

ORIGINAL SCIENTIFIC PAPER

# Copper in fruit and vegetable products intended for human consumption and sold in the local market in the Republic of Serbia, 2015–2019

Milana Lazović<sup>1,2</sup> | Vladimir Tomović<sup>1</sup> | Biljana Bajić<sup>2</sup> | Isidora Kecojević<sup>2</sup> | Danica Mrkajić<sup>2</sup> | Ana Joksimović<sup>2</sup> | Mila Tomović<sup>3</sup> | Aleksandra Martinović<sup>4</sup> | Dragan Vujadinović<sup>5</sup> | Milenko Smiljanić<sup>5</sup> | Vesna Đorđević<sup>6</sup>

<sup>1</sup>University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Republic of Serbia

<sup>2</sup>A BIO TECH LAB d.o.o., Vojvode Putnika 87, 21208 Sremska Kamenica, Republic of Serbia

<sup>3</sup>Technical School “Pavle Savić”, Šajkaška 34, 21138 Novi Sad, Republic of Serbia

<sup>4</sup>University of Donja Gorica, Faculty for Food Technology, Food Safety and Ecology, Oktoih 1, 81000 Podgorica, Montenegro

<sup>5</sup>University of East Sarajevo, Faculty of Technology Zvornik, Karakaj 34A, 75400 Zvornik, Republic of Srpska, Bosnia and Herzegovina

<sup>6</sup>Institute of Meat Hygiene and Technology, Kačanskog 13, 11040 Belgrade, Republic of Serbia

## Correspondence

Vladimir Tomović

Email: tomovic@uns.ac.rs

## Abstract

The concentration of copper (Cu) was determined in 110 samples of fruit (n = 31) and vegetable products (n = 79), collected during the period from January 2015 to December 2019. Fruit and vegetable products originate from 17 countries, including Serbia. Samples were analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES). Measurable levels of Cu were found in all analysed samples. Overall, Cu levels ranged from 0.065 to 14.050 mg kg<sup>-1</sup>, with an average of 1.314 mg kg<sup>-1</sup>. Only 3 (2.73%) of fruit and vegetable products exceeded the maximum levels set by Serbian Regulation which was valid until the end of 2019.

**Keywords:** fruit products, vegetable products, copper

## 1. INTRODUCTION

Copper (Cu), an essential mineral, is naturally present in some foods and is available as a dietary supplement. It is a cofactor for several enzymes (known as “cuproenzymes”) involved in energy production, iron metabolism, neuropeptide activation, connective tissue synthesis, and neurotransmitter synthesis (Collins 2014; Food Institute of Medicine Nutrition Board 2001; Prohaska 2012). One abundant cuproenzyme is ceruloplasmin (CP), which plays a role in iron metabolism and carries more than 95%

of the total copper in healthy human plasma (Hellman & Gitlin 2002). Copper is also involved in many physiologic processes, such as angiogenesis; neurohormone homeostasis; and regulation of gene expression, brain development, pigmentation, and immune system functioning (Collins 2014). In addition, defense against oxidative damage depends mainly on the copper-containing superoxide dismutases (Allen & Klevay 1994; Owen 1982). The richest dietary copper sources include shellfish, seeds and nuts, organ meats, wheat-bran cereals, whole-grain prod-

**Table 1.** Maximum levels (mg kg<sup>-1</sup> wet weight) for copper in fruit and vegetable products before 2020 (Serbian Regulation 2014; 2015; 2018a; 2018b) amended in 2019.

Metal	Fruit and vegetable products	MLs
Copper	Fruit juices, concentrated fruit juices, fruit syrups and citrus base (after dilution)	5.0
	Fruit products in metal containers and other types of packaging, including fried and dry roasted seeds	10.0
	Vegetable products in metal containers and other types of packaging	5.0
	Triple concentrated tomato paste	20.0

ucts, and chocolate (Collins 2014; Prohaska 2012). The absorption of copper is strongly influenced by the amount of copper in the diet (Food Institute of Medicine Nutrition Board 2001).

Though an essential micronutrient for man, Cu is toxic at high levels. An overload of this metal easily leads to Fenton-type redox reactions, resulting in oxidative cell damage and cell death. However, Cu toxicity as a result of dietary excess is generally not considered a widespread health concern, probably as a result of the homeostatic mechanisms controlling Cu absorption and excretion (Bost et al. 2016; Turnlund, Keyes, Kim, & Domek 2005). In EFSA2008 EFSA established an Acceptable Daily Intake (ADI) of 0.15 mg Cu kg<sup>-1</sup> bw per day (corresponding to 10 mg day<sup>-1</sup> for a 70-kg adult). However, the Acceptable Daily Intake (ADI) for copper from all sources in food will be reduced from 0.15 mg kg<sup>-1</sup> of body weight (bw) to 0.07 mg kg<sup>-1</sup> bw based on an updated evaluation of the scientific evidence (EFSA (European Food Safety Authority) 2022). In the EU, there are no regulations surrounding copper maximum levels in fruits and vegetables products. In Serbia, maximum levels for copper in fruit and vegetable products were valid until the end of 2019 (Serbian Regulation 2014; 2015; 2018a; 2018b) amended in 2019. These maximum levels are summarised in Table 1.

In Serbia, fruit and vegetable products quality is regulated by the Regulation on the quality of fruit jams, jellies, marmalades, "Pekmeza" and sweetened chestnut purees (Serbian Regulation 2015), Regulation on the quality of on the fruit juices and certain related products intended for human consumption (Serbian Regulation 2018b) amended in 2019 and 2020 and Regulation on the quality of fruit and vegetable products (Serbian Regulation 2020), amended in 2021.

To date, no reports have analysed the copper concentration in commercial fruit and vegetable products. Thus, the aim of this study was to determine the concentration of copper in fruit and vegetable products intended for human consumption and available in the Serbian market and to compare them with maximum levels established for these food products by the Serbian legislation which was valid until the end of 2019.

## 2. MATERIALS AND METHODS

From January 2015 to December 2019 concentration of Cu was determined in 31 samples of fruit products and in 79 samples of vegetable products. Detailed characteristics of the analysed samples are presented in Table 2.

The methods for sample preparation and analysis of the concentration of Cu in the collected fruit and vegetable products and quality control using the standard reference material were conducted as described in detail in (Lazović et al. 2022; 2023). Validation data by analysing standard reference material are presented in Table 3. In all analysed samples, Cu concentration was reported as mg kg<sup>-1</sup> wet weight. Primary samples of each fruit and vegetable products were taken from eight different packages where five fruit and vegetable products were taken randomly from each package. The examined fruit and vegetable products did not contain inedible parts.

## 3. RESULTS AND DISCUSSION

The individual concentrations of the copper in all samples of fruit (n = 31) and vegetable products (n = 79) are shown in the supplementary material. The copper concentrations in all analysed samples were above the detection limit.

The individual copper concentration in the fruit and vegetable products ranged from 0.065 (apple juice) to 14.050 mg kg<sup>-1</sup> (dried apple), with an average of 1.676 mg kg<sup>-1</sup>, and from 0.073 (apple juice) to 12.880 mg kg<sup>-1</sup> (dried apple), with an average of 1.173 mg kg<sup>-1</sup>, respectively. The ML for copper set by Serbian Regulation which was valid until the end of 2019 was exceeded in 1 fruit products samples (3.13%; 1 out of 31: dried apple) and in 2 vegetable products samples (2.53%; 2 out of 79: beet-root juice and tomato powder). Overall, Cu levels ranged from 0.065 to 14.050 mg kg<sup>-1</sup>, with an average of 1.314 mg kg<sup>-1</sup>. Only 3 (2.73%) of fruit and vegetable products exceeded the maximum levels set by Serbian Regulation which was valid until the end of 2019. Elevated copper concentrations were determined in the fruit and vegetable products before placing fruit and vegetable products on the market.

In conclusion, the obtained results for copper concentration in fruit and vegetable products indicate presence of this metal in the food. Thus, presence of copper

**Table 2.** Characteristics of the analysed fruit and vegetable products and the concentration ranges (mg kg<sup>-1</sup>) for Cu.

Fruit and vegetable products	n	Country of origin	Range of Cu concentration
<b>Fruit products</b>			
Apple juice	1	Serbia	0.065
Dried apple	2	Poland, Turkey	1.087–14.050
Frozen apple puree	1	Serbia	0.273–0.327
Apricot jam	1	Serbia	0.512
Frozen apricot puree	1	Serbia	0.395
Banana powder	1	France	1.650
Blackberry juice	1	Serbia	0.095
Dried cranberry	1	Greece	0.274
Dried fig	2	France, Turkey	1.523–2.421
Dried grape	4	Iran, Turkey	2.870–3.887
Plum jam	1	Serbia	0.367–0.614
Dried papaya	1	Thailand	0.934
Dried pineapple	1	Thailand	1.595
Dried plum	3	Argentina, Greece, France	1.186–2.623
Frozen plum	3	Serbia	0.159–0.599
Frozen raspberry	1	Serbia	0.731
Frozen sour cherry	3	Serbia	0.901–2.750
Frozen sour cherry puree	1	Serbia	1.290
Frozen strawberry	1	Serbia	0.609
<b>Vegetable products</b>			
Fermented algae	6	Croatia, North Macedonia, Serbia	0.158–1.912
Pasteurized artichokes	1	Italy	0.085
Beetroot juice	1	Slovenia	12.880
Beetroot powder	1	Poland	4.210
Frozen broccoli	3	Serbia	0.256–0.374
Broccoli powder	1	China	2.570
Frozen butternut puree	1	Serbia	0.268
Dried carrot	4	China, Poland, Serbia	1.869–3.362
Frozen carrot	2	Serbia	0.374–1.060
Frozen cauliflower	2	Poland, Serbia	0.075–0.636
Dried chickpea	1	Greece	1.279
Dried ginger	1	India	2.112
Dried green bean	6	Serbia	0.248–0.394
Dried onion	5	France, Germany, India	0.118–3.356
Frozen peas	4	Serbia	0.251–1.083
Dried pepper	1	Croatia	4.065
Frozen pepper	11	Serbia	0.291–1.610
Pickled peperoni pepper	1	North Macedonia	0.153
Frozen pepper puree	1	Serbia	0.672
Pickle	1	Serbia	0.206
Potato gnocchi	1	Austria	1.359
Frozen pumpkin	1	Serbia	0.230
Pasteurized ratatouille	1	North Macedonia	0.090
Sauerkraut	3	Serbia	0.079–0.450
Dried spinach	1	India	6.697
Frozen spinach	1	Serbia	0.390
Frozen sweetcorn	1	Serbia	0.101
Sterilized sweetcorn	1	Serbia	0.231
Tomato juice	3	Serbia	0.314–0.368
Double concentrated tomato paste	2	Italy, Spain	0.167–0.203
Tomato powder	1	Italy	10.710
Frozen mixed vegetables	8	Serbia	0.189–0.728

**Table 3.** Validation data (mg kg<sup>-1</sup>) by analysing standard reference material.

Metal	LOD	LOQ	Certified	Measured
Copper	0.016	0.055	0.140	0.128

in food cannot be ignored due to their significance impact on human health, which is in accordance with new EFSA recommendation.

#### 4. ACKNOWLEDGEMENTS

This research was funded by the Ministry of Education, Science and Technological Development, Republic of Serbia under Grant [451-03-47/2023-01/200134]. Also, this research has been done in liaison with the activities defined by the grant for the establishment and implementation of the research-innovation-scientific program “Centre of Excellence (CoE) for digitalization of microbial food safety risk assessment and quality parameters for accurate food authenticity certification (FoodHub)”, financed by the Ministry of Education, Science, Culture and Sports of Montenegro under Grant No [01-3660/2].

#### REFERENCES

- Allen, K. G. D., & Klevay, L. M. (1994). Copper: an antioxidant nutrient for cardiovascular health. *Current Opinion in Lipidology*, 5(1), 22–28. <https://doi.org/10.1097/00041433-199402000-00005>
- Authority), E. E. F. S. (2008). *Conclusion regarding the peer review of the pesticide risk assessment of the active substance copper compounds*. (Pages: 1–101 Volume: 187)
- Bost, M., Houdart, S., Oberli, M., Kalonji, E., Huneau, J.-F., & Margaritis, I. (2016). Dietary copper and human health: Current evidence and unresolved issues. *Journal of Trace Elements in Medicine and Biology*, 35, 107–115. <https://doi.org/10.1016/j.jtemb.2016.02.006>
- Collins, J. F. (2014). *Modern nutrition in health and disease*. Baltimore, MD: Lippincott Williams & Wilkins.
- EFSA (European Food Safety Authority). (2022). *Re-evaluation of the existing health-based guidance values for copper and exposure assessment from all sources: Draft opinion for public consultation*.
- Food Institute of Medicine Nutrition Board. (2001). *Dietary reference intakes for vitamin a, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc*. Washington, DC: National Academies Press.
- Hellman, N. E., & Gitlin, J. D. (2002). Ceruloplasmin metabolism and function. *Annual Review of Nutrition*, 22(1), 439–458. <https://doi.org/10.1146/annurev.nutr.22.012502.114457>
- Lazović, M., Tomović, V., Vasiljević, I., Kecojević, I., Tomović, M., Martinović, A., ... Đorđević, V. (2022). Cadmium, lead, mercury, and arsenic in fresh fruits and fruit products intended for human consumption in the Republic of Serbia, 2015–2017. *Food Additives & Contaminants: Part B*, 15(4), 283–291. <https://doi.org/10.1080/19393210.2022.2106313>
- Lazović, M., Tomović, V., Vasiljević, I., Kecojević, I., Tomović, M., Martinović, A., ... Đorđević, V. (2023). Cadmium, lead, mercury and arsenic in fresh vegetables and vegetable products intended for human consumption in the Republic of Serbia, 2015–2017. *Food Additives & Contaminants: Part B*, 16(2), 102–119. <https://doi.org/10.1080/19393210.2023.2169359>
- Owen, C. A. J. (1982). *Biochemical aspects of copper: Copper proteins, ceruloplasmin, and copper protein binding*. Park Ridge, NJ: Noyes Publications.
- Prohaska, J. R. (2012). *Present knowledge in nutrition*. Washington, DC: Wiley-Blackwell.
- Serbian Regulation. (2014). *Pravilnik o maksimalno dozvoljenim količinama ostataka sredstava za zaštitu bilja u hrani i hrani za životinje i o hrani za životinje za koju se utvrđuju maksimalno dozvoljene količine ostataka sredstava za zaštitu bilja: Službeni glasnik RS, broj 29 (2014), 37 (2014), 39 (2014), 72 (2014), 80 (2015), 84 (2015), 35 (2016), 81 (2016), 21 (2017) & 81 (2017)*.
- Serbian Regulation. (2015). *Pravilnik o kvalitetu voćnih džemova, želea, marmelade, pekmeza i zaslađenog kesten pirea: Službeni glasnik RS, broj 101*.
- Serbian Regulation. (2018a). *Pravilnik o maksimalno dozvoljenim količinama ostataka sredstava za zaštitu bilja u hrani i hrani za životinje i o hrani za životinje za koju se utvrđuju maksimalno dozvoljene količine ostataka sredstava za zaštitu bilja: Službeni glasnik RS, 22 (2018), 90 (2018), 76 (2019) & 81 (2019)*.
- Serbian Regulation. (2018b). *Pravilnik o voćnim sokovima i određenim srodnim proizvodima namenjenim za ljudsku upotrebu: Službeni glasnik RS, broj 103 (2018), 94 (2019), 2 & 84 (2020)*.
- Serbian Regulation. (2020). *Pravilnik o kvalitetu proizvoda od voća i povrća: Službeni glasnik RS, broj 128 & 130 (2021)*.
- Turnlund, J. R., Keyes, W. R., Kim, S. K., & Domek, J. M. (2005). Long-term high copper intake: effects on copper absorption, retention, and homeostasis in men. *The American Journal of Clinical Nutrition*, 81(4), 822–828. <https://doi.org/10.1093/ajcn/81.4.822>