

CONCENTRATIONS OF SELECTED METALS (NA, K, CA, MG, FE, CU, ZN, AL, NI, PB, CD) IN COFFEE

KONCENTRACIJE IZBRANIH KOVIN (NA, K, CA, MG, FE, CU, ZN, AL, NI, PB, CD) V KAVI

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ABSTRACT

Keywords:

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Introduction: The health benefits and detrimental effects of coffee consumption may be linked to chemical compounds contained in coffee beans. The aim of our study was to evaluate the concentration of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), copper (Cu), zinc (Zn), aluminum (Al), nickel (Ni), lead (Pb) and cadmium (Cd) in green and roasted samples of coffee beans purchased in Bosnia and Herzegovina, and to determine the potential health implications at current consumption level.

Methods: The concentrations were determined using a microwave high-pressure mineralization and atomic absorption spectrometer that measures total metal (ionic and non-ionic) content.

Results: The average metal concentrations (μg element/g coffee) in the green coffee beans were; Na: 18.6, K: 19898, Ca: 789, Mg: 1758, Fe: 60, Cu: 14, Zn: 3.6, Al: 4.2, Ni: 0.415, Pb: 0.076, and Cd: 0.015, while, in the roasted; Na: 23, K: 23817, Ca: 869, Mg: 1992, Fe: 41.1, Cu: 11.4, Zn: 5.41, Al: 4.19, Ni: 0.88, Pb: 0.0169, and Cd: 0.0140.

Conclusion: The level of investigated metals at the present level of consumption of coffee in Bosnia falls within the limits recommended as safe for health.

IZVLEČEK

Ključne besede:

kavna infuzija,
zelena kava,
pražena kava,
koncentracija kovin

Uvod: Zdravstvene prednosti in škodljivi učinki uživanja kave so lahko povezani z kemijskimi spojinami v kavnih zrnih. Cilj študije je oceniti koncentracije naslednjih spojin: natrij (Na), kalij (K), kalcij (Ca), magnezij (Mg), železo (Fe), baker (Cu), cink (Zn), aluminij (Al), nikelj (Ni), svinec (Pb) in kadmij (Cd) v zelenih in praženih vzorcih kavnih zrn, kupljenih v Bosni in Hercegovini, ter določiti morebitne zdravstvene posledice glede na trenutno raven uživanja.

Metode: Koncentracije so bile določene z uporabo visokotlačne mineralizacije z mikrovalovi in atomske absorpcijske spektrometrije, ki merijo skupno vsebino kovine (ionska in neionska).

Rezultati: Povprečna koncentracija kovin (μg elementa/g kave) v zelenih kavnih zrnih je bila: Na: 18,6, K: 19898, Ca: 789, Mg: 1758, Fe: 60, Cu: 14, Zn: 3,6, Al: 4,2, Ni: 0,415, Pb: 0,076 in Cd: 0,015; v praženih zrnih pa: Na: 23, K: 23817, Ca: 869, Mg: 1992, Fe: 41,1, Cu: 11,4, Zn: 5,41, Al: 4,19, Ni: 0,88, Pb: 0,0169 in Cd: 0,0140.

Zaključek: Raven preverjenih kovin na trenutni stopnji uživanja kave v Bosni in Hercegovini se nahaja znotraj omejitev, ki so priporočene kot zdrave za zdravje.

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1 INTRODUCTION

Coffee is, after water, amongst the most popular beverages consumed in the world (1). Numerous studies suggest that moderate coffee consumption has beneficial health impacts on humans. Coffee infusions show protective potential against oxidative stress through the presence of antioxidants and active components (2-4). They increase the antioxidant plasma capacity and might increase glutathione levels and thus reduce the levels of DNA damage (5, 6). Furthermore, some studies imply that habitual coffee consumption could protect against Parkinson's and Alzheimer's disease (7, 8). Coffee consumption may also be linked to improvements in fecal microbiota and colonic fermentation, may reduce the risk of developing liver, colorectal and prostate cancer as well as brain tumors (9-11). The meta-analysis by Lukic et al. confirmed the protective effect of coffee consumption on the risk of endometrial cancer. Additionally, authors suggest that increased coffee intake might be particularly beneficial for women with obesity (12). On the other hand, increased long-term coffee consumption may cause, among others: increasing plasma homocysteine and LDL (Low Density Lipoprotein) level, gastrointestinal disturbances (4, 13, 14). Moreover, repeated doses of coffee throughout the day may be linked to an elevation of cortisol secretion in the afternoon hours (15). What is even more, maternal consumption of coffee during pregnancy may increase the risk of the occurrence acute childhood leukemia (16, 17). It is also suggested that coffee consumption is a risk factor for osteoporosis in postmenopausal women (18).

The contamination of food may be caused by various compounds found in the environment e.g. high doses of fertilizers or plant protection chemicals. These compounds, taken with food and then absorbed in the digestive tract, may have an influence on body cells and tissues. On the other hand, potential contamination may derive from package and storage, pollution, fungi and molds (19, 20). The amount of compounds taken with coffee infusions depend on their contents in coffee beans, level of consumption and pattern of drinking coffee infusions, which is linked to the geographical region. In Europe, the highest coffee consumption is observed in Finland, 12 kg per capita/year, and in Bosnia and Herzegovina (B&H) it is 6.2 kg per capita/year (21).

The aim of this study was to evaluate the concentration of selected metals: Na, K, Ca, Mg, Fe, Cu, Zn, Al, Ni, Pb and Cd in coffee and determine the difference in their concentration between green and roasted coffee beans. Additionally, we investigated if the level of studied metals, at the current level of consumption of coffee in B&H, is within the recommended limits safe for health.

2 MATERIALS AND METHODS

Coffee infusions in Bosnia are prepared in a traditional way, which is widespread in the Balkans, the Middle East, Eastern Europe, North Africa, the Caucasus and Bali, known as Turkish coffee. During the first step roasted ground coffee is added to boiling water in the pot and heated until the foam level is rising. Afterwards, the coffee is flooded with a small amount of cold water. At this time the coffee is partially precipitating. Next, the coffee is heated until the foam level rises again. After a few minutes the coffee is ready to drink (19).

2.1 Coffee Samples

The coffee beans were roasted and purchased in small local stores in Sarajevo, B&H. Coffee roasting was carried out in specialized drum furnaces by store employees. The process of roasting can be described as follows: the gas flame under the drum heats and burns the coffee beans, the temperature being around 200°C immediately after roasting. After this process, the beans are cooled down by air at ambient temperature.

We tested two samples of green coffee beans (G 1-2) and six (R 1-6) roasted. Two pairs of the same coffee beans, before and after roasting were examined: G 1a and R 1a and G 2b and R 2b. The measurements of metal concentration were performed in triplicate from each coffee sample.

2.2 Instrument

Grinded coffee beans weighing 1 ± 0.01 g were digested with a mixture of concentrated HNO₃ and HClO₄ acids (5 and 1 mL, respectively) and then diluted to 25 mL with water. Coffee infusions were prepared by boiling 10 ± 0.1 g of coffee in 200 mL of water. Coffee brewing time was 5 min. After cooling the infusions to 20°C, 25 mL were taken for mineralization with a mixture of concentrated HNO₃ and HClO₄ acids (2.5 and 1 mL, respectively). After mineralization, the samples were diluted to 50 mL with water.

Mineralizations of coffee beans and coffee infusions were carried out using a high pressure microwave mineralizer, Speedwave Xpert (Bergof, Eningen, Germany). Metals were determined using the Hitachi Polarized Zeeman Atomic Absorption Spectrometer ZA3000 Series (Hitachi High-Technologies Corporation, Tokyo, Japan). Ca, K, Na, Mg were determined using the flame atomic absorption spectroscopy method (FAAS) in the air-acetylene flame with Zeeman correction. Fe, Cu, Zn, Al, Pb Cd and Ni were measured by the flameless technique in a graphite furnace atomic absorption spectroscopy (GFAAS). Mili-Q water (18.2M Ω) was used to prepare coffee infusions and dilutions. Standardized calibration solutions

dedicated for metal determination by atomic absorption with a concentration of 1000 mg/L were used for the calibration curves; for Mg, Ca, K, Na and Fe (Scharlau Chemie s.a., Barcelona, Spain), and for Zn, Cu, Pb, Cd Ni and Al (Merck, Darmstadt, Germany). Reliability of the analytical method was tested using a reference material - fish muscle ERM-BB422 (European Reference Materials, European Commission - Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium). The recovery of elements was in the range of 95-105%, and the precision for the reference material was 1.2-10.1%.

2.3 Statistical Analysis

The measurements of metal concentration were performed in triplicate from each coffee sample. For quantitative variables in each group, the minimum and maximum values, the arithmetic mean, SD and IQR were calculated. The differences of metals' concentration were performed using the ANOVA test.

3 RESULTS

The ranges of values of metals' concentration (μg element/g coffee) in the samples of green coffee beans are presented in Table 1a. In the samples of roasted coffee beans, there were: Na: 13.0-36.3, K: 20300-32933, Ca 750-939, Mg: 1800-2127, Fe: 35.2-49.1, Cu: 6.5-16.5, Zn: 4.96-6.18, Al: 1.74-6.01, Ni: 0.69-1.16, Pb: 0.0115-0.0215 and Cd: 0.0111-0.0222 $\mu\text{g/g}$ of coffee. The average contents of Na, K, Ca, Mg, Zn, Ni and Cd in roasted coffee samples compared to green coffee were higher, while average contents for Al have not changed, and for three metals: Fe, Cu and Pb were lower (see Table 1a and 1b). The ranges of values of metals' concentration ($\mu\text{g}/100\text{mL}$) in the coffee infusions were as follows: Na: 25.5-63.9, K: 81467-132333, Ca: 1037-1827, Mg: 4600-8463, Fe: 8.93-24.50, Cu: 1.20-6.86, Zn: 5.53-13.17, Al: 2.03-8.43, Ni: 0.78-1.82, Pb: 0.133-0.558, and Cd: 0.036-0.061 (see Table 2).

Table 1a. Concentration of metals in green coffee ($\mu\text{g/g}=\text{ppm}$).

No of green coffee	Na	K	Ca	Mg	Fe	Cu	Zn	Al	Ni	Pb	Cd
G1a	10.6	19583	695	1733	75.1	18.5	4.04	5.65	0.44	0.1436	0.0145
G 2b	26.6	20213	882	1783	45.2	9.4	3.09	2.73	0.39	0.0084	0.0152
Mean	18.6	19898	789	1758	60	14	3.6	4.2	0.415	0.076	0.015
SD	± 11.31	± 445.48	± 132.23	± 35.36	± 21.14	± 6.43	± 0.67	± 2.06	± 0.04	± 0.0956	± 0.0005
IQR	(8)	(315)	(93.5)	(25)	(14.95)	(4.55)	(0.48)	(1.46)	(0.03)	(0.068)	(0.0004)

Table 1b. Concentration of metals in roasted coffee ($\mu\text{g/g}=\text{ppm}$).

No of roasted coffee	Na	K	Ca	Mg	Fe	Cu	Zn	Al	Ni	Pb	Cd
R 1a	24.2	20300	868	2127	41.8	16.5	5.07	3.53	0.72	0.0202	0.0124
R 2b	36.3	22133	888	2120	49.1	10.3	6.18	6.01	0.69	0.0131	0.0126
R 3	21.6	32933	864	2097	37.4	13.3	5.16	4.25	1.14	0.0115	0.0111
R 4	14.3	25167	904	2007	36.2	6.9	4.96	4.44	0.71	0.0196	0.0222
R 5	13.0	20867	750	1803	46.7	14.6	5.89	5.17	0.84	0.0215	0.0120
R 6	28.6	21500	939	1800	35.2	6.5	5.22	1.74	1.16	0.0155	0.0135
Mean	23	23817	869	1992	41.1	11.4	5.41	4.19	0.88	0.0169	0.0140
SD	± 8.80	± 4779.12	± 64.30	± 153.91	± 5.80	± 4.13	± 0.50	± 1.47	± 0.22	± 0.0041	± 0.0041
IQR	(11.4)	(3383)	(35)	(260.3)	(9)	(6.5)	(0.63)	(1.28)	(0.35)	(0.006)	(0.001)

Samples G 1 and G 2- green; R 1 to R 6- roasted; G 1a and R 1a and G 2b and R 2b- pairs of the same coffee beans, before and after roasting; SD- standard deviation; IQR- interquartile range

Table 2. Concentration of metals in coffee infusions, ($\mu\text{g}/100\text{mL}$).

No of coffee	Na	K	Ca	Mg	Fe	Cu	Zn	Al	Ni	Pb	Cd
R 1a	57.0	86933	1277	6593	11.30	2.82	6.10	4.93	0.78	0.558	0.042
R 2b	59.8	95667	1633	8463	24.50	2.62	13.17	4.63	1.63	0.357	0.059
R 3	42.8	132333	1037	6893	15.87	6.86	6.13	8.33	1.62	0.163	0.041
R 4	25.5	103533	1233	4600	8.93	2.15	5.53	5.40	0.82	0.133	0.036
R 5	19.6	81467	1263	7380	16.13	2.70	6.67	8.43	1.04	0.192	0.061
R 6	63.9	95267	1827	8073	15.27	1.20	8.13	2.03	1.82	0.140	0.046
Mean	44.8	99200	1378	7000	15.33	3.04	7.62	5.63	1.29	0.257	0.048
SD	± 18.71	± 17941	± 292.36	± 1369.18	± 5.33	± 1.95	± 2.86	± 2.43	± 0.46	± 0.168	± 0.010
IQR	(29.3)	(12550)	(303.5)	(1231.8)	(3.8)	(0.5)	(1.66)	(2.89)	(0.75)	(0.17)	(0.015)

SD- standard deviation; IQR- interquartile range

All analyzed metals passed from ground coffee beans to coffee infusions. The highest average diffusion showed K and Mg, more than 83 and 70%, respectively. The average level of diffusion from 38 to 27% showed: Na, Pb, Ca, Ni and Zn and Al. While, the lowest: Fe, Cu and Cd, each less than 11% (see Table 3).

Table 3. Penetration of metals to coffee infusions, (%).

No of coffee	Na	K	Ca	Mg	Fe	Cu	Zn	Al	Ni	Pb	Cd
R 1a	47.1	85.6	29.4	62.0	5.4	3.4	24.0	28.0	55.3	6.8	21.5
R 2b	32.9	86.4	36.8	79.8	10.0	5.1	42.6	15.4	54.4	9.4	47.6
R 3	39.6	80.4	24.0	65.8	8.5	10.3	23.8	39.2	28.2	7.3	28.1
R 4	35.7	82.3	27.3	45.8	4.9	6.2	22.3	24.3	13.6	3.2	23.2
R 5	30.2	78.1	33.7	81.8	6.9	3.7	22.6	32.6	17.9	10.3	24.9
R 6	44.7	88.6	38.9	89.7	8.7	3.7	31.1	23.3	18.0	6.8	31.4

The analysis in pairs of the same coffee beans, before and after roasting showed that, in roasted coffee beans (R 1a), concentrations of Na, Ca, Zn and Ni were significantly higher than in green coffee beans (G 1a), while in roasted beans R 2b, concentrations of Na, K, Mg, Zn, Al, Ni and Pb were significantly higher than in green beans G 2b. It should be noted that, in green coffee beans (G 1a), concentrations of Al and Pb were significantly higher than in roasted coffee beans (R 1a) (see Table 4).

Table 4. Empirical levels of significance for differences of metals' concentrations by ANOVA test.

Metal	G 1a vs. R 1a	G 2b vs. R 2b
Na	<0.001*	0.013*
K	0.509	0.008*
Ca	<0.001*	0.802
Mg	0.050	0.003*
Fe	0.004	0.427
Cu	0.335	0.235
Zn	0.017*	0.007*
Al	0.004*	0.0066*
Ni	0.020*	0.012*
Pb	<0.001*	0.030*
Cd	0.173	0.135

*statistically significant differences

4 DISCUSSION

Coffee beans from miscellaneous geographical areas are characterized by different organoleptic features and chemical composition (20, 22, 23). The final content of elements in the coffee beans is also influenced by technological processes: drying, burning, roasting and storage (19, 20). Mineral components and toxic elements pass to the beverage during the brewing process. Their final content in infusion is influenced by methods of brewing and occurrence other mineral components that could be present e.g. in water used to prepare beverage (24).

On the one hand metals play an important role in the human body e.g. as components of enzymes. On the other hand, their increased supply may cause adverse health effects, like damage to internal organs, endocrine disruption and poor reproductive capacity and genotoxicity linked to cancers. They may also be involved in the pathogenesis of neurodegenerative diseases (25-28). Moreover, it should be noted that lead accumulates in the human body, causing distant effects (29).

The tolerable upper intake level (mg), which exceeds a recommended intake for the examined elements per year (for adults with average body weight 70 kg), is as follows: Na: 730000, K: 2775000-12775000 (probably oral lethal dose for human varies), Ca: 912500, Cu: 1825, Zn: 9125, Al: 3650, Ni: 365, Pb: 91, Cd: 9.125. Very large doses of magnesium, higher than 1825000 mg, are associated with its toxicity, and oral dose of 1533000 mg Fe can be lethal (30-34).

The exposure on metals from coffee is usually a long-term low-concentration exposure. Coffee is a rich source of elements and compounds. The data on the differences in concentrations of metals in coffee beans is important due to the popularity of this beverage and the occurrence of a safe consumption limit for elements that come from the diet, dietary supplements and the environment and topped up by coffee. In addition, compounds contained in coffee may affect the course of treatment e.g. in bipolar affective disorder, by affecting the blood concentration of lithium (35).

The findings we obtained suggest that roasting of coffee beans may affect the content of some metals, and drying may cause increase in concentration of the elements. In coffee samples before roasting the concentrations of Na, K, Ca, Mg, Zn, Ni (for G 1a) and K, Mg, Zn, Ni, Pb (for G 2b) were lower than after the roasting process. However, in coffee sample G 1a: Fe, Cu and Pb, the concentration of metals was lower after roasting. The ranges of estimated intake of investigated metals per capita/year, based on coffee consumption obtained from (21) were: Na: 80.6-225.1; K: 125860--204184.6; Ca: 4650-5821.8; Mg: 11160-13187.4; Fe: 218.2-304.4; Cu 40.3-102.3; Zn:30.8-38.3; Al:

10.8-37.3; Ni: 4.3-7.2; Pb: 0.07-0.13; Cd: 0.07-1.14 mg/ per capita/year, and none of the metals tested exceeded the level that could pose a health risk. Our previous study of coffee purchased in Bosnia has shown similar values for Ni intake 3.83-5.68, but higher values for Pb 4.76-7.56 mg/ per capita/year (36). Unfortunately, in the previous study, we did not investigate green coffee beans.

Generally, the number of reports concerning content of metals in green coffee beans is limited in comparison to roasted coffee beans reports. Stelmach et al. and Nogaim et al., have analyzed mineral components in green coffee beans from Africa, America, Asia and Yemen, respectively (37, 38). Authors reported similar to ours values for Cu and Fe. However, Nogaim et al. have observed higher values for Pb (0.599-7.989 µg/g) in Yemeni green coffee beans (38). This confirms that coffee beans growing on different geographical areas are characterized by different chemical composition. Unfortunately, in this research the content of elements after roasting was not determined. Taking into account the results obtained in other studies, which showed that the content of Pb after roasting compared to green coffee beans increased, it would be an interesting issue to investigate. Długaszek et al. have assessed the content of selected elements in Colombian coffee beans purchased in Poland. Authors observed similar Al and Ca concentrations, but lower Mg, Fe, Zn, Ni, Cu and Cd in comparison to our results for Brazilian coffee beans purchased in Bosnia. The authors observed higher than ours Pb content (0.02-0.06 µg/g), which is linked to higher estimated intake of Pb: 0.122-0.366 mg per capita/year. Additionally, a lower intake of coffee in Poland than in Bosnia has been observed (2.4 vs. 6.2 kg per capita /year, respectively) (24). Other authors, Grembecka et al. have also investigated the metal content in roasted coffee beans from Africa, America, Asia and Oceania. They received values comparable to ours for: Zn, Cu, Fe and Ni, but Pb and Cd concentrations were below their method detection limits (23).

In 2015, Oliveira et al. have analyzed mineral contents in infusions prepared from roasted coffee beans from: Brazil, Ethiopia, Colombia, India, Mexico, Honduras, Guatemala, Papua New Guinea, Kenya, Cuba, Timor, Mussulo and China. Authors have noted similar values for Na, as in our studies of coffee infusions, but lower values for: Ca, Mg, K and Fe (39). The authors observed that the mineral profiles of the beverages were linked to both, inter- and intracontinental differences. It is interesting that Mn and Ca were found to be the best chemical descriptors for origin of coffee beans. South American origin coffees were on average richer in the analyzed elements, except for Ca, while coffee beans from Central America had lower mineral contents (excluding Mn). Unfortunately, among the above mentioned studies authors rarely investigated these elements, so such comparison is impossible.

Ashu and Chandravanshi studied content of selected metals in coffee infusions in Ethiopian coffee beans and noted similar Ca, Fe and Cu concentrations compared to our results, but higher values for Na and Zn, and lower values for K and Mg (20). Pb and Cd concentrations were below their method detection limits, just like in research by Grembecka et al. (23).

Average intakes of Na, K, Ca, Mg, Fe, Cu, Zn, Al, Ni, Pb and Cd (mg/per capita/year), based on the average metal content of roasted coffee purchased in Bosnia (see table 1b) and coffee consumption in B&H were: 142.6, 147665.4, 5387.8, 12350.4, 254.82, 70.68, 33.54, 25.98, 5.46, 0.105, 0.071 respectively. Note that the intake values are the entire population averages, which means that coffee drinkers will tend to ingest more coffee and metals than values shown.

Therefore further investigations are needed, especially on metals that have harmful effects on health, and also those that accumulate in the body, like Pb. Research should focus on countries with high coffee consumption. Again, the fact that even low levels of some metals, e.g. zinc, may interfere with HDL (High Density Lipoprotein) concentrations, Pb is accumulated and the effects of its accumulation can be distant in time should be taken into account (29, 40).

5 CONCLUSION

All in all, the level of studied components in coffee purchased in Bosnia is within the recommended limits.

CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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ETHICAL APPROVAL

Not applicable.

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