RESEARCH

United States Grown and Imported Rice on Sale in Las Vegas: Metal(loid)s Composition and Geographic Origin Discrimination

Desta Woldetsadik[1,2] · Douglas B. Sims[2] · Mark C. Garner[2] · Amanda C. Hudson[2] · Joshua Monk[2] · Bethany Braunersrither[2] · Whitney Nyamedea Adepa Sunshine[2] · Lovely Warner-McRoy[2] · Shaezeen Vasani[2]

Abstract

Concentrations of metal(loid)s, Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Se, Sr, V and Zn, were determined in rice on sale in Las Vegas. The rice samples were grown in five different countries, the USA, Thailand, India, Pakistan, and Bangladesh. The elemental concentrations in rice grain were determined using inductively coupled plasma mass spectrometry (ICP-MS) following hot block-assisted digestion. The accuracy of the laboratory procedure was verified by the analysis of rice flour standard reference material (NIST SRM 1568b). The mean metal(loid) contents in rice of various geographic origins were 3.18–5.91 mg kg^{-1} for Al, 0.05–0.12 mg kg^{-1} for As, 3.64–41 µg kg^{-1} for Cd, 5.11–12 µg kg^{-1} for Co, 0.12–0.14 mg kg^{-1} for Cr, 1.5–1.91 mg kg^{-1} for Cu, 3.04–4.98 mg kg^{-1} for Fe, 4.2–10.4 mg kg^{-1} for Mn, 0.21–0.41 mg kg^{-1} for Ni, 0.02–0.07 mg kg^{-1} for Se, 0.68–0.88 mg kg^{-1} for Sr, 3.64–5.26 µg kg^{-1} for V, and 16.6–19.9 mg kg^{-1} for Zn. respectively. The mean concentration of As in US rice was significantly higher than in Indian, Pakistani, and Bangladeshi rice. On the other hand, it was found a significantly low mean level of Cd in US-grown rice. It was also found that the concentrations of metal(loid)s in black and brown rice on sale in Las Vegas were statistically similar, except for Mn and Se. The geographic origin trace-ability of rice grain involved the use of ICP-MS analysis coupled with chemometrics that allowed their differentiation based on the rice metal(loid) profile, thus confirming their origins. Data were processed by linear discriminant analysis, and US and Thai rice samples were cross-validated with higher accuracy (100%). This authentication quickly discriminates US rice from the other regions and adds verifiable food safety measures for consumers.

Keywords Rice · Metal(loid)s · United States · Las Vegas · Geographic origin discrimination · LDA

Introduction

Rice is the seed of a monocot plant, *Oryza sativa* L., from the Poaceae family. It is a staple food for half of the earth's population. Among the world's most important grains, rice is second after maize. Global rice production is estimated to be 508.7 million metric tons [1]. Most of the world's rice (75%) is transplanted under flooded conditions, while the remainder is direct-seeded [2]. In the 2021/22 fiscal year, Americans and US residents consumed 14.5 kg of rice per

✉ Desta Woldetsadik
  destowol@yahoo.com; desta.woldetsadik@wu.edu.et

✉ Douglas B. Sims
  douglas.sims@csn.edu

  Mark C. Garner
  mark.garner@csn.edu

  Amanda C. Hudson
  amanda.hudson@csn.edu

  Joshua Monk
  joshua.monk@csn.edu

  Bethany Braunersrither
  bbraunersrither@gmail.com

  Whitney Nyamedea Adepa Sunshine
  sunshinesika@yahoo.com

  Lovely Warner-McRoy
  Lovely576825@gmail.com

  Shaezeen Vasani
  shaezeenv@gmail.com

1 Department of Soil and Water Resources Management, Wollo University, Dessie, Ethiopia

2 Present Address: College of Southern Nevada, Las Vegas, Nevada, USA

capita [3]. In the USA, rice is cultivated in five states, but the USA must also import a large amount of rice from Asian countries, including Thailand, India, Pakistan, and Bangladesh every year to meet consumption demands [4]. Rice is an important source of both essential and potentially toxic elements [5]. Selected elements, including Cu, Fe, Mn, Se, and Zn, are responsible for the synthesis of several enzymes and gene expression regulation [6–8]. Other elements, such as As and Cd, are considered toxic, posing a health risk to humans [9, 10].

Some rice-growing regions command a premium price in the world market and are vulnerable to economic adulteration and mislabelling. For this reason, cultivation area and rice cultivar are crucial factors in market prices [11]. In this sense, consumers' interest in foods with traceable origins and geographic indication status is growing, and robust analytical tools are necessary to authenticate them [11–13]. Food safety monitoring programs require the authenticity of the origin of food to be tracked. Market regulations have been introduced in several countries to guarantee food safety [14, 15]. In 2009, the US House of Representatives passed the Food Safety Enhancement Act (HR2749 RS) requiring the disclosure of full information regarding the geographical origin of foods grown in the USA or foods intended for import into the USA [16].

However, there is still a lack of scientific information to ensure the implementation of safety regulations. Previous studies widely evidenced and recognized that the multi-element composition of rice reflects the soil composition and agro-climates in which it is grown and, thus, could be used as an indicator of its geographical origin [11, 12, 17]. However, the traceability of food depends not only on reliably measured data but also on appropriate chemometric data-processing methods such as principal component analysis (PCA) and linear discriminant analysis (LDA) [17]. Because rice is a newly emerging crop in terms of cultivation in the USA, it is reasonable to verify the quality and geographic origins of US-grown rice using analytical methods in combination with statistical analysis. However, to the best of our knowledge, no studies have been previously reported on the geographic discrimination of rice on sale in Las Vegas. Thus, the aims of this study were to determine the metal(loid) profile of rice on sale in Las Vegas and to discriminate US-grown rice from imported rice grains based on the metal(loid) profile coupled with the LDA model.

Materials and Methods

Chemicals and Reagents

Nitric acid (69% HNO_3) was obtained from J.T. Baker (Center Valley, PA, USA). The wash-nitric acid blank and tune solution for ICP-MS were obtained from Agilent Technologies (Santa Clara, CA, USA). An ICP-MS grade solution containing 1000 μg mL^{-1} single-element from CPI International (Santa Rosa, CA, USA) was used to prepare the calibration curve. An internal standard solution (Li, Sc, Y, In, Tb, and Bi) from CPI International (Santa Rosa, CA, USA) was also used during the ICP-MS analysis. Rice flour (NIST-1568b) certified reference material (CRM) used for method validation was obtained from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

Collection of Rice Samples

A total of 54 rice samples were purchased from stores in Las Vegas, USA. Based on the package label information, these samples represented 8 countries (USA (20), Thailand (12), India (7), Bangladesh (6), Pakistan (6), Argentina (1), Spain (1), and Sri Lanka (1)). For milling, 100 g of individual samples was taken and powdered using ADL multi-purpose grinder. The samples were packed in polyethylene bags and stored at room temperature prior to digestion.

Sample Digestion and Analyses

Rice samples were digested using the Hot Block digestion method (EPA Method 3050b). Briefly, 0.25 g of rice flour sample was placed in a 50 ml polyethylene vial (Environmental Express, Charleston, SC) followed by 5 ml of concentrated HNO_3. The vials were placed in a heating block (Environmental Express, Charleston, SC) and loosely covered with caps then heated at 95 °C for 2 h. After cooling to room temperature, 5 ml of HNO_3 was added and heated until the disappearance of brown fume appeared. Then, after cooling to room temperature, 2 ml of distilled water and 3 ml of 30% H_2O_2 were added and heated and 30% H_2O_2 was added and heated again until effervescence subsided. After cooling, the digestate was made into 20 ml with distilled water and filtered using a 0.22-μm pore size syringe filter. Elemental analyses (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Se, Sr, V, and Zn) were carried out by using an Agilent 7850 ICP-MS (Agilent Technologies, CA, USA) equipped with a Peltier-cooled quartz spray chamber (Scott type), a quartz torch (2.5 mm i.d.), and a low flow concentric nebulizer (0.2 mL min^{-1}). Each sample was analyzed in triplicate. The ICP-MS operating conditions are presented in Tables S1 and S2. The detection limit (DL) and quantification limit (QL) were calculated as the concentration that provided 3 and 10 times the signal of the blank for each element, respectively. Method DLs are given in Table S3.

Quality Control and Assurance

For quality control and quality assurance purposes, new polyethylene vials were used throughout the sample digestion

and preparation steps. The reagents used for the preparation of the calibration standard solutions and treatments were analytical grades. Internal standards were automatically added using the ICP-MS instrument. The mean values and RSD for the elements in the CCV-100 solution are 98.9–102 and 0.5–1.4 µg L^{-1}, respectively. The CRM was prepared and analyzed in the same way as the samples, observing good agreement between certified and analyzed values with recovery values ranging from 89 to 117% for Al, As, Cd, Cu, Fe, Mn, Se, and Zn. Rice flour samples were also spiked with Ag, Co, Cr, Ni, Sr, and V for recovery tests. The recoveries of the six elements were ranged from 80 to 121%.

Statistical Analysis

Data were analyzed using Statistical Package for Social Sciences (SPSS) version 23 and XLSTAT (Addinsoft, NY, USA). The normal distribution and homogeneity of variance were tested using Kolmogorov-Smirnov's and Levene's tests, respectively. In cases of non-normal distribution, the data were log-transformed. Whenever data/transformed data satisfied these assumptions, the mean concentrations of analyzed elements were statistically evaluated by analysis of variance (ANOVA) or Student's t test. The Kruskal-Wallis test was used in combination with Dunn's multiple comparisons otherwise. Linear discriminant analysis (LDA) was used to discriminate the geographic origins of rice grains. LDA is a supervised classification method that maximizes the variation between groups and minimizes variation within a group by creating new variables (discriminant functions), which are linear combinations of the original variables. Statistical significance was established at $p < 0.05$.

Results and Discussion

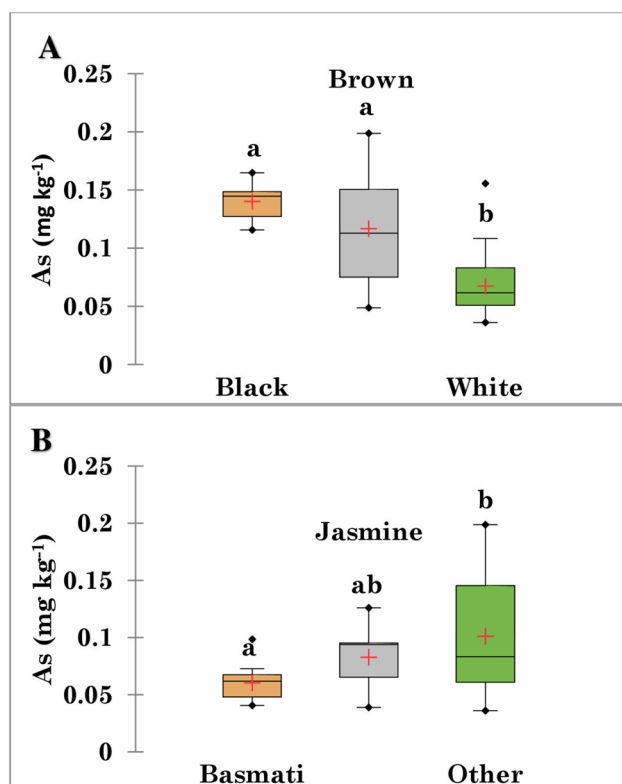### Metal(loid) Concentration in Rice

Aluminum

Aluminum is ubiquitous in the environment. Aluminum has no recognized biological function in humans [18]. Prolonged exposure to Al is related to neurodegenerative diseases such as Alzheimer's [19]. On average, an adult in the USA eats roughly 7–9 mg of aluminum per day [20]. Cereals are the main Al contributors [21]. In this study, US rice exhibited a significantly lower mean Al content (3.2 mg kg^{-1}) compared with rice from the other geographic origins. The mean Al concentrations were 5.4, 4.8, and 4.2 mg kg^{-1} in black, brown, and white rice, respectively (Fig. S1). Antoine et al. [21] found higher levels of Al in rice samples from Jamaica, with concentrations ranging from 6.1 to 23.4 mg kg^{-1} in white rice and 7.4 to 43 mg kg^{-1} in brown rice. The mean

values of Al for basmati and jasmine rice were 9.30 and 14.7 mg kg^{-1}, respectively (Fig. S1).

Arsenic

Arsenic is a metalloid and its presence in the environment is the result of both natural geologic processes and environmental pollution. Arsenic has been linked to a wide range of deleterious health impacts, including cancers [22, 23], diabetes [24], and cardiovascular diseases [25]. Furthermore, As exposure is also associated with elevated genotoxic effects [26]. Rice, a staple crop that is grown in paddy fields, may pose a particular health concern as it accumulates tenfold higher levels of inorganic arsenic (i-As), an established human carcinogen, than any other grain [27, 28]. The mean As concentrations in USA (103 µg kg^{-1}) and Thai (115 µg kg^{-1}) rice samples were significantly higher than concentrations found for Bangladesh, India, and Pakistan rice samples. Similarly, rice grown in some regions of the USA has been reported to have higher mean total As concentrations than rice grown in other geographic regions [27, 29], which may be related to the increase in As contamination in paddy soils. Likewise, a two-and-a-half-fold higher mean As concentration was obtained in US rice samples compared to Pakistani rice samples sold in Almadinah Almunawarah markets, KSA [30]. On the other hand, three individual rice samples from Argentina, Spain, and Sri Lanka exhibited As concentrations of 176 µg kg^{-1}, 314 µg kg^{-1}, and 50 µg kg^{-1}, respectively. For minimizing As exposure due to rice consumption, knowing where As is elevated in rice grains can help choose lower concentration grains based on growing regions [31]. A maximum residue limit (MRL) of 200 µg kg^{-1} is set for inorganic-arsenic (i-As) [32]. Although only total As concentrations were determined in this study, one white rice sample may only exceed the MRL if the i-As of this sample exceeds 63.6% of the total As. Moreover, all the analyzed rice samples contained total As concentrations far lower than the MRLs value stipulated by the Food Safety and Standards Authority of India (FSSAI) [33]. In fact, rice grown in the USA contains lower concentrations of i-As [27, 29].

The As content in rice also varies with color. In the present study, black and brown rice contained significantly higher concentrations than white rice (Fig. 1). Consistent with this, Chen et al. [34] reported that brown rice has two times higher level of As than white rice. Only recently, TatahMentan et al. [4] studied the toxic element contents of rice samples from various geographic origins, including the USA and China, and found that brown and black rice contained higher levels of As than white rice. In the case of white rice, the bran and germ (or most of it) are removed during polishing, whereas black and brown rice with the bran still intact may have a higher fiber content than white rice but also have higher As levels [4, 35]. Arsenic
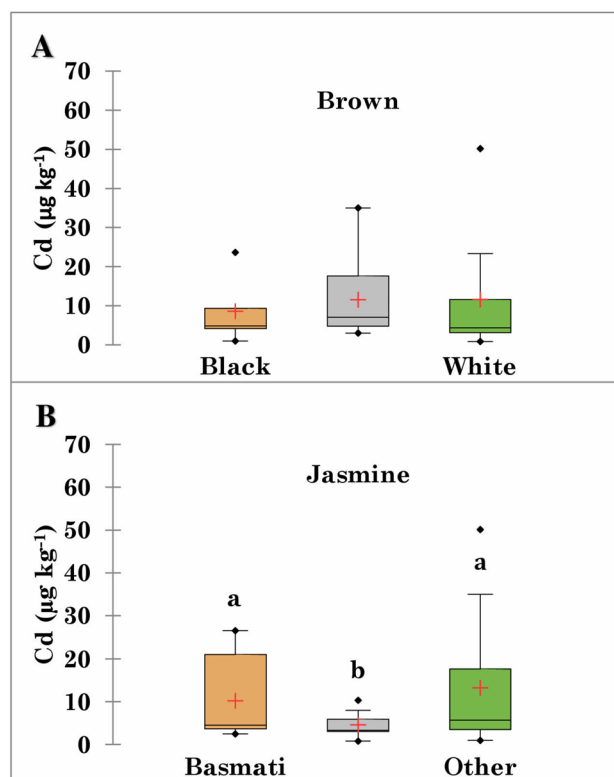
Fig. 1 Box plot of As concentration in rice samples based on (**A**) color and (**B**) brand. + indicates mean value; dash line indicates median value; bars represent the 1st and 3rd quartile

Fig. 2 Cd content in rice based on (**A**) color and (**B**) brand. + indicates mean value; dash line indicates median value; bars represent the 1st and 3rd quartile

accumulation also varies by brand. Basmati rice contained less As than rice samples under the "other" category (Fig. 1). On the other hand, basmati rice exhibited significantly similar As content to jasmine rice. This is not consistent with the results of Zavala et al. [36] who reported that basmati and jasmine rice exhibited higher As levels. Conversely, jasmine rice from Thailand had a higher mean As (130 µg kg^{-1}) compared with basmati rice from India and Pakistan (60 µg kg^{-1}) [37].

Cadmium

Cadmium is a toxic heavy metal and a carcinogenic environmental pollutant [38]. Food represents the major source of cadmium exposure pathway [39]. Long-term Cd exposure may be associated with bone defects, high blood pressure, and myocardial dysfunction [40]. Irrespective of rice varieties, the mean concentrations of Cd in rice on sale in Las Vegas ranged from 3.64 µg kg^{-1} (Pakistan) to 41 µg kg^{-1} (Bangladesh). The mean Cd concentrations in rice samples from the USA (5.33 µg kg^{-1}), Thailand (7.18 µg kg^{-1}), and Pakistan were significantly lower than those rice samples originating from Bangladesh and India (16.5 µg kg^{-1}). Similarly, several previous studies reported that the mean Cd

concentrations in Bangladeshi rice were the highest (88 µg kg^{-1}, [39]; 73 µg kg^{-1}, [41]). A far higher mean concentration of Cd, 750 µg kg^{-1}, in Bangladeshi rice samples was also observed by Kormoker et al. [42]. A particular concern from Cd exposure is infants; stricter standards are in place in the EU for Cd in processed baby foods (40 µg kg^{-1}) [43], and 100% of Bangladeshi rice samples failed this standard, making it unsuitable for use in making baby foods. The mean Cd concentration in rice from the USA was 5.33 µg kg^{-1}, which is considerably comparable with the value (6.2 µg kg^{-1}) reported by Rahman et al. [39]. While countries such as Argentina, Spain, and Sri Lanka have been less considered, the results presented were for single samples, and Cd concentrations were 4.8, 6.7, and 28.5 µg kg^{-1}, respectively. Shi et al. [31] established a global context for Cd in rice grain. They found that the Americas were typically low in cadmium, but the Indian sub-continent and certain regions of Bangladesh were universally elevated. The mean Cd concentrations in rice samples from five different geographic origins were well below the European ML of 200 µg kg^{-1} [43].

The mean Cd concentrations were 8.6, 11.5, and 11.6 µg kg^{-1} in black, brown, and white rice, respectively (Fig. 2). In a 2001 market survey on rice on the Swedish market, the

mean Cd concentration was similar between white (20 μg kg^{-1}) and brown (21 μg kg^{-1}) but the variation in Cd among geographic origins of rice was considerable, indicating the influence of soil, climatic, and management variables [37]. The mean concentrations of Cd in basmati and jasmine rice were 10.3 μg kg^{-1} and 4.64 μg kg^{-1}, respectively. Previously, Jorhem et al. [37] reported non-considerable variation in Cd between basmati (23 μg kg^{-1}) and jasmine (18 μg kg^{-1}) rice. Basmati rice from Pakistan contained remarkably higher Cd concentration than the concentration presented in the present study [44].

Cobalt

Cobalt is an essential oligo element, particularly as a constituent of vitamin B12 (cobalamine) and some metalloproteins; however, excessive exposure to this element causes goiter and reduced thyroid activity [45, 46]. For example, cobalt intoxication has been a well-documented cause of cardiomyopathy for over 50 years; however, it has mostly been known in the context of so-called Quebec beer drinkers' cardiomyopathy [47, 48]. Historically, Quebec beer drinkers' cardiomyopathy was characterized by congestive heart failure caused by the addition of small amounts of cobalt chloride as a foam stabilizer by certain breweries in Canada and the USA [47, 48]. Moreover, cobalt intoxication is an increasingly recognized and life-threatening problem associated with hip prostheses [49]. Yet Co is needed in trace amounts in cobalamine to avoid megaloblastic anemia [48]. In the present study, the mean Co concentration varied between 5.53 μg kg^{-1} (Bangladesh) and 11.9 μg kg^{-1} (Thailand), with a significant difference between Thai (12.0 μg kg^{-1}) and USA (6.52 μg kg^{-1}) rice. Similar lower concentrations were previously reported by Rahman et al. [39] and Shraim et al. [30]. Conversely, Naseri et al. [50] reported a range of mean Co concentrations (110–440 μg kg^{-1}) in domestic and imported rice from Iran. Black and brown rice contained significantly higher concentrations than white rice (Fig. S2). The mean content of white rice is somewhat lower than reported in other studies [5, 21]. The mean concentration of Co in jasmine rice (11.5 μg kg^{-1}) was about two times higher than in basmati rice (6.2 μg kg^{-1}) (Fig. S2).

Chromium

Chromium has high redox potential, and it can exist in various oxidation states, including the most important +3 (trivalent), and +6 (hexavalent) states [51]. Several studies have shown that exposure to hexavalent chromium [Cr (VI)] is associated with several types of cancer and is increasingly being recognized as a neurotoxicant [52]. On the other hand, Cr(III) is generally regarded as less toxic and is argued to be potentially therapeutic for type II diabetes [53]. In the

USA, Cr(VI) is released to the environment primarily from stationary point sources resulting from human activities, and these sources contribute an estimated 900–970 tons of Cr(VI) emissions per year [54]. In this study, mean Cr concentrations in rice on sale in Las Vegas varied from 0.117 (Thailand) to 0.140 mg kg^{-1} (India). Likewise, the mean Cr concentration in rice from the USA was 0.120 mg kg^{-1}. Naseri et al. [50] found an average of 0.47 mg kg^{-1} in Thai rice samples collected from retail stores in Shiraz, Iran. On the other hand, some studies have indicated excessive levels of Cr in rice from the wastewater-irrigated sites in India [55, 56].

Despite the non-statistical significance among black, brown, and white rice for Cr (Fig. S3), brown rice presented the highest mean concentration (0.131 mg kg^{-1}) followed by white rice (0.122 mg kg^{-1}). Likewise, a relatively lower mean Cr concentration (0.056 mg kg^{-1}) was obtained in the USA white rice samples sold in Brisbane, Australia [30]. Similarly, Jorhem et al. [37] reported a remarkably lower mean Cr concentration (0.008 mg kg^{-1}) for brown, white, and parboiled rice from the Swedish market study. Basmati rice presented the highest mean Cr content (0.141 mg kg^{-1}) against 0.118 mg kg^{-1} for jasmine and "other" rice brands.
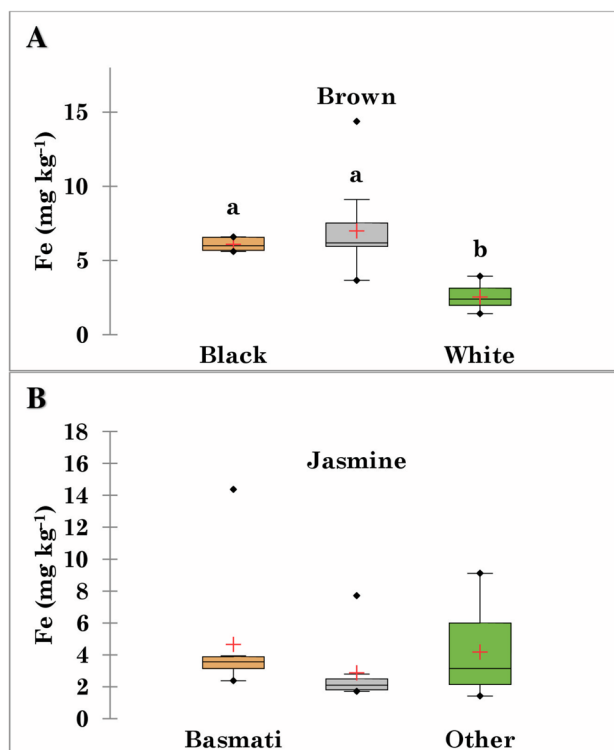
Copper

Copper is an essential trace element that is required by humans in several metabolic processes, including hemoglobin synthesis, iron oxidation, neurotransmitter biosynthesis, cellular respiration, and pigment formation [57, 58]. For adults, the recommended dietary allowance for Cu is 0.9 mg per day. Consequently, Cu deficiency is rare; however, the hematologic manifestations associated with Cu deficiency, such as anemia, osteoporosis, leukopenia, and neutropenia, are well documented [59]. The mean Cu contents in Indian (1.9 mg kg^{-1}) and Pakistani (1.8 mg kg^{-1}) rice on sale in Las Vegas were significantly higher than those found in Thai (1.5 mg kg^{-1}) and USA (1.5 mg kg^{-1}) rice. A relatively comparable mean Cu (1.01 mg kg^{-1}) concentration was found in US rice collected from Almadinah Almunawarah markets, KSA [30]. Conversely, the mean Cu concentration in US rice of the present study was about twofold lower than that reported by TatahMentan et al. [60]. Similarly, Shraim [30] found a mean Cu concentration of 4.4 mg kg^{-1} in US rice collected from Brisbane, Australia. Previous studies reported a lower mean Cu concentration in Bangladeshi rice [39, 41], which is comparable with the present study. The mean concentration of Cu in brown rice was significantly higher than that in white rice (Fig. 3). A recent study by TatahMentan et al. [60] showed that the mean Cu concentration in brown rice was nearly 1.4-fold higher than found in white rice. The Cu content in basmati rice differed significantly from jasmine (Fig. 3).
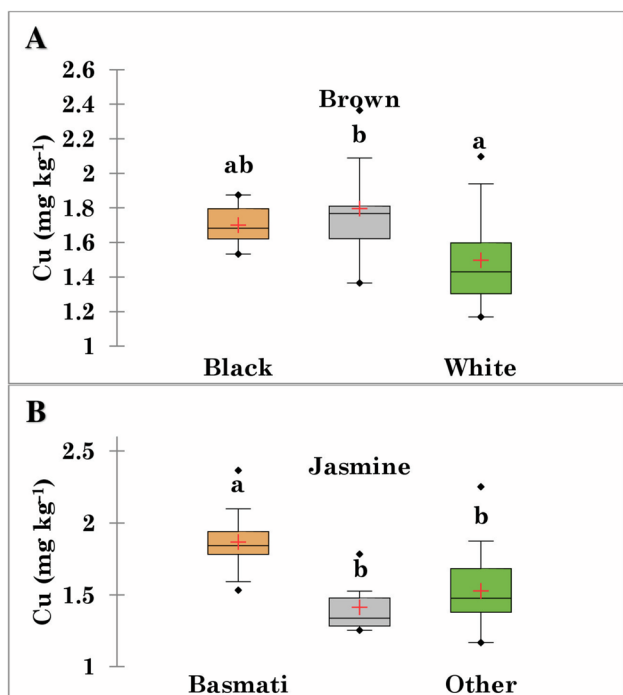
Fig. 3 Box plot of Cu concentration in rice samples based on (**A**) color and (**B**) brand. + indicates mean value; dash line indicates median value; bars represent the 1st and 3rd quartile

Fig. 4 Box plot of Fe concentration in rice samples based on **A** color and **B** brand. + indicates mean value; dash line indicates median value; bars represent the 1st and 3rd quartile

Iron

Iron deficiency is the most common nutritional deficiency. Globally, more than two billion people suffer from Fe deficiency annually [61, 62]. Iron deficiency and anemia are associated with impaired neurocognitive development and immune function in different life stages [63]. The mean concentrations of Fe in rice on sale in Las Vegas ranged from 3.0 mg kg^{-1} (Bangladesh) to 5 mg kg^{-1} (India). Iron was observed in lower concentrations ranging from 1.4 to 9.1 mg kg^{-1}, with a mean value of 4 mg kg^{-1} in US rice. These results agree with those obtained by Shraim [30] who reported a mean level of 3.3 mg kg^{-1} for Fe, in US rice samples collected from Brisbane, Australia. The literature is quite extensive for Fe in rice and reports concentrations between 1.75 and 47 mg kg^{-1} [30, 60, 64]. It is worth noting that regular rice consumption in different forms would cause Fe malnutrition among vegetarians. On the other hand, significant differences in the contents of Fe were observed among rice colors (Fig. 4). Likewise, the mean Fe concentration in brown rice was about fourfold higher than that in white rice [60]. Although genetic variations exist for Fe content in grains of rice germplasms, commonly grown rice varieties are poor sources of Fe [62]. However, when comparing the mean Fe concentration between basmati and jasmine rice, the values are very similar and showed no significant difference (Fig. 4). Dumitrascu et al. [65] also observed comparable Fe concentrations between basmati and jasmine rice.

Manganese

Manganese is an essential micronutrient that plays a primary role in the activation of several enzymes [7]. Because of its ubiquity in the environment, Mn deficiency is unlikely. The mean Mn contents in US (10.2 mg kg^{-1}) and Thai (10.4 mg kg^{-1}) rice on sale in Las Vegas were significantly higher than those found in Pakistani rice (4.2 mg kg^{-1}). On the other hand, relatively low Mn concentrations have been reported for US rice samples collected from Almadinah Almunawarah markets in KSA with a mean Mn concentration of 5.2 mg kg^{-1} [30]. Conversely, TatahMentan et al. [60] found an average of 15 mg kg^{-1} in rice samples cultivated in four states (California, Louisiana, Arkansas, and Texas) in the USA. The mean contents of black and brown rice samples were significantly higher than white rice. TatahMentan et al. [60] reported mean Mn concentrations of 11 mg kg^{-1} and 29.2 mg kg^{-1} for white and brown rice, respectively. Basmati rice had a significantly lower mean Mn content than the "other" category, whereas there was no significant difference between basmati and jasmine (Fig. S4).

Nickel

Nickel is generally not considered an essential nutrient for higher animals or humans because it lacks a clearly defined specific biochemical function [66]. Excessive exposure to Ni may cause oxidative stress in various organs in animals and humans, including liver and kidney damage [67, 68]. The mean Ni content is significantly lower in US rice (0.214 mg kg^{-1}) compared to Bangladeshi rice (0.362 mg kg^{-1}) and Indian rice (0.412 mg kg^{-1}), respectively. The mean Ni concentration in samples from the five geographic origins was below the ML set forth by the United Nations Food and Agriculture Organization and World Health Organization (FAO/WHO) [69]. Nickel concentrations in rice in the present study were comparable to the levels reported for Chinese and Spanish rice [70, 71]. On the other hand, relatively high Ni concentrations have been reported for US rice samples collected from Brisbane, Australia, with a mean Ni concentration of 1.93 mg kg^{-1} [30]. Conversely, nearly all rice samples collected from Almadinah Almunawarah markets in KSA contained no detectable Ni [30].

Figure S5 also compares the mean content of Ni among black, brown, and white rice. Rahman et al. [39] reported the highest mean Ni concentration in brown rice (0.268 mg kg^{-1}) compared to white rice (0.07 mg kg^{-1}). Kruskal-Wallis analysis showed that the Ni content was significantly similar among black, brown, and white rice. For Ni, basmati rice had a significantly higher Ni content than jasmine, whereas there was no significant difference between jasmine and "other" brands.

Selenium

Selenium is an essential constituent of many antioxidant enzymes such as glutathione peroxidase and selenoprotein P in humans and animals [72, 73]. The deficiency of this element has been associated with various clinical consequences including cardiovascular diseases, type 2 diabetes, and an increased risk of certain cancers [73, 74]. In fact, a trace quantity of Se is required to maintain good health in both animals and humans. The Institute of Medicine has set the Recommended Dietary Allowance for Se at 55 µg per day for adults [75]. Despite the importance of Se in promoting growth and maintaining healthy heart muscle, rice is scarcely investigated in terms of total Se content and Se speciation. In this study, the mean Se content in rice ranged from 0.02 (Bangladesh) to 0.07 mg kg^{-1} (India). The mean Se content in rice grown in the USA was 0.035 mg kg^{-1}, regarded as seriously low-selenium rice. There are factors that limit rice Se levels, including geochemistry, and soil composition [76].

According to Kelly et al. [77], rice grown in one of the recognized rice-growing regions in the USA (Arkansas) is characterized by relatively high concentrations of Se (0.125–0.4 mg kg^{-1}). Likewise, considerable regional diversity in Se concentrations in US rice was observed by Williams et al. [76]. On the other hand, Zhang et al. [78] analyzed Se content in rice grown in a Se-rich environment in China and reported that Se concentrations in rice were between 0.05 and 0.3 mg kg^{-1}.

For Se in rice grain, the difference between white and brown rice was non-significant (Fig. S6). The mean Se concentration in white rice observed in this study for US rice is nearly five times lower than the result of Williams et al. [76] who found a mean value of 0.180 mg kg^{-1}. Mean Se content in basmati rice was significantly higher than in jasmine rice (Fig. S6). The mean Se concentration found in this study for basmati rice is supported by Naeem et al. [79] who found mean levels from 0.04 to 0.05 mg kg^{-1}.

Strontium

Strontium is an alkali earth metal with no reported biological role in the human body [80]. The mean Sr contents detected differed significantly between Bangladeshi (0.68 mg kg^{-1}) and US rice (0.88 mg kg^{-1}). The mean Sr in brown rice was significantly higher than that in white rice (Fig. S7). The mean content of Sr in brown rice was 0.93 mg kg^{-1}, which was lower than in the previous study conducted by Antoine et al. [21]. On the other hand, the mean contents of basmati and jasmine differed non-significantly.

Zinc

Zinc is an essential component of the catalytic site or sites of at least one enzyme in every enzyme classification, which has a diverse range of functions, including the synthesis of nucleic acids and specific proteins [6]. The mean Zn concentrations in rice samples from India and Pakistan were significantly lower than Zn in Thai rice. The US rice had a mean Zn concentration of 18 mg kg^{-1}. This result is consistent with a recent study by TatahMentan et al. [60]. However, Zn concentrations in US rice were generally higher in this study than those by Shraim [30]. In this study, black and brown rice contained significantly higher Zn concentrations than white rice (Fig. 5). Similar results had been reported in US rice grown in California, Louisiana, Arkansas, and Texas [30]. They found that brown rice contained a 1.5-fold higher Zn concentration than white rice. Basmati rice contained significantly lower mean Zn than jasmine rice (Fig. 5).
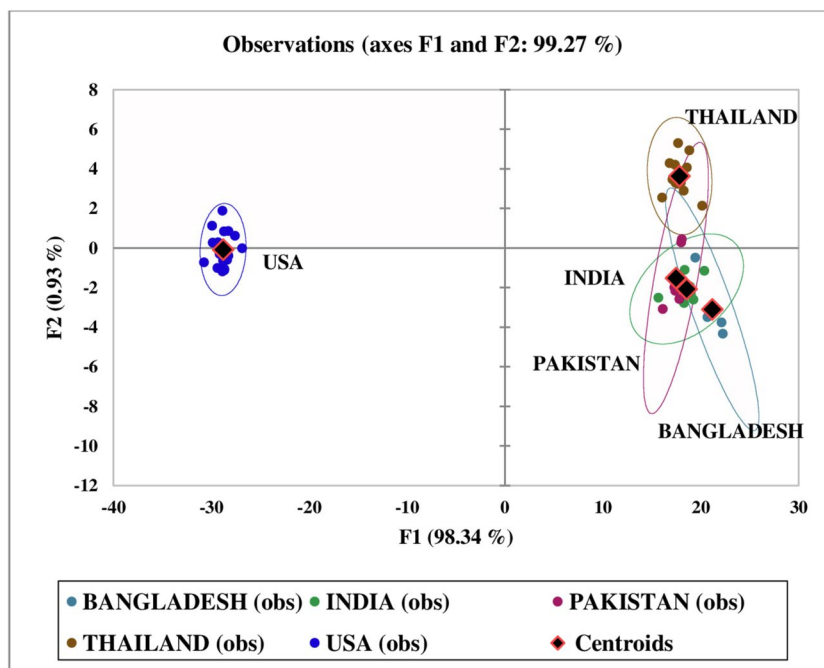
Linear Discriminant Analysis

Linear discriminant analysis was performed to check whether metal(loid) profile could be used to discriminate samples according to the country of origin of the rice samples. Metal(loid)s that demonstrated significant variation among countries of origins were used as chemical descriptors in the statistical analysis to classify the different rice samples based on their geographic origin: USA, Thailand, India, Bangladesh, and Pakistan. The LDA
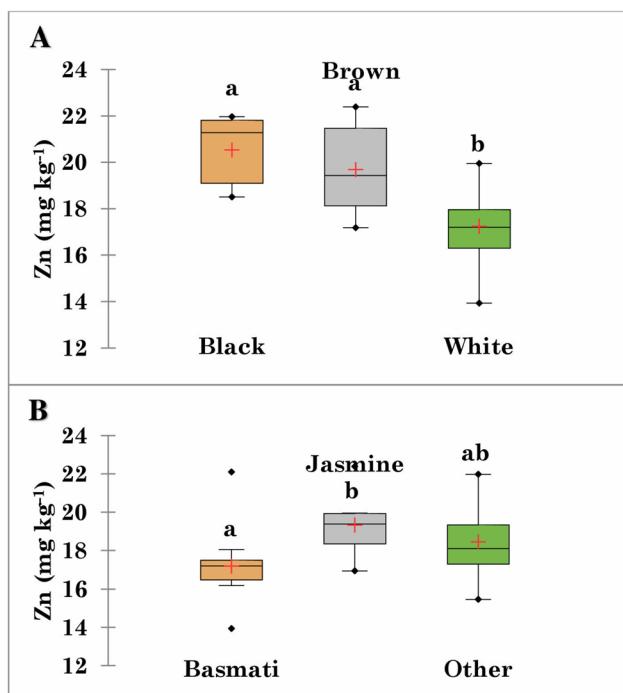
Fig. 5 Box plot of Zn concentration in rice samples based on (**A**) color and (**B**) brand. + indicates mean value; dash line indicates median value; bars represent the 1st and 3rd quartile

model showed a Wilks' λ value proximal to zero (0.00004), suggesting that group means were different [81, 82]. The first discriminant function (F1) accounted for 98.3% of the total variance, while the second discriminant function (F2) accounted for 0.93% of the total variance. Prior and posterior classifications and membership probabilities summarize the observations' reclassification and allow one to quickly see the percentage of well-classified observations [83]. The influential standardized canonical discriminant function coefficients for F1 were Ag (1.332), Cd (0.739), and Mn (0.698) and for F2, Zn (1.046), Sr (−0.961), Cd (−0.776), Se (−0.724), and As (0.690). Previous studies adopting discriminant models found that Cu, Ag, Zn, and Cr were the critical elemental markers for determining rice geographic authentication [84, 85]. The results of the LDA showed 100% correctly classified samples. LDA indicated that all US rice samples formed a dense cohort that was well separated from the Asian rice samples (Fig. 6). On the other hand, LDA showed that Indian rice formed an overlapped cohort with Pakistani rice. Nonetheless, Thailand was properly separated from the studied Asian region.

To check the reliability of the developed classification model, a cross-validation method was used to compute the classification and probability of rice samples [11]. According to the confusion cross-validation results, 100% of US rice samples were correctly classified. In addition, Thai rice samples were cross-validated with a higher accuracy (100%) than Pakistani (83.3%) and Bangladeshi (66.7%) (Table S4). This confirms that US-grown and Thai rice samples show unique elemental fingerprint characteristics that can be differentiated from other geographic origins. LDA struggles to group and separate the samples from India, where the accuracy is low (57.1%). As shown in Table S4, three Indian rice samples were misclassified as Pakistani rice samples. Similarly, two Bangladeshi rice samples were misclassified as Indian samples. On the other hand, one Pakistani rice sample was misclassified as an Indian sample. Therefore, for Indian/Bangladeshi rice samples, it is worth noting that the narrow

Fig. 6 Linear discriminant analysis scatter plot of the first two discriminant functions (F1 and F2) for rice grown in the USA, Thailand, India, Pakistan, and Bangladesh

variance of the metal(loid) profile and its origin can be misclassified. This can be attributed to the closeness of India, Bangladesh, and Pakistan in terms of location. Yet the total correct results of cross-validation reached 82.24% These results show that soil has a great influence on rice element composition and, consequently, geographic origin discrimination [86]. Furthermore, local climate and agricultural practices also influence the elemental composition of rice. Using LDA, it is impossible to misclassify Bangladeshi/Indian/Pakistani/Thai rice for US rice, which resolves fraud issues for rice cultivated in the USA.

Conclusion

This research reports on the metal(loid) composition of 51 rice samples from five countries on sale in Las Vegas. It was found that the concentrations of metal(loid)s in black and brown rice were statistically similar, except for Mn and Se. The concentrations of potentially toxic elements in the analyzed rice samples were below the MRL values, indicating no potential health risks associated with the consumption of rice on sale in Las Vegas. In fact, potential health risks associated with dietary intakes of toxic elements from the consumption of rice are related to both concentrations and intake patterns. For Las Vegas, intake patterns by different community groups should be studied to estimate dietary intakes of potentially toxic elements. Distinct separations between samples cultivated in the USA and those in the four Asian countries were observed using LDA models and selected metal(loid)s were identified as descriptors that could determine rice geographic origin discrimination. The confusion matrix showed that 100% of US and Thai rice samples were correctly classified. On the other hand, the distribution of metal(loid) composition of Indian and Pakistani rice showed some similarity, making it difficult to do 100% discrimination for these samples. The metal(loid) marker found in this study may provide critical insight regarding the geographic authentication of rice on sale in Las Vegas to improve food safety with potential application for other cereals following further validation.

Declarations

References

1. FAO (Food and Agriculture Organization of the United Nations) (2020) Crop prospects and food situation - Quarterly Global Report No. 1, Crop Prospects and Food Situation #1. http://www.fao.org/3/cb3672en/cb3672en.pdf. Accessed 17 May 2023
2. Nawaz A, Rehman AU, Rehman A, Ahmad S, Siddique KH, Farooq M (2022) Increasing sustainability for rice production systems. J Cereal Sci 103:103400
3. Statista (2023) Rice consumption in the U.S. 2022/23. https://www.statista.com/statistics/255981/total-us-rice-consumption/. Accessed 5 May 2023
4. TatahMentan M, Nyachoti S, Okwori OF, Godebo TR (2023) Elemental composition of rice and lentils from various countries: a probabilistic risk assessment of multiple life stages. J Food Compos Anal 115:104852
5. Pedron T, Oliveira GS, Paniz FP, de Moura SF, Masuda HP, dos Santos MC, Rocha BA, Pereira RM, Batista BL (2021) Determination of chemical elements in rice from Singapore markets: distribution, estimated intake and differentiation of rice varieties. J Food Compos Anal 101:103969
6. Fierke C (2000) Function and mechanism of zinc. J Nutr 130:1437S-1446S
7. Horning KJ, Caito SW, Tipps KG, Bowman AB, Aschner M (2015) Manganese is essential for neuronal health. Annu Rev Nutr 35:71–108
8. Zoroddu MA, Aaseth J, Crisponi G, Medici S, Peana M, Nurchi VM (2019) The essential metals for humans: a brief overview. J Inorg Biochem 195:120–129
9. Edwards JR, Prozialeck WC (2009) Cadmium, diabetes and chronic kidney disease. Toxicol Appl Pharmacol 238(3):289–293
10. Zheng L, Kuo CC, Fadrowski J, Agnew J, Weaver VM, Navas-Acien A (2014) Arsenic and chronic kidney disease: a systematic review. Curr Environ Health Rep 1:192–207
11. Cheajesadagul P, Arnaudguilhem C, Shiowatana J, Siripinyanond A, Szpunar J (2013) Discrimination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry. Food Chem 141(4):3504–3509
12. Gonzálvez A, Armenta S, De La Guardia M (2011) Geographical traceability of "Arròs de Valencia" rice grain based on mineral element composition. Food Chem 126(3):1254–1260
13. Zhi L, Yuan W, Yudi H, Wei L, Bin L, Guiyuan M (2023) Multi-stable isotope and multi-element origin traceability of rice from

the main producing regions in Asia: a long-term investigation during 2017–2020. Food Chem 412:135417

14. 178/2002/EC (Official Journal L 31, 02/01/2002, pp. 1–24). Regulation of the European Parliament and of the council of January 28, 2002, laying down the general principles and requirements of food law, establishing the EFSA and laying down procedures in matters on food safety (General Food Law)

15. Liu Z, Mutukumira AN, Chen H (2019) Food safety governance in China: From supervision to coregulation. Food Sci Nutr 7(12):4127–4139

16. FDA (Food and Drug Administration) (2009) H.R.2749 - Food Safety Enhancement Act of 2009. https://www.congress.gov/bill/111th-congress/house-bill/2749. Accessed 23 May 2023

17. Liu Z, Zhang W, Zhang Y, Chen T, Shao S, Zhou L, Yuan Y, Xie T, Rogers KM (2019) Assuring food safety and traceability of polished rice from different production regions in China and Southeast Asia using chemometric models. Food Control 1(99):1–0

18. Filippini T, Tancredi S, Malagoli C, Cilloni S, Malavolti M, Violi F, Vescovi L, Bargellini A, Vinceti M (2019) Aluminum and tin: food contamination and dietary intake in an Italian population. J Trace Elem Med Biol 52:293–301

19. Bondy SC (2014) Prolonged exposure to low levels of aluminum leads to changes associated with brain aging and neurodegeneration. Toxicology 315:1–7

20. Agency for Toxic Substances and Disease Registry (ATSDR) (2008) Toxicological profile of aluminium. https://www.atsdr.cdc.gov/toxprofiles/tp22.pdf. Accessed 24 May 2023

21. Antoine JM, Fung LA, Grant CN, Dennis HT, Lalor GC (2012) Dietary intake of minerals and trace elements in rice on the Jamaican market. J Food Compos Anal 26(1–2):111–121

22. Chung JY, Yu SD, Hong YS (2014) Environmental source of arsenic exposure. J Prev Med Public Health 47(5):253

23. López-Carrillo L, Hernández-Ramírez RU, Gandolfi AJ, Ornelas-Aguirre JM, Torres-Sánchez L, Cebrian ME (2014) Arsenic methylation capacity is associated with breast cancer in northern Mexico. Toxicol Appl Pharmacol 280(1):53–59

24. Grau-Pérez M, Kuo CC, Spratlen M, Thayer KA, Mendez MA, Hamman RF, Dabelea D, Adgate JL, Knowler WC, Bell RA, Miller FW (2017) The association of arsenic exposure and metabolism with type 1 and type 2 diabetes in youth: the SEARCH case-control study. Diabetes Care 40(1):46–53

25. Wu F, Jasmine F, Kibriya MG, Liu M, Cheng X, Parvez F, Islam T, Ahmed A, Rakibuz-Zaman M, Jiang J, Roy S (2015) Interaction between arsenic exposure from drinking water and genetic polymorphisms on cardiovascular disease in Bangladesh: a prospective case-cohort study. Environ Health Perspect 123(5):451–457

26. Banerjee M, Banerjee N, Bhattacharjee P, Mondal D, Lythgoe PR, Martínez M, Pan J, Polya DA, Giri AK (2013) High arsenic in rice is associated with elevated genotoxic effects in humans. Sci Rep 3(1):2195

27. Meharg AA, Williams PN, Adomako E, Lawgali YY, Deacon C, Villada A, Cambell RC, Sun G, Zhu YG, Feldmann J, Raab A (2009) Geographical variation in total and inorganic arsenic content of polished (white) rice. Environ Sci Technol 43(5):1612–1617

28. Davis MA, Signes-Pastor AJ, Argos M, Slaughter F, Pendergrast C, Punshon T, Gossai A, Ahsan H, Karagas MR (2017) Assessment of human dietary exposure to arsenic through rice. Sci Total Environ 586:1237–1244

29. Williams PN, Price AH, Raab A, Hossain SA, Feldmann J, Meharg AA (2005) Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. Environ Sci Technol 39(15):5531–5540

30. Shraim AM (2017) Rice is a potential dietary source of not only arsenic but also other toxic elements like lead and chromium. Arab J Chem 10:S3434–S3443

31. Shi Z, Carey M, Davidson E, Meharg C, Meharg AA (2021) Avoiding rice-based cadmium and inorganic arsenic in infant diets through selection of products low in concentration of these contaminants. Expos 13(2):229–235

32. EFSA (European Food Safety Authority) (2014) Dietary exposure to inorganic arsenic in the European population. EFSA J 12:3597. https://efsa.onlinelibrary.wiley.com/10.2903/j.efsa.2014.3597

33. FSSAI (Food Safety and Standards Authority of India) (2017) Manual for food safety, 17th edn

34. Chen HL, Lee CC, Huang WJ, Huang HT, Wu YC, Hsu YC, Kao YT (2016) Arsenic speciation in rice and risk assessment of inorganic arsenic in Taiwan population. Environ Sci Pollut Res 23:4481–4488

35. Meharg AA, Zhao FJ (2012) Arsenic in rice grain. Arsenic & rice. Springer, Dordrecht. https://doi.org/10.1007/978-94-007-2947-6_2

36. Zavala YJ, Gerads R, Gürleyük H, Duxbury JM (2008) Arsenic in rice: II. Arsenic speciation in USA grain and implications for human health. Environ Sci Technol 42(10):3861–3866

37. Jorhem L, Åstrand C, Sundström B, Baxter M, Stokes P, Lewis J, Grawe KP (2008) Elements in rice from the Swedish market: 1. Cadmium, lead and arsenic (total and inorganic). Food Addit Contam 25(3):284–292

38. Uraguchi S, Fujiwara T (2012) Cadmium transport and tolerance in rice: perspectives for reducing grain cadmium accumulation. Rice 5:1–8

39. Rahman MA, Rahman MM, Reichman SM, Lim RP, Naidu R (2014) Heavy metals in Australian grown and imported rice and vegetables on sale in Australia: health hazard. Ecotoxicol Environ Saf 100:53–60

40. Duruibe JO, Ogwuegbu MOC, Egwurugwu JN (2007) Heavy metal pollution and human biotoxic effects. Int J Phys Sci 2(5):112–118

41. Ahmed MK, Shaheen N, Islam MS, Habibullah-Al-Mamun M, Islam S, Banu CP (2015) Trace elements in two staple cereals (rice and wheat) and associated health risk implications in Bangladesh. Environ Monit Assess 187:1–1

42. Kormoker T, Proshad R, Islam MS, Shamsuzzoha M, Akter A, Tusher TR (2021) Concentrations, source apportionment and potential health risk of toxic metals in foodstuffs of Bangladesh. Toxin Rev 40(4):1447–1460

43. EC (European Commission) (2006) European Union Commission. Regulation No 1881/2006 setting maximum levels for certain contaminants in foodstuffs. Off J Eur Union 2006:L364/5 (Available online: https://eur-lex.europa.eu/legal-content/IT/ALL/?uri=CELEX%3A32006R1881, Accessed 18 Apr 2023)

44. Tariq F, Wang X, Saleem MH, Khan ZI, Ahmad K, Saleem Malik I, Munir M, Mahpara S, Mehmood N, Ahmad T, Memona H (2021) Risk assessment of heavy metals in basmati rice: implications for public health. Sustainability 13(15):8513

45. Lauwerys R, Lison D (1994) Health risks associated with cobalt exposure—an overview. Sci Total Environ 150(1–3):1–6

46. Barceloux DG, Barceloux D (1999) Cobalt. J Toxicol Clin Toxicol 37(2):201–216

47. Bonenfant JL, Miller G, Roy PE (1967) Quebec beer-drinkers' cardiomyopathy: pathological studies. Can Med Assoc J 97(15):910

48. Maisch B (2016) Alcoholic cardiomyopathy: the result of dosage and individual predisposition. Herz 41(6):484

49. Dahms K, Sharkova Y, Heitland P, Pankuweit S, Schaefer JR (2014) Cobalt intoxication diagnosed with the help of Dr House. Lancet 383(9916):574

50. Naseri M, Vazirzadeh A, Kazemi R, Zaheri F (2015) Concentration of some heavy metals in rice types available in Shiraz market and human health risk assessment. Food Chem 175:243–248

51. Sharma P, Singh SP, Parakh SK, Tong YW (2022) Health hazards of hexavalent chromium (Cr (VI)) and its microbial reduction. Bioengineered 13(3):4923–4938

52. Wise JP Jr, Young JL, Cai J, Cai L (2022) Current understanding of hexavalent chromium [Cr (VI)] neurotoxicity and new perspectives. Environ Int 158:106877

53. Peng M, Yang X (2015) Controlling diabetes by chromium complexes: the role of the ligands. J Inorg Biochem 146:97–103

54. ASTDR (Agency for Toxic Substances and Disease Registry) (2012) Toxicological profile for Chromium. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA

55. Singh A, Sharma RK, Agrawal M, Marshall FM (2010) Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. Food Chem Toxicol 48(2):611–619

56. Mohanty M, Pattnaik MM, Mishra AK, Patra HK (2011) Chromium bioaccumulation in rice grown in contaminated soil and irrigated mine wastewater—a case study at South Kaliapani chromite mine area, Orissa. India Int J Phytoremediation 13(5):397–409

57. Balamurugan K, Schaffner W (2006) Copper homeostasis in eukaryotes: teetering on a tightrope. Biochim Biophys Acta, Mol Cell Res 1763(7):737–746

58. Prohaska JR (2014) Impact of copper deficiency in humans. Ann N Y Acad Sci 1314(1):1–5

59. Cakic M, Mitic Z, Nikolic G, Savic I, Savic IM (2013) Design and optimization of drugs used to treat copper deficiency. Expert Opin Drug Discovery 8(10):1253–1263

60. TatahMentan M, Nyachoti S, Scott L, Phan N, Okwori FO, Felemban N, Godebo TR (2020) Toxic and essential elements in rice and other grains from the United States and other countries. Int J Environ Res Public Health 17(21):8128

61. World Health Organization (WHO) (2016) Iron deficiency anaemia. http://www.who.int/nutrition/topics/ida/en. Accessed 19 Apr 2023.

62. Pradhan SK, Pandit E, Pawar S, Pradhan A, Behera L, Das SR, Pathak H (2020) Genetic regulation of homeostasis, uptake, biofortification and efficiency enhancement of iron in rice. Environ Exp Bot 177:104066

63. Gupta PM, Perrine CG, Mei Z, Scanlon KS (2016) Iron, anemia, and iron deficiency anemia among young children in the United States. Nutrients 8(6):330

64. Giri S, Singh AK (2017) Human health risk assessment due to dietary intake of heavy metals through rice in the mining areas of Singhbhum Copper Belt, India. Environ Sci Pollut Res 24:14945–14956

65. Dumitrascu C, Fiamegos Y, de la Calle Guntiñas MB (2021) Feasibility study on the use of elemental profiles to authenticate aromatic rice: the case of Basmati and Thai rice. Anal Bioanal Chem 413(20):4947–4957

66. Nielsen F (2021) Nickel Adv Nutr 12(1):281

67. Pereira MC, Pereira ML, Sousa JP (1998) Evaluation of nickel toxicity on liver, spleen, and kidney of mice after administration of high-dose metal ion. J Biomed Mater Res 40(1):40–47

68. Wu B, Liu Y, Zhen J, Mou P, Li J, Xu Z, Song B (2022) Protective effect of methionine on the intestinal oxidative stress and microbiota change induced by nickel. Ecotoxicol Environ Saf 244:114037

69. FAO/WHO (Nations Food and Agriculture Organization/World Health organization) (2011) FAO/WHO food standards programme codex committee on contaminants in foods. Fifth Session. ftp//ftpfaoorg/codex/meetings/CCCF/cccf5/cf05_INFpdf. Accessed 02 May 2023.

70. Cheng WD, Zhang GP, Yao HG, Wu W, Xu M (2006) Genotypic and environmental variation in cadmium, chromium, arsenic, nickel, and lead concentrations in rice grains. J Zhejiang Univ Sci B 7:565–571

71. Aguilera-Velázquez JR, Calleja A, Moreno I, Bautista J, Alonso E (2023) Metal profiles and health risk assessment of the most consumed rice varieties in Spain. J Food Compos Anal 117:105101

72. Burk RF, Hill KE, Nakayama A, Mostert V, Levander XA, Motley AK, Johnson DA, Johnson JA, Freeman ML, Austin LM (2008) Selenium deficiency activates mouse liver Nrf2–ARE but vitamin E deficiency does not. Free Radic Biol Med 8:1617–1623

73. Kumar BS, Priyadarsini KI (2014) Selenium nutrition: how important is it? Biomed Prev Nutr 4(2):333–341

74. Rayman MP (2002) The argument for increasing selenium intake. Proc Nutr Soc 61(2):203–215

75. FNB (Food and Nutrition Board, Institute of Medicine, National Academy of Sciences) (2000) Dietary reference intakes for vitamin c, vitamin e, carotenoids and selenium. National Academy Press, Washington DC

76. Williams PN, Lombi E, Sun GX, Scheckel K, Zhu YG, Feng X, Zhu J, Carey AM, Adomako E, Lawgali Y, Deacon C (2009) Selenium characterization in the global rice supply chain. Environ Sci Technol 43(15):6024–6030

77. Kelly S, Baxter M, Chapman S, Rhodes C, Dennis J, Brereton P (2002) The application of isotopic and elemental analysis to determine the geographical origin of premium long grain rice. Eur Food Res Technol 214:72–78

78. Zhang M, Pang Y, Yi Q, Huang J, Huang X, Huang Q, Xu P, Tang S (2020) Comparative effectiveness of Se translocation between low-Se and high-Se rice cultivars under Se fertilization. Ecotoxicol Environ Saf 205:111372

79. Naeem A, Aslam M, Ahmad M, Asif M, Yazici MA, Cakmak I, Rashid A (2021) Biofortification of diverse basmati rice cultivars with iodine, selenium, and zinc by individual and cocktail spray of micronutrients. Agronomy 12(1):49

80. Bonjour JP, Guéguen L, Palacios C, Shearer MJ, Weaver CM (2009) Minerals and vitamins in bone health: the potential value of dietary enhancement. Br J Nutr 101(11):1581–1596

81. Pellerano RG, Mazza SS, Marigliano RA, Marchevsky EJ (2008) Multielement analysis of Argentinean lemon juices by instrumental neutronic activation analysis and their classification according to geographical origin. J Agric Food Chem 56(13):5222–5225

82. Zhao H, Yu C, Li M (2017) Effects of geographical origin, variety, season and their interactions on minerals in tea for traceability. J Food Compos Anal 63:15–20

83. Demianová A, Bobková A, Lidiková J, Jurčaga L, Bobko M, Belej Ľ, Kolek E, Poláková K, Iriondo-DeHond A, del Castillo MD (2022) Volatiles as chemical markers suitable for identification of the geographical origin of green Coffea arabica L. Food Control 136:108869

84. Chung IM, Kim JK, Lee JK, Kim SH (2015) Discrimination of geographical origin of rice (Oryza sativa L.) by multielement analysis using inductively coupled plasma atomic emission spectroscopy and multivariate analysis. J Cereal Sci 65:252–259

85. Opatić AM, Nečemer M, Budič B, Lojen S (2018) Stable isotope analysis of major bioelements, multi-element profiling, and discriminant analysis for geographical origins of organically grown potato. J Food Compos Anal 71:17–24

86. Chung IM, Kim JK, Lee KJ, Park SK, Lee JH, Son NY, Jin YI, Kim SH (2018) Geographic authentication of Asian rice (Oryza sativa L.) using multi-elemental and stable isotopic data combined with multivariate analysis. Food Chem 40:840–849