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Identification and Quantification of Heavy Metals Concentrations in *Pistacia*

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Abstract

The levels of heavy metals are very important in pistachio nuts, because the edible nuts have an important and increasing role in human nutrition. Pistachio is one of the native nuts of Iran which contains high genetic resources, but there is insufficient information regarding nutritional properties and other elements like heavy metals. The objective of the present study was to investigate and compare heavy metals contents in the kernels of various pistachio samples including: 'Daneshmandi', 'Sephid', 'Garmeh', 'Momtaz', 'Ahmad Aghaei', 'Badami Zarand', *Pistacia atlantica* Desf. ('Baneh'), *Pistacia vera* 'Sarakhs' and chance seedling as 'Non-grafted 1', 'Non-grafted 2' and 'Non-grafted 3'. Inductively coupled plasma emission spectrophotometer (ICP) was used for the determination of aluminium, chromium, nickel, copper, strontium, arsenic, cadmium and cobalt concentrations in pistachio kernels. This study showed that there were significant differences among the samples in all measured heavy metals except the arsenic, cadmium and cobalt. The content of aluminium varied from 3.22 to 9.59 (mg kg^{-1} of dry matter) and chromium concentration from 0.60 to 1.86 (mg kg^{-1} of dry matter). The nickel content of examined pistachio samples was found between 0.43 and 3.63 (mg kg^{-1} of dry matter) and copper ranged from 3.20 to 12.33 (mg kg^{-1} of dry matter). The strontium content was observed between 4.96 and 24.93 (mg kg^{-1} of dry matter). The contents of arsenic, cadmium and cobalt not reported, because their amounts were lower than the detection limit of the applied measuring method (ICP). These data demonstrated that the concentrations of heavy metals in pistachios varied by cultivar.

Keywords: chemical analysis, cultivar, human diet, pistachio, trace elements

Introduction

Heavy metals have positive and negative effects on the human health. According to Munoz-Olivas *et al.* (2001), Jalbani *et al.* (2007) heavy metals can be classified as potentially toxic (aluminium, arsenic, cadmium, etc.,) and essential (copper, iron, zinc, etc.). Humans are exposed to heavy metals in many different ways such as; by ingestion of contaminated water and food, and by inhalation of air pollutants or contaminated soil particles (Bordajandi *et al.*, 2004). Long-term exposures to toxic elements can be very harmful even at low concentration but the intake of too much of essential metals can also cause produce toxic effects (Celik and Oehlenschlager, 2007).

In the near past years, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of contaminated foodstuffs by pesticides and heavy metals or toxins (D'Mello, 2003). There have been studies on heavy metals in mango and almond (Ademoroti, 1986), strawberry (Ward and Savage, 1994), plantain (Selema and Farago, 1996), quince and grape (Pinochet *et al.*, 1999), lemon, sweet orange and grape fruits (Gorinstein *et al.*, 2001), orange (Rossini *et al.*, 2003), chiku, papaya, mango, muskmelon and apple (Parveen *et al.*, 2003), banana, pineapple and papaya (Santos *et al.*, 2004), date palm (Williams *et al.*, 2005) and apricot (Davarynejad *et al.*, 2010; Saracoglu *et al.*, 2009).

Pistachio (*Pistachia vera* L.) belongs to the Anacardiaceae family, and is one of the important tree nuts. It has been cultivated widely in Iran, Turkey, Syria, Greece, Italy and United States, and its cultivation has increased in recent years (Kucukoner and Yurt, 2003). Iran is one of the most important pistachio producers and exporters in the world, and its total production in 2008 was 635,577 tons (FAO, 2008). The popularity of pistachio is mainly due to their nutritional components including; fatty acids, minerals, vitamins, sterols, phenolic compounds and antioxidant properties (Tsantili *et al.*, 2010). It is widely consumed as a snack food, both raw and roasted, confectionery ingredient in cakes, ice cream, bread and sauces.

In spite of various pistachio cultivars grown in different regions of the Iran, the heavy metals of Iranian pistachio cultivars have not been evaluated in detail. Such data will assist in the cultivar selection for safety food production to meet market demand and the conception of healthy diet. Therefore, the aim of the present study was to analyze and compare the heavy metals concentrations in the kernels of various pistachio samples grown in Iran. In addition, differences between pistachio of commercial, non-grafted and wild groups were compared.

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Materials and methods

Pistachio samples

Pistachio samples were studied: 'Daneshmandi', 'Sephid', 'Garmeh', 'Momtaz', 'Ahmad Aghaei', 'Badami Zarand' (Commercial group), *Pistacia atlantica* Desf. ('Baneh'), *Pistacia vera* 'Sarakhs' (Wild group) and chance seedling as 'Non-grafted 1', Non-grafted 2' and 'Non-grafted 3' (Non-grafted group). The samples at commercial maturity stage were hand harvested in 2009. Mature trees (18 year-old) randomly selected to represent the population of the plantation from Feyzabad of the Khorasan-e-Razavi province, Iran. Feyzabad is located on the north east part of Iran at 35˚01'N latitude and 58˚78'E longitude. The average temperature, the amount of rainfall and relative humidity in growing season of 2009 were 28.65'C, 20 mm and 26%, respectively. Soil is a sand-loam, EC = 4.12 (ds m^{-1}) and soil pH = 7.21. The trees were spaced 6 and 3 m between and along the rows, respectively. Trees were irrigated every 24 days and fertilized with 50 kg h^{-1} of nitrate ammonium. All samples were grown under the same geographical conditions and with the same applied agronomic practices. The air dried pistachio nuts were used for chemical analysis in four of replications.

Chemical analysis of heavy metals

Samples were prepared in accordance with Hungarian standard (MSZ-08-1783-15, 1985). Kernels were digested with concentrate HNO3-H2O2 digester mixture: 5 g fresh kernel was digested at 120°C during three hours in a Teflon digestor. Digested samples were diluted with distilled water to 100 cm3. Examined elements were measured by Thermo Jarrell Ash Poly-scan 61E and Thermo Electron Corporation IRIS Intrepid II XDL Inductively coupled plasma emission spectrophotometers (ICP) (Davarynejad *et al*., 2010).

Statistical analysis

This experiment was conducted according to completely randomized design with 4 replications (each replicate contained 5 individual kernels). Data were analyzed by Statistical Analysis System (SAS) software version 9.1 using analysis of variance (ANOVA) and differences among means were determined for significance at $P < 0.05$ using Tukey's test.

Results and discussion

Aluminium

A great variation in terms of aluminium content was observed among the pistachio samples (3.22-9.59 mg kg^{-1} of dry matter) and the differences were statistically significant (Fig. 1). The highest amount of aluminium was observed in 'Baneh', followed by 'Non-grafted 1' and 'Sephid', while the lowest was in 'Garmeh'. Also, the mean values of aluminium were significantly different among the three groups of pistachio. The aluminium content of the wild, non-grafted and commercial groups comprised 7.77, 6.70 and 5.36 mg kg^{-1} of dry matter, respectively (Fig. 2).

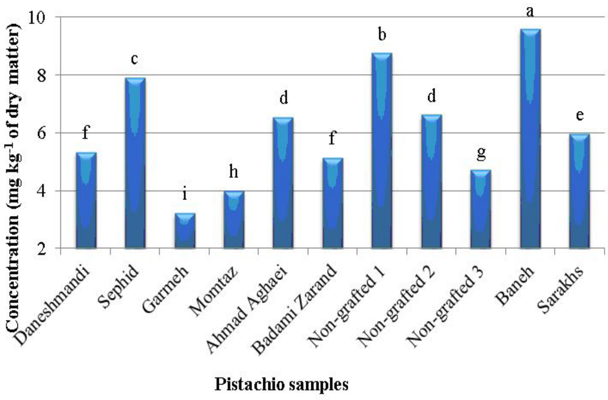

Fig. 1. The aluminium concentration of eleven Iranian pistachio samples. (Each column with different letters is significantly different ($P < 0.05$)

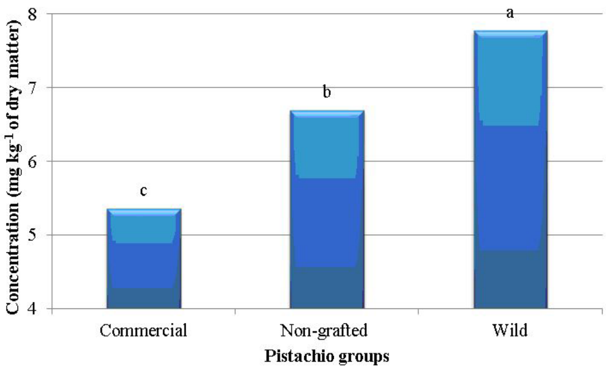

Fig. 2. The aluminium concentration of three Iranian pistachio groups. (Each column with different letters is significantly different ($P < 0.05$)

The aluminium concentration of pistachio samples have not been studied in detail yet. Saracoglu *et al.* (2009) reported that the aluminium concentration in dried apricot samples of Turkey ranged from 0.08 to 0.22 mg kg^{-1} of dry matter. The content of aluminium in plants is depended on several factors, like plant species (Biego *et al.*, 1998).

Aluminium (Al) is an abundant element in earth's crust, but it's not considered to be an essential element in humans. The uptake of aluminium can take place through food, breathing and by skin contact. Long lasting uptakes of significant concentrations of aluminium can lead to serious health effects such as; damage to the central nervous system, dementia, memory loss, listlessness, severe trembling and kidney patients (Narin *et al.*, 2004; Shokrollahi *et al.*, 2008). Based on WHO statistics (WHO, 1989), the permissible aluminium dose for an adult is quite high (60 mg day^{-1}). The average content of aluminium of pistachio samples was 6.16 mg kg^{-1} of dry matter. In this study, we found low concentrations of aluminium in studied pistachio samples, which may not be harmful to human health. It means that an adult can eat approximately 10 kg pistachio a day to reach this threshold (not calculating other sources).

Chromium

Significant variation in chromium concentration was found among the eleven samples of pistachio and the values ranged from 0.60 to 1.86 (mg kg^{-1} of dry matter). The highest level of chromium was observed for 'Daneshmandi', followed by 'Garmeh', while the lowest was in 'Non-grafted 3' (Fig. 3). The results also showed that the chromium content was not significantly different between groups of commercial and wild, while significantly differences were observed between groups of non-grafted and commercial or groups of non-grafted and wild. The samples of commercial had the highest chromium content (1.14 mg kg^{-1} of dry matter) while the non-grafted samples had the lowest chromium content (0.78 mg kg^{-1} of dry matter) (Fig. 4).

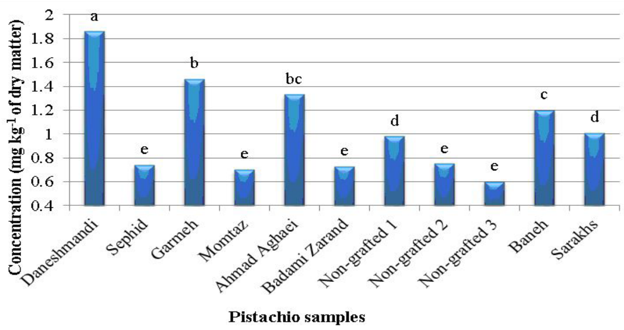

Fig. 3. The chromium concentration of eleven Iranian pistachio samples. (Each column with different letters is significantly different ($P < 0.05$)

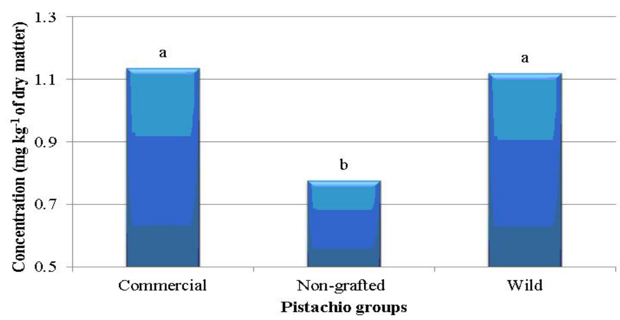

Fig. 4. The chromium concentration of three Iranian pistachio groups. (Each column with different letters is significantly different ($P < 0.05$)

The chromium level of pistachio samples have not been investigated in detail yet. The chromium content was found in the range of 3.23-6.43 mg kg-1 in apricots of Pakistan by Zahoor and Zahoor (2003) and in the range of 0.32-0.64 mg kg^{-1} in the apricots of Turkey by Saracoglu *et al.* (2009). Although, there are very low concentrations of chromium (Cr) in the human body, it is a beneficial element and essential for human growth and development. It is important role in glucose, lipid and protein metabolism (Cobo *et al.*, 1995; Jirapinyo *et al.*, 1985; Offenbacher and Pi-Sunyer, 1988). For most people eating food that contains chromium is the main route of chromium uptake as chromium occurs naturally in many vegetables, fruits, meats, yeasts and grains. Nowadays, the exhaustion of chromium is a real danger, because of the abundant consumption of high sugar foods that increase the exhaustion of it. Of course the intake of too much of chromium can also cause harmful health effects for instance hepatitis, gastritis, ulcers and lung cancer (Parveen *et al.*, 2003).

According to Saracoglu *et al.* (2009) a range of chromium intake between 50 and 200 µg day^{-1} is recommended for adults. Our results indicated that the mean content of chromium in pistachio samples was 1.03 mg kg^{-1} of dry matter. It means that pistachio is an excellent source of chromium. Eating 200 g pistachio per day covers the daily intake of an adult.

Nickel

In this study, the differences in nickel content among the pistachio samples were significant ranging from 0.43 to 3.63 mg kg^{-1} of dry matter. The highest concentration of nickel was observed for 'Garmeh', followed by 'Sephid', 'Non-grafted 1', 'Daneshmandi' and 'Momtaz' while the lowest was in 'Ahmad Aghaei' (Fig. 5). There was a significant difference between the commercial group and the other groups (wild and non-grafted).

The mean nickel contents of the commercial, non-grafted and wild groups were 1.50, 0.96 and 0.94 mg kg^{-1} of dry matter, respectively (Fig. 6).

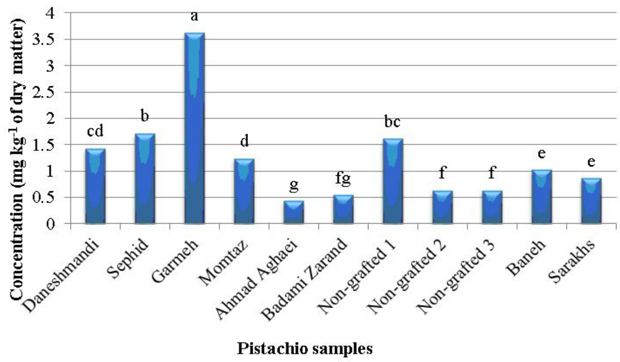

Fig. 5. The nickel concentration of eleven Iranian pistachio samples. (Each column with different letters is significantly different ($P < 0.05$)

The nickel level of pistachio has been reported as 0.36 to 13.8 mg kg^{-1} (Cabrera *et al.*, 2003; Soylak *et al.*, 2006).

The nickel values obtained in the current study were greater than those reported by Cabrera *et al.* (2003), while lower than those reported by Soylak *et al.* (2006). The variation may the result of other factors such as; the different pistachio samples, production place and method used in the experiments. Soylak *et al.* (2006) reported that the level of nickel as 17.41 mg kg^{-1} for almond and 25.80 mg kg^{-1} for walnut. The level of nickel in the studied pistachio samples was lower than other nuts.

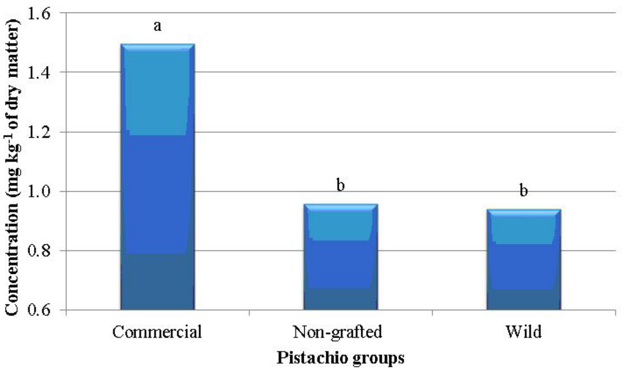

Fig. 6. The nickel concentration of three Iranian pistachio groups. (Each column with different letters is significantly different (P < 0.05)

Nickel (Ni) is a trace element; its physiological role in plants is similar to cobalt. Its role in human body is not as clear, but it may be beneficial as an activator of some enzyme systems in small quantities (Saracoglu *et al.*, 2009). Foodstuffs naturally contain small amounts of nickel. Several kinds of vegetables, fruits and meats are fine for consumption in regard to nickel content. The uptake of too large quantities of nickel can cause adverse effects such as; lung cancer and nickel allergy (Onianwa *et al.*, 2000; Parveen *et al.*, 2003).

Based on WHO (WHO, 1994), the content of nickel recommend for daily intake is 100 and 300 µg. We found that the average level of nickel of examined pistachio samples was 1.25 mg kg^{-1} of dry matter. Based on our results, pistachio is regarded as excellent nickel source for humans, but the excessive consumption may be result in harmful effects.

Copper

There were significant differences in the copper content of pistachio samples and the values ranged from 3.20 to 12.33 (mg kg^{-1} of dry matter). Among the studied samples, 'Baneh' had the highest amount of copper and 'Non-grafted 2' had the lowest copper content (Fig. 7). Statistically significant differences in copper content were found among groups of wild (10.89 mg kg^{-1} of dry matter), commercial (8.18 mg kg^{-1} of dry matter) and non-grafted (5.59 mg kg^{-1} of dry matter) (Fig. 8).

Cabrera *et al.* (2003) stated the content of copper was found as 9.20 mg kg^{-1} in pistachio in Spain. Soylak *et al.* (2006) reported that the concentration of copper was 24.90 mg kg^{-1} in pistachio in Turkey. Our results were lower than values observed by Soylak *et al.* (2006), while our results were in agreement with values reported by Cabrera *et al.* (2003). Sattar *et al.* (1989) showed that the level of copper was 6.20 mg kg^{-1} for almond and 7.74 mg kg^{-1} for walnut. The copper levels of almond and walnut samples from Spain have been reported as 11.1 and 22 mg kg^{-1}, respectively (Cabrera *et al.*, 2003). Edible nuts are regarded as good source of copper. Cashew nuts provide the most copper with 2.2 mg (111% RDA) per 100 gram serving, Other nuts high in copper include; hazelnuts (88% RDA), brazil nuts (87% RDA), walnuts (79% RDA), pistachios (66% RDA), pine nuts (66% RDA), peanuts (65% RDA), pecans (60% RDA), and almonds (59% RDA) (USDA, 2009).

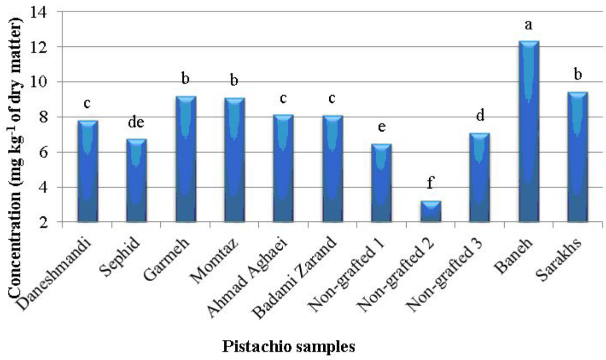

Fig. 7. The copper concentration of eleven Iranian pistachio samples. (Each column with different letters is significantly different (P < 0.05)

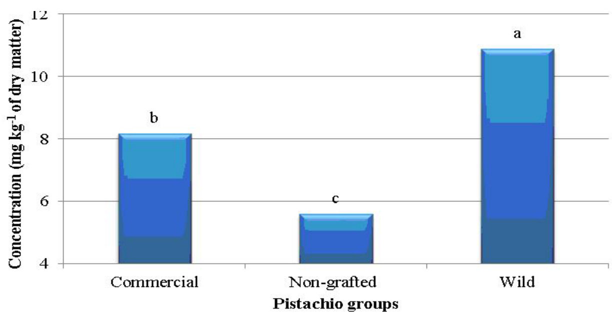

Fig. 8. The copper concentration of three Iranian pistachio groups. (Each column with different letters is significantly different (P < 0.05)

Copper (Cu) is a trace element that plays an essential role in our life and health. It is known to be vital for many biological systems such as; enzymes function (super oxide dismutase), skin and hair pigmentation, helps in the iron intake, maintenance of connective tissue and many other functions (Saracoglu *et al.*, 2009). Although, humans can handle proportionally large concentrations of copper, exposure too much copper can cause eminent health problems such as; hepatic and kidney damage, methanoglobinemia and hemolytic anemia (Banerjee *et al.*, 2010).

The daily quantity of ingested copper foods has been estimated between 1 and 3 mg day^{-1} (WHO, 1994). The mean concentration of copper of pistachio samples was 7.96 mg kg^{-1} of dry matter. The data of this study also confirmed that the pistachio is a rich source of copper and approximately 250 g pistachio serves the recommended daily intake for an adult.

Strontium

The highest and the lowest strontium level were detected in 'Daneshmandi' and 'Non-grafted 2', respectively (Fig. 9). The results also showed that there was a significant difference between the commercial group and the other groups (wild and non-grafted). The strontium level of the non-grafted, wild and commercial groups comprised 11.21, 11.52 and 16.73 mg kg^{-1} of dry matter, respectively (Fig. 10).

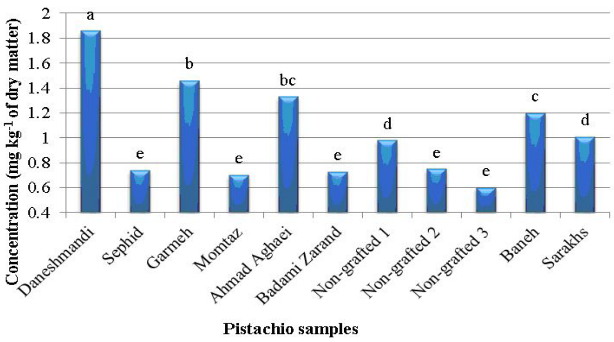

Fig. 9. The strontium concentration of eleven Iranian pistachio samples. (Each column with different letters is significantly different (P < 0.05)

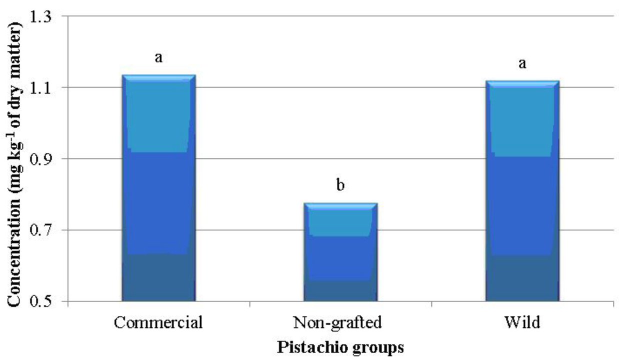

Fig. 10. The strontium concentration of three Iranian pistachio groups. (Each column with different letters is significantly different (P < 0.05)

The strontium level of pistachio samples have not been studied in detail yet. Foods containing strontium ranged from very low (e.g. in corn (0.4 ppm) and orange (0.5 ppm) to high (e.g. in cabbage (45 ppm), onions (50 ppm) and lettuce (74 ppm). Foodstuffs that contain significantly high concentrations of strontium are spices, grains, leafy vegetables and dairy products.

Strontium (Sr) is a trace mineral in the diet. Strontium bears a chemical resemblance to calcium and can displace it at times. Strontium improves the cellular makeup of bones and teeth, promotes bone development and density. It has a role in osteoblasts and osteoclasts. The uptake of high strontium concentrations is generally not known to be a great danger to human health. However, for children exceeded strontium uptake may be a health risk, because it can cause problems with bone growth and disruption of bone development. When the uptake is very high it may cause anaemia and oxygen shortages, and at extremely high concentrations it is even known to cause cancer as a result of damage to the genetic materials in cells (ATSDR, 2004). However, this effect can only occur when strontium uptake is in the thousands of ppm range.

It is estimated that the average person consumes 1 to 5 mg of strontium per day in food and water. The mean level of strontium of pistachio samples was 14.27 mg kg^{-1} of dry matter. According to our study, pistachio is regarded as an excellent strontium source for humans because eating 100-200 g pistachio a day covers the recommended daily intake.

Conclusion

Statistically significant differences were observed between pistachio of samples and groups investigated in all measured heavy metals except the arsenic, cadmium and cobalt. The contents of arsenic, cadmium and cobalt not reported, because their amounts were lower than the detection limit of the applied measuring method (ICP). Since all eleven pistachio samples used in this research were grown in the same location using similar agronomic practices, the differences in examined heavy metal content indicates that cultivar was the main factor determining the concentration of heavy metals in pistachio. The present study also showed that the pistachio contains high contents of strontium followed by copper, aluminium, nickel and chromium. In addition, the results provide important information on the nutritional values of pistachio samples which can be useful for selection of superior desirable pistachio genotypes for bringing to commercial cultivation. However, further investigations need to study other cultivars in Iran and explore their nutritional factors.

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