 ppm) among all the raisin samples analyzed. All raisin samples exhibited copper concentrations below the permissible limit recommended by FAO/WHO (2011) [17], which is 0.3 ppm for fruits. No statistically significant difference was observed among the raisin varieties with respect to Cu concentration ($p = 0.636$). Manzoor et al. [24] quantified the concentrations of several metals, including Cu, in ten different dried fruits, including raisins, and reported a copper concentration of 0.018 ppm, which was within the permissible range recommended by FAO/WHO [17]. Therefore, the results of the present study closely agree with and are comparable to those reported by Manzoor et al. [24].

The total amount of Cu in the adult human body is approximately 100–200 mg, with most of it present as a component of proteins and enzymes. High concentrations of Cu are found primarily in the liver, brain, kidneys, heart, bones, and muscles. Cu can readily change its oxidation state, facilitating electron transfer and helping maintain cellular redox balance. It is also involved in several important physiological processes, including the synthesis of collagen, neurotransmitters, and melanin, as well as mitochondrial respiration [31]. However, excessive or prolonged Cu exposure can have adverse health effects. Chronic exposure to elevated copper levels may cause skin irritation and itching, conjunctival and respiratory tract irritation, gastrointestinal symptoms such as vomiting and abdominal pain, and loss of appetite. Excessive Cu accumulation may also promote oxidative stress and cellular damage. At sufficiently high concentrations, Cu can interfere with hemoglobin metabolism and contribute to anemia. Therefore, maintaining Cu homeostasis is essential, as both Cu deficiency and excessive Cu exposure can adversely affect human health [32].

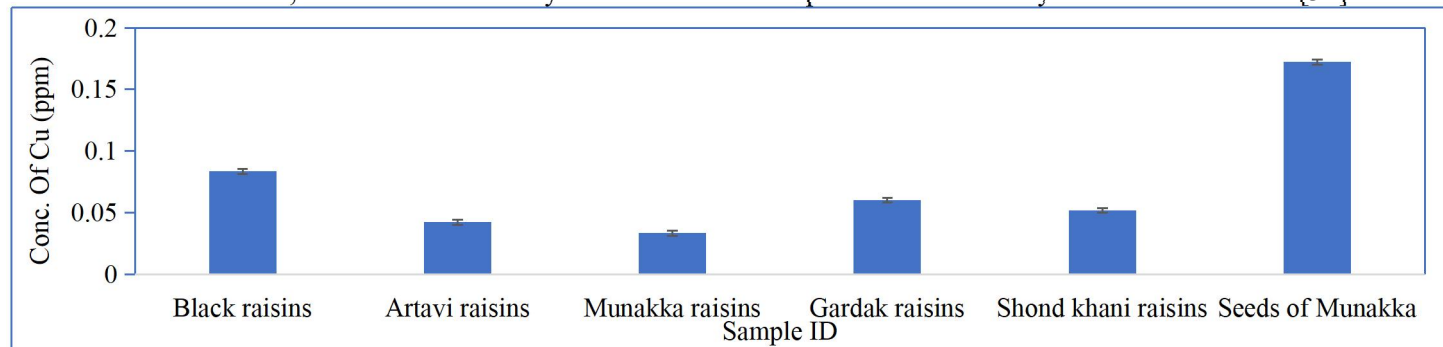


Figure 5: Concentration of Cu in five different varieties of raisins and Seeds of Munakka raisins.

3.5. Concentration of Zn in Different Samples of Raisins

The analysis of all raisin samples revealed that the seeds of Munakka had the highest Zn concentration (0.2623 ± 0.0072 ppm), followed by the flesh of Munakka raisins (0.1550 ± 0.0012 ppm), Gardak raisins (0.1485 ± 0.0057 ppm), Artavi raisins (0.1339 ± 0.0055 ppm), and Black raisins (0.1084 ± 0.0053 ppm). In contrast, Shond Khani raisins exhibited the lowest Zn concentration (0.0989 ± 0.0129 ppm). The Zn concentrations in all raisin samples were within the permissible

limit reported by FAO/WHO (2011) [17], which is 20 ppm for fruits. A statistically significant difference was observed among the raisin varieties with respect to Zn concentration ($p = 4.61 \times 10^{-10}$).

Khalid et al. [36] investigated the phytochemical composition and elemental profiles of six different raisin varieties (Haita, Sundar Khani, Kishmishi, Tour, Pahari, and Sahibi) from Balochistan Province. They reported the highest Zn concentration in Pahari raisins (5.42 ppm) and the lowest concentration in Kishmishi raisins (2.40 ppm). In comparison, the Zn concentrations observed in the present study were considerably lower than those reported by Khalid et al. [36]. Zn is the 24th most abundant element in the Earth's crust and is an essential element for humans, animals, microorganisms, and plants [33]. It occurs naturally in water, air, and soil. Anthropogenic activities, including the application of sewage sludge, fertilizers, and agrochemicals, can increase zinc release and accumulation in the environment. The average concentration of zinc in soil is approximately 55 $\mu\text{g/g}$, although it varies with geological and environmental conditions. Zn is also released into soils through rock weathering. Zn is an essential micronutrient for plants and plays important roles in carbohydrate and protein metabolism, membrane function, and plant defense against pathogenic attacks [34]. At the cellular level, zinc is involved in numerous biochemical and physiological processes across living organisms. In humans, zinc is essential for normal immune function and overall growth and development. Both inadequate and excessive zinc intake can adversely affect human health. Prolonged inadequate dietary zinc intake can impair growth and development, while zinc deficiency may adversely affect the skeletal, central nervous, epidermal, reproductive, and immune systems [35].

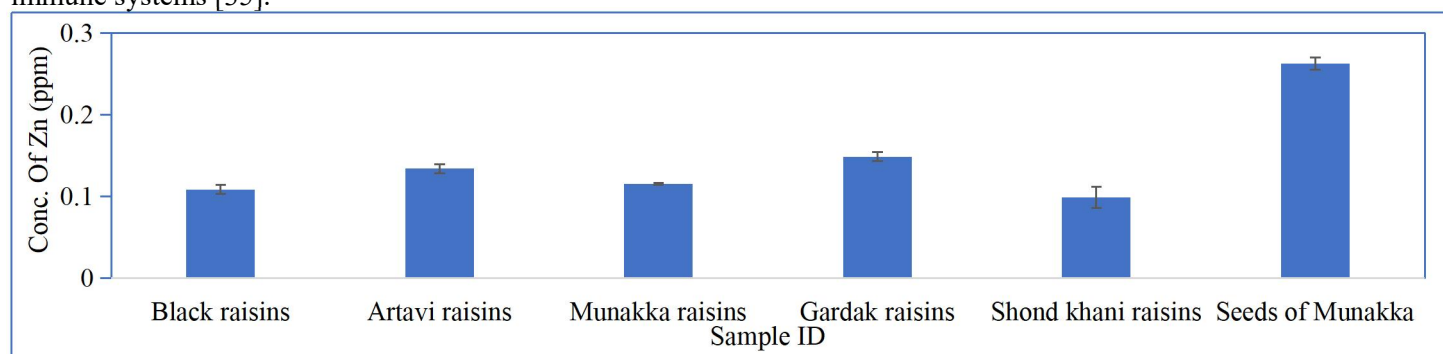


Figure 6: Concentration of Zn in five different varieties o raisins and Seeds of Munakka raisins.

3.6. Concentration of As in Different Samples of Raisins

In the present study, arsenic concentrations were below the detection limit in Artavi and Shond Khani raisins. The highest arsenic concentrations were detected in the Seeds of Munakka raisins (0.0109 ± 0.00015 ppm) and Gardak raisins (0.0097 ± 0.00025 ppm), followed by Black raisins (0.0047 ± 0.00025 ppm). The lowest detectable arsenic concentration was observed in the Flesh of Munakka raisins (0.0034 ± 0.00035 ppm). The arsenic concentrations in all raisin samples were within the permissible limit reported by FAO/WHO (2011) [17], which is 0.1 ppm for fruits. No statistically significant difference was observed among the raisin varieties with respect to arsenic concentration ($p = 0.768$).

Arsenic is a toxic metalloid that exhibits properties of both metals and non-metals and is considered a non-essential toxic element, similar to lead (Pb), chromium (Cr), cadmium (Cd), and mercury (Hg) [37, 38]. Arsenic originates from biogenic, geogenic, and anthropogenic sources. Major anthropogenic and environmental sources include fossil fuel combustion, fungicide and herbicide use, mining activities, volcanic eruptions, wood preservatives, and arsenic-containing animal feed additives [39]. Research has confirmed the carcinogenic effects of arsenic, while other adverse health effects include hearing loss, cardiovascular disease, diabetes, neurobehavioral and neurological disorders, respiratory disorders, anemia, developmental abnormalities, and adverse reproductive and pregnancy outcomes [40, 41]. The measured arsenic concentration generally represents total arsenic. It does not distinguish among its different chemical species or oxidation states, particularly inorganic arsenic species such as arsenite [As(III)] and arsenate [As(V)]. Fang et al. [42] determined the concentrations of arsenic and nine other metals in Thompson seedless raisins collected from Turpan City, China, using graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Arsenic concentrations were below 0.007 ppm in all samples, below the permissible limit of 1 ppm reported for Singapore, Malaysia, and Australia and the relevant WHO guideline. Therefore, the concentrations reported in this study closely agreed with those reported by Fang et al. [42].

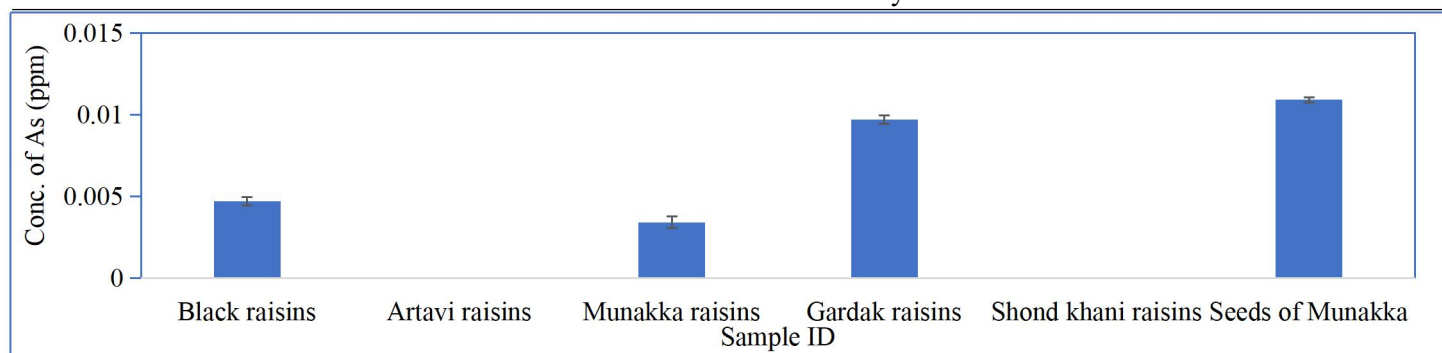


Figure 7: Concentration of As in five different varieties of raisins and Seeds of Munakka raisins.

4. Conclusion

In the present study, six metals, Pb, Cd, Ni, Cu, Zn, and As, were determined by inductively coupled plasma mass spectrometry (ICP-MS) in the five different varieties of raisins, Black raisins or Kala kishmish, Artavi raisins, Munakka raisins, Gardak raisins, and Shond khani raisins collected from Quetta markets. The findings demonstrated substantial variation in elemental concentrations among the investigated raisin varieties, indicating differences in their elemental profiles and the potential sources of contamination. Metal concentrations were within the permissible range recommended by FAO/WHO (2011), except for lead, which was higher in all raisin samples. Comparison with established permissible values also showed that certain metals warrant particular attention from a food-quality and food-safety perspective. Metal concentration variations were attributed to the growing medium, soil type, environment, agrochemical use, wastewater irrigation, and raisin processing. Higher lead concentrations in all samples emphasize the need for continued monitoring to ensure food quality and safety. Further investigations integrating dietary intake, potential exposure assessment, and bioaccessibility would provide a more comprehensive understanding of the potential food-safety implications of heavy-metal exposure through raisin consumption. Advanced technologies are recommended to remediate the metal; machine-learning (ML) models offer an alternative by learning nonlinear relationships between input variables and remediation outcomes, enabling prediction of lead removal efficiency, adsorption capacity, contaminant mobility, and optimal treatment conditions. Emerging technologies such as Machine Learning (ML), Internet of Things (IoT), and Artificial Intelligence (AI) may support rapid detection of heavy-metal contamination in foods, including raisins, as well as real-time data collection and food-safety assessment. Together with X-ray-based techniques, they may enable sensitive, non-destructive screening. Recent studies highlight the potential of machine learning (ML) for heavy-metal remediation. Integrating ML with Explainable Artificial Intelligence (XAI) can improve the interpretability of lead contamination prediction, identify key factors affecting lead removal, and optimize efficient and sustainable remediation strategies.

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Authors' Contributions

All the authors made significant contributions to the study. Najeeb Ullah conducted experiments and prepared the initial Draft. Attiq-Ur-Rehman conceived and designed the study. Naqeeb Ullah arranged the chemicals and lab facilities. Sami Ullah interpreted data and prepared the Draft. Ghulam Mustafa Khan reviewed and edited the Draft.

Conflict of Interest: The authors declare no conflict of interest.

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