Comparative Study on Minerals in Peel and Pulp of Peach (Prunus persica L.) Fruit

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In this study, variations of minerals contents between peel and pulp parts of six different peach varieties originated from Serbia were investigated by using inductively coupled plasma optical emission spectrophotometry and one-way analysis of variance (ANOVA) with Tukey’s post-hoc test. The content of fifteen elements was determined and content of K was highest among macroelements and Fe among microelements in both parts of the peach fruit. Also, peach peel had higher levels of all minerals with the exception of K. Greater differences between the peel and the pulp and the same parts of different types of peaches are observed in the case of macroelements than the microelements. Hg and Cd are not detected while the contents of Pb and As are below prescribed values.

Keywords: peach, minerals, ICP-OES determination, statistical analysis

Peaches are classified as Prunus persica L. and belong to the Rosaceae family. Its fruits with golden yellowish flesh are one of a favorite that are used in diet because of their refreshing sour-sweet taste. Natural sugars, organic acids, phenolic acids, vitamins (C and A), flavonoids and anthocyanin compounds, minerals and dietary fibers are among the major constituents of peach fruits, which contribute to the nutritional quality of both fresh fruits and the juices i.e. these constituents certainly elevate the nutritional status of the peach fruit. 100 g portion of peach fruits should have 165 kJ; 0.91 g of protein; 0.25 g of total lipid; 9.54 of carbohydrate; 8.39 g of sugars; 1.5 g of dietary fiber; 6.6 mg of vitamin C; 88.9 g of water etc. [1]. Dietary intake of peach can reduce the generation of reactive oxygen species and provide protection from several chronic diseases. Many published reports reveal that peel of various fruits (apple, persimmons, pear) contains higher amount of phenolics and flavonoids as compared to their flesh parts [2,3].

The plants translocate some quantities of metals from soil, water and air to their roots, trees, branches, leaves, fruits and seeds. Many factors affect the bioavailability of metals: the total metal soil concentration, pH, the organic matter content, redox conditions, etc. Also, the plant genotype is the most important factor affecting the metals adoption [4]. Healthy plant growth requires not only macronutrients (N, P, K, S, Ca, and Mg) but also micronutrients such as Co, Cu, Fe, Mn, Mo, Ni, and Zn which are essential for plant metabolism in trace amounts [5]. Some of necessary microelements may interfere with physiological processes and could be harmful for plants and may affect human health when they are present at excessive levels [6]. The assessment of metals content, especially heavy metals, in fruits is an important issue with regards to human health and represents one of the factors in the evaluation of their quality.

Extensive use of fertilizers, inorganic and livestock manures (e.g. cattle, sheep, poultry, etc.), metal-based pesticides, insecticides and herbicides play an important role in increasing the mineral contents of soils and plant tissues. Also, the polluted environment, the fuel combustion, contaminated food transport and supply chains, poor market sanitary conditions and the use of contaminated or waste water for irrigation purposes, may contribute to the increased content of heavy metals in food.

The different chemical compounds used to supply N, P, and K for plant growth contain trace amounts of heavy metals as impurities. Pesticide, insecticides and fungicides were based on compounds which contain Cu, Hg, Pb, or Zn. Cd is found predominantly in phosphoric fertilizers and Fe in some inorganic fertilizers which are regularly added to soil [5,7]. Matei et al. found that over a period of six years, the concentration of Cd is increased twenty times because of fuel combustion from highway and town which can be the major pathway trough Cd is released into the atmosphere [3].

Nutrient levels in foods are variable. In the case of fruits, mineral levels can be affected by factors such as the variety of the produce item, time of harvest, ripeness, climate, soil conditions including fertilizer application, and storage and marketing conditions. There are a lot of literature data about minerals contents of whole peaches fruit. Matei et al. determined Cd, Cu, Zn, and Pb in fresh fruits [3]. The most abundant heavy metal was Cu (2.47 mg kg⁻¹), followed by Zn (1.5236 mg kg⁻¹) and Cd (0.0228 mg kg⁻¹) while Pb was not detected. All determined contents are below the recommendable maximum limits for metals in fruits: 0.05 mg kg⁻¹ for Cd; 0.1 mg kg⁻¹ for Pb and 5 mg kg⁻¹ for Cu and Zn [8]. Radwan and Salama analyzed dried peaches samples from Egyptian markets and found elevated values: 0.38 mg kg⁻¹ Pb, 6.22 mg kg⁻¹ Zn, 0.01 mg kg⁻¹ Cd and 1.46 mg kg⁻¹ Cu [7]. Peach samples of one area in Libya contain 1.87 mg kg⁻¹ Cu; 5.87 mg kg⁻¹ Zn and 0.02 mg kg⁻¹ Cd [9]. Ashhammary and Al-Horayess, determined minerals concentrations in peaches of the three major agricultural Saudi companies and their results show that Fe is dominant (176.33 mg kg⁻¹), followed by Ca (150.33 mg kg⁻¹); Mg (25.47 mg kg⁻¹); Cu (19.93 mg kg⁻¹); Zn (12.74 mg kg⁻¹); Mn (8.74 mg kg⁻¹); Cd (0.099 mg kg⁻¹) (DW) [5]. Cunningham et al. detected 230 mg 100g⁻¹ K; 1 mg 100g⁻¹ Na; 5 mg 100g⁻¹ Ca; 11 mg 100g⁻¹ Mg; 0.3 mg 100g⁻¹ Fe and 0.1 mg 100g⁻¹ Zn in composite sample of several unpeeled row peach cultivars [10]. Peach juice and peach nectar samples are often the subject of metals contents determination [11,12].

Component parts of the peach fruit, namely flesh or pulp and peel are, not much studied [2,13]. The objective of present work was to compare elemental composition among pulp and peel of the various peach cultivars from Serbia as well as to compare obtained values with the

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established national and international standards and recommendations. Optical emission spectrometer with inductively coupled plasma (ICP-OES) as a multi-element technique for the detection of major, minor and trace elements in different complex samples which combines qualities such as a relatively low detection limits, high capacity for the simultaneous and precise detection for short intervals over wide concentration ranges, was used for this purpose.

**Experimental part**

**Materials and methods**

**Sample collection and preparation**

The analyzed six varieties of peaches (Radmilovcanka and Vesna as domestic cultivars; June Gold; Blake; Hale and Adria as cultivars from American continent) originated from Southeast Serbia (district of Niš) orchards which are approximately the same age without significant agricultural measures and with the same type of soil. Fully ripened fresh fruits of the five randomly selected trees were collected at the peak of the harvest period during June-September 2013, depending on the varieties. Samples were transported in closed polyethylene bags, washed thoroughly first by tap water followed by acidified and deionized water and peeled to separate pulp and peel. The homogenized composite samples (about 10 g) were frozen until dry-digested mineralization process in furnace with the controlled temperature in the range from 500 to 4500 °C for 24 h. After the complete digestion the cooled dry residues were dissolved in 2.5 ml HNO3 (1:1, v/v), filtered through Whatman No. 42 filter paper and transferred to a 50 ml volumetric flask with deionized water [14]. All necessary measures of contamination prevention were taken at all steps in process.

**Instrumentation**

The iCAP 6000 inductively coupled plasma optical emission spectrometer which combines an Echelle optical design and a charge injection device (CID) solid state detector (Thermo Scientific, Cambridge, United Kingdom) was used for analysis the metals contents. Analyses were made in triplicate and the mean values are reported. The blank sample involving the addition of all used reagents was processed to make corrections for each of the element were selected based upon the tables of known interferences, baseline shifts and the background correction (the highest signal-to-background ratio) which was manually selected for the quantitative measurements.

**Reagents**

The multi-element standard solution (Ultra Scientific, USA, Item ICM-240, EPA Method 200.7 LPC Solution of 30 analytes) of 20.00±0.10 mg L−1 was used as a stock solution for calibration. Matrix of multi-standard was 2% HNO3, with traces of tartaric acid in deionized water with low values of total organic carbon (TOC<50 mg L−1). Analytical grade 65% nitric acid (Merck, Darmstadt, Germany) was used for complete mineralization of analyzed samples. All the solutions were prepared using high purity deionized water.

**Statistical analysis**

All ICP-OES measurements were carried out in triplicate, presented as mean ± standard deviation (SD) and the results were subjected to statistical analysis. One-way analysis of variance (ANOVA) with Tukey’s post-hoc test was done to determine significant differences, considering a level of significance of less than 5% (p<0.05) using a statistical package IBM SPSS 20, US. [15].

**Results and discussions**

The determined minerals were classified according to the criteria of the World Health Organization into the following groups: the essential macroelements (Na, K, Mg, Ca, and P) (table 1); essential trace elements and trace elements that are probably essential (Cr, Cu, Fe, Mn, Ni, Zn, and B) (table 2) and toxic and potentially toxic-some elements (Al, As, and Pb) (table 3) [16]. All metals contents were calculated on a wet weight basis (mg kg−1 WW). Tables with determined elements concentrations also contain the results of one-way analysis of variance with Tukey’s post-hoc test.

Macromolecules have great significance for the human body: potassium as an element with big role in ionic balance and cell function and it is important for proper cardiac contraction, for the proper functioning of the intestines and muscles; calcium is responsible for the development and growth of bones and teeth; it is necessary for muscle contraction, nerve transfer signal and for secretion of hormones and enzymes; magnesium plays different roles in the body, and some are not as certain yet. Potassium is necessary for muscle and nerve cell functions, and also helps maintain proper bone density. Magnesium is important for bone health, nerve function, and muscle contractions. Calcium is important for bone density and muscle and nerve function. Iron is important for the production of red blood cells and the transport of oxygen in the body. Zirconium is a key element in the development and growth of bones and teeth. It is also necessary for muscle contraction, nerve transfer signal and for secretion of hormones and enzymes. Magnesium plays a role in several important processes in the body, including energy production, muscle function, and blood pressure regulation.

| Varieties       | Fruit part | Na   | K     | Mg     | Ca   | P     |
|-----------------|------------|------|-------|--------|------|-------|
| Radmilovcanka   | pulp       | 39±2 | 461±3 | 38±2   | 14±2 | 55±3  |
|                 | peel       | 22±2 | 343±3 | 12±2   | 20±2 | 45±3  |
| Blake           | pulp       | 192±2| 493±5 | 92±2   | 15±2 | 54±5  |
|                 | peel       | 39±2 | 405±5 | 19±2   | 27±2 | 54±5  |
| Hale            | pulp       | 14±2 | 182±18| 87±2   | 14±2 | 50±4  |
|                 | peel       | 21±2 | 122±12| 11±2   | 27±2 | 56±4  |
| Vesna           | pulp       | 11±2 | 606±5 | 94±2   | 11±2 | 57±4  |
|                 | peel       | 11±2 | 460±5 | 100±2  | 16±2 | 47±4  |
| Adria           | pulp       | 34±2 | 606±49| 94±2   | 22±2 | 56±5  |
|                 | peel       | 31±2 | 521±44| 111±2  | 29±2 | 53±4  |

Table 1

The content of essential macromolecules ±SD (mg kg−1 WW) in peel and pulp parts of peach fruit

SD-standard deviation for triplicate determination; mean values in the same column with the same small letters indicate no significant differences (p<0.05) between the pulps and between the peels of different cultivars, separately.
K is the most abundant element in the both parts of fruits whose content ranges from 1822 mg kg\(^{-1}\) to 6605 mg kg\(^{-1}\) WW in the pulp and from 1223 mg kg\(^{-1}\) to 5287 mg kg\(^{-1}\) WW in the peel. The tested elements are more present in the peel than in the pulp except for K which is also the case in the work of Manzoor et al. [2]. Higher values of determined elements follow next descending order: K\(\geq\)Mg\(\geq\)Ca in both parts of fruit. Basar determined P, N, K, Ca, and Mg in flesh and peel of three cultivars (Redhaven, Glohaven and J. H. Hale) from seven orchards in Turkey for each cultivar and these contents were similar in all of the cultivars and the amount of the elements in the same part did not significantly differ [13]. P and K were accumulated in significantly higher concentrations in pulp than in the peel unlike other determined elements. K and N were found below the sufficiency levels in the both flesh and peel samples while Ca content was only found deficient in the pulp samples according to Food and Agriculture Organization of the United Nations which reported critical values only for whole fruit. The order is as follows: K\(\geq\)N\(\geq\)Ca in both of the fruit parts which is the case in the work of Manzoor et al. [2]. Higher values of macroelements were detected in the aforementioned works because the fact that analyzed samples were oven-dried at 70\(^\circ\)C for 72 h. Mean values of the three cultivars are as follows: Ca 60 mg kg\(^{-1}\) (6%); Mg 90 mg kg\(^{-1}\) (22.5%); P 200 mg kg\(^{-1}\) (20%) and K 1900 mg kg\(^{-1}\) (54.29%).

Differences ranging up to an order of magnitude which is in accordance with the percentage of water in the fruit peaches (about 88%) [17].

### Essential trace elements (B, Fe, Cu, Zn, Mn, Ni, Cr) in a certain amount are necessary for normal growth and development of plants and also for customers that use them in the diet. Manganese takes part in carbohydrates metabolism and is known as an antioxidant; iron is a core of red blood cells; zinc is reported as a coenzyme for over 200 enzymes and its sufficient is essential to neutralize the toxic effects of cadmium and excessive absorption of zinc suppresses copper and iron absorption; copper as biocatalyst is an essential trace element, necessary for body pigmentation, for maintenance of a healthy central nervous system, prevention of anemia but its toxicity is a much overlooked contributor to many health problems; nickel is involved in iron metabolism (it affects the absorption of iron from foods) and plays the important role in the formation of red blood cells; it is necessary in the metabolism of sugars, fats, hormones, and cell membranes; chromium helps the metabolism of glucose, regulates the level of insulin and maintain healthy levels of cholesterol and other fats in the blood; boron is important

### Table 2

| Varieties | Fruit part | Cr | Cu | Fe | Mn | Ni | Zn | B |
|-----------|------------|----|----|----|----|----|----|---|
| Redhaven  | pulp       | 0.07±0.003 \(^{\pm}\) 0.02  | 0.84±0.06  | 3.6±0.2 | 0.33±0.03  | 0.17±0.04 \(^{\pm}\) 0.02  | 0.7±0.03  | 4.3±0.1 |
|           | peel       | 0.09±0.003 \(^{\pm}\) 0.04  | 1.0±0.04  | 9.3±0.2 | 0.6±0.07  | 0.19±0.06 \(^{\pm}\) 0.04  | 0.88±0.04  | 6.5±0.2 |
| June Gold | pulp       | 0.07±0.003 \(^{\pm}\) 0.02  | 1.57±0.06  | 9.6±0.2 | 0.62±0.03  | 0.5±0.06  | 0.79±0.03 \(^{\pm}\) 0.2  | 5.6±0.2 |
|           | peel       | 0.08±0.003 \(^{\pm}\) 0.04  | 1.5±0.04  | 10.1±0.2 | 0.73±0.06  | 0.61±0.02  | 0.71±0.02  | 5.7±0.2 |
| Blake     | pulp       | 0.08±0.003 \(^{\pm}\) 0.02  | 0.98±0.04  | 9.6±0.2 | 0.32±0.01  | 0.13±0.01  | 0.7±0.03  | 4.2±0.2 |
|           | peel       | 0.09±0.003 \(^{\pm}\) 0.04  | 1.47±0.06  | 13±2  | 0.7±0.04  | 0.2±0.02  | 0.8±0.05 \(^{\pm}\) 0.2  | 7.2±0.2 |
| Hale      | pulp       | 0.08±0.003 \(^{\pm}\) 0.02  | 3.5±0.07  | 17±2  | 0.36±0.04  | 0.12±0.06  | 0.7±0.04  | 1.4±0.07 |
|           | peel       | 0.11±0.003  | 4.0±0.05  | 17±2  | 0.75±0.04  | 0.3±0.02  | 0.7±0.06  | 4.6±0.2 |
| Vena      | pulp       | 0.12±0.003  | 16.4±0.07  | 10.6±0.2 | 0.47±0.05  | 0.9±0.004 | 0.78±0.04  | 9.6±0.3 |
|           | peel       | 0.09±0.003 \(^{\pm}\) 0.04  | 0.61±0.04  | 4.8±0.2 | 0.46±0.04  | 0.08±0.03  | 0.76±0.05  | 7.2±0.2 |
| Adria     | pulp       | 0.09±0.003 \(^{\pm}\) 0.02  | 1.31±0.05  | 10.6±0.3 | 0.59±0.02  | 0.04±0.004 \(^{\pm}\) 0.02  | 0.78±0.04  | 9.8±0.3 |

SD-standard deviation for triplicate determination; mean values in the same column with the same capital letters indicate no significant differences (p<0.05) between pulp and peel of the same cultivars; mean values in the same column with the same small letters indicate no significant differences (p<0.05) between the pulps and between the peels of different cultivars, separately.
The content of potentially toxic and toxic elements ± SD* (mg kg⁻¹ WW) in peel and pulp parts of peach fruit

| Varieties     | Fruit part | Al   | As   | Pb   |
|---------------|------------|------|------|------|
| Khmilocevskaja| pulp       | 2.7±0.2 | 0.04±0.003 | 0.01±0.001 |
|               | peel       | 7.4±0.3  | 0.05±0.004 | 0.01±0.003 |
| June Gold     | pulp       | 5.3±0.3  | 0.05±0.003  | 0.01±0.001  |
|               | peel       | 12.4±0.5 | 0.07±0.003  | 0.01±0.002  |
| Blake         | pulp       | 4.0±0.2  | 0.04±0.003 | 0.02±0.003 |
|               | peel       | 11.8±0.3 | 0.07±0.002  | 0.02±0.002  |
| Hale          | pulp       | 7.5±0.3  | 0.06±0.002 | 0.02±0.003 |
|               | peel       | 9.1±0.3  | 0.06±0.003  | 0.02±0.003  |
| Verna         | pulp       | 3.1±0.2  | 0.03±0.002 | 0.009±0.001 |
|               | peel       | 4.5±0.2  | 0.03±0.002  | 0.01±0.001  |
| Adra          | pulp       | 6.5±0.3  | 0.07±0.002 | 0.009±0.001 |
|               | peel       | 7.5±0.3  | 0.04±0.003 | 0.010±0.001 |

Conclusions

The assessment of metals in peach represents one of the factors in the evaluation of their quality. In the present work, the minerals of different parts (peel and pulp) of six varieties of peach fruit were evaluated. K is the most abundant macroelement in the both parts of fruits while Fe is the most common essential trace element. All

Organization of the United Nations. Ni concentrations were above the tolerable levels in the both fruit peel and pulp. Examined elements follow the next descending order: Fe>Zn>Cu>Mn>Ni>Co>Cr in the pulp and in the peel: Fe>Cu>Zn>Mn>Ni>Co>Cr. The average amounts in the pulp are as follows: Fe 12.53 mg kg⁻¹; Mn 3.29 mg kg⁻¹; Zn 7.47 mg kg⁻¹; Cu 6.42 mg kg⁻¹; Cr 0.20 mg kg⁻¹; Ni 1.66 mg kg⁻¹; Co 0.45 mg kg⁻¹; while in peel samples: Fe 41.82 mg kg⁻¹; Mn 4.76 mg kg⁻¹; Zn 8.26 mg kg⁻¹; Cu 9.83 mg kg⁻¹; Cr 0.32 mg kg⁻¹; Ni 1.78 mg kg⁻¹; Co 0.48 mg kg⁻¹.

Lead has neurological effects on human health, especially the younger population; cadmium is carcinogenic for human and toxic to plants; arsenic accumulates in the body, especially in the hair, skin and some internal organs and inorganic trivalent arsenic is particularly toxic; mercury is a powerful neurotoxin and it can cause damage to the brain, kidneys and lungs and is especially dangerous for pregnant women and children. The maximum allowable concentrations (MAC values) of Pb, Cd, Hg and As in fresh fruits (1.05, 0.02 and 0.1 mg kg⁻¹, respectively) are defined by national regulation: The provisions on maximal allowed amounts of pesticides, metals, metalloids and other toxic substances, chemotherapeutics, anabolics and other substances that can be found in food [18]. Hg and Cd are not detected while the contents of Pb and As are below these values in all tested samples. The contents of As and Pb are ranged from 0.034 to 0.070 mg kg⁻¹ and from 0.009 to 0.026 mg kg⁻¹, respectively, and the less differences in content between the parts of the fruit as well as between the tested varieties are obvious, especially for Pb. The content of Al is greater in the peel of all samples then in pulp even more than three times. It is also evident that all the analyzed peach varieties show statistically significant differences regarding the content of this element. Maximum levels (MLs) for heavy metals in foodstuffs have been set by Commission Regulation [8]. The European Communities set maximum levels (MLs) to be 0.10 mg kg⁻¹ WW for Pb and 0.05 mg kg⁻¹ for Cd. There are no statutory limits for As and Hg levels in fruit at EU level. Basar determined significantly higher concentrations, as average amounts, of Pb (1.67 mg kg⁻¹ DW) in pulp then in peel samples (0.56 mg kg⁻¹ DW) and these concentrations were above the tolerable levels in the both fruit parts [13]. Matal et al. found 0.0228 mg kg⁻¹ Cd in whole fruit while lead is not detected while Chiștayokov et al. found 0.01 mg kg⁻¹ Cd in Egypt samples of whole peach fruit [2,19].

Conclusions

The assessment of metals in peach represents one of the factors in the evaluation of their quality. In the present work, the minerals of different parts (peel and pulp) of six varieties of peach fruit were evaluated. K is the most abundant macroelement in the both parts of fruits while Fe is the most common essential trace element. All

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examined macroelements are more present in the peel than in the pulp with the exception of K which is also the case in the earlier works. It follows that removal of peel from peach fruits may induce significant nutrient losses and because of that the intake of fruits along with their peels can be more beneficial as a potential source of high-value components. Significant differences in the mean content of all investigated macroelements between the pulp and the peel of peach fruits in all investigated cultivars exist. Differences in the metals content in the same part of the fruit of different species are smaller and at least in the case of P. The tested macroelements are present in the following descending order: K>P>Ca>Na>Mg and the contents of examined trace elements follow the next descending order: Fe>B>Cu>Zn>Mn>Ni>Cr in the peel and the pulp of almost all samples. Much smaller differences in the content of trace elements between the peel and the pulp of the same species and between different parts of the same type are present. Hg and Cd are not detected while the contents of Pb and As are below values prescribed by relevant regulations. On the base of obtained results and recommendations of USDA it can be said that this fruit can serve as a good source of essential metals for humans.

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