

Concentration of Micro- and Macro-Elements in Green and Roasted Coffee: Influence of Roasting Degree and Risk Assessment for the Consumers

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Abstract

The aim of the present study was to determine concentrations of 15 macro- and micro-elements in 10 commercially available plantation Arabica coffee brands. The elemental concentration was studied in 50 samples of green and roasted coffee beans of various roasting degrees and their infusions. There were four different roasting degrees: City + (C+), Full city (FC), Full city ++ (FC++), and Dark (D). The attention was given to the impact of the roasting process on the elemental composition. Statistically significant differences were found between the green coffee beans and the different roasting degrees in both macro- and micro-elements. The results showed that roasting degrees affected the concentration of elements in resulting infusions. Dietary intakes for macro- and micro-elements based on RDA and PTWI (in the case of Al) were calculated. Based on the RDA values for macro- and micro-elements, it can be concluded that coffee infusions are not an important source of elements in nutrition. In the case of Al, consumption of coffee was considered non-hazardous based on the PTWI value.

Keywords Green coffee \cdot Roasted coffee \cdot Elemental composition \cdot Roasting degree \cdot Risk assessment

Introduction

Coffee belongs to the most popular non-alcoholic beverages worldwide [1]. Coffee consumption has increased by 1.90% over the past 3 years to 9.4 million tons per year [2]. This commodity has an enormous economic importance [3]. Its pleasant flavor and aroma together with beneficial influence on health are the main causes of its still increasing consumption [3, 4]. Due to

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great public interest, numerous researches have focused on its biological and physiological implications [3, 5–8]. Coffee is suggested to have a role in prevention of chronic diseases such as *diabetes mellitus* type 2, Parkinson's disease, and liver disease [9] or may even decrease the risk of colorectal cancer [8, 9].

The genus *Coffee* (family *Rubiaceae*) includes around 90 different species with *C. arabica* and *C. canephora* (also known as *C. robusta*) having the strongest economical value

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[10, 11]. Arabica and Robusta coffees differ in many aspects, such as their ideal growing climates or chemical composition [10]. *C. arabica* represents approximately 60% of the world's production [2] and is a superior source of enjoyable flavor and fragrance [4, 12]. *C. canephora* accounts for around 40% of the global coffee market [2]. As it name suggests, Robusta plants are stronger, more resistant to diseases, and less demanding to climate conditions. Robusta coffee beans contain more caffeine, more soluble solids and elements, and have higher amount of antioxidant substances than *C. arabica* [4, 12].

Green seeds are raw unprocessed seeds of coffee fruits. They are considerably different in a number of aspects from roasted coffee regularly consumed around the world [4, 12]. The effect of roasting on the chemical changes in the processed product is obvious and alternations of some coffee constituents, such as proteins or dietary fiber, are described in numerous publications [13–15]. Particular attention is devoted to the effect of roasting on the concentration of chlorogenic acids and their derivates [16, 17].

Among elements that can be found in the green coffee beans (3.5–4.5%), potassium is the major macro-element accounting for 40% of the total elemental concentration [3, 10, 18]. The remaining concentration is represented by sodium, magnesium, phosphorus, calcium, sulfur, and trace elements including zinc, strontium, silicon, manganese, iron, copper, barium, boron, and aluminum [3, 10, 18-21]. Differences in elemental concentration of green coffee beans between C. arabica and C. robusta are not significant, although the total mineral content is slightly lower in C. arabica beans (3.5–4.5%) compared to C. robusta (3.9–4.5%) [10]. In a study by Martín et al. [11], concentrations of Cu, Mn, and P were found to be discriminating variables between C. arabica and C. robusta coffee types. However, still, the diverse amounts of elements in coffee beans reflect the character of various factors including physiological characteristics and cultivation condition [3, 4].

Regular consumption of coffee imposes an impact on determination of chemical composition with a great emphasis on elemental composition [22, 23]. To secure food quality and safety, the levels of essential, non-essential, and toxic elements are important to be known and controlled [21, 23]. A number of experimental works have been focused on elemental composition of different coffee samples [19, 21, 23–25] and/or coffee brews [19, 23, 25–27]. Notable attention is understandably put on hazardous or toxic elements [27, 28], since high concentrations of several heavy metals have been found in some coffee samples [19, 22, 27, 28].

The variability of mineral composition in context of processing and production conditions is discussed by Cruz et al. [12]. However, the knowledge about changes in elemental composition due to roasting is still not very ample [24]. As far as we know, the only investigation of metal concentration alternations in raw and roasted coffee beans was conducted by Van Cuong et al. [24]. Therefore, the aim of the present study was to determine concentrations of 15 macro- and micro-elements in 10 commercially available plantation Arabica coffee and their infusions. Since the applied technological food processing can to certain extent alter the final chemical composition of a product, the attention was predominantly put on the effect of roasting process on the elemental concentration changes. Based on the data on the concentration of the studied elements in the hot water coffee infusions, dietary element intake was defined and whether regular consumption of two cups of coffee per day might pose a potential health risk for a consumer in a long run.

Materials and Methods

Chemicals and Reagents

Nitric acid \geq 69% (trace purity) and hydrogen peroxide \geq 30% (trace purity) used for sample mineralization were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Steiheim, Germany). Ultra-pure water (ddH₂O) (18.2 M Ω cm⁻¹, 25 °C) was treated in a Simplicity 185 purification system (Millipore SAS, Molsheim, France).

Coffee Samples

The study was focused on 10 green coffee brands, namely: Costa Rica (La Pastora Tarrazú) washed; Brazil Santos (NY 2, Scr. 17/18, strictly soft); Brazil Santos (Scr. 17/18, pulped natural); India Plantation AA (Pampabampara Singly estate, washed); Indonesia Java Blawan (A/WP-1'x', washed); Indonesia Sumatra Mandheling (pulped natural); Kenya AA+ (Joshua Rehm, AA+, Masai, washed); Ethiopia Harrar (Hand Picked GR. 4, Cert. No. 0298, Long Beary Eeast, unwashed); Ethiopia Sidamo (GR. 2, Cert. No. 0036, washed); Ethiopia Sidamo Honeybird (unwashed) obtained from commercial producer and/or distributor (Barzzuz spol. s r. o., Banská Bystrica, Slovak Republic). Each of the coffee brands was divided into five different categories. First category consisted of green coffee samples (G) and the rest consisted of four different roasting degrees: City + (C+), Full city (FC), Full city ++ (FC++), and Dark (D). The coffee samples were roasted in Toper TKMX-15 (Toper PF, Izmir, Turkey) in the company Barzzuz (Banská Bystrica, Slovakia). The roasting conditions for particular roasting degrees are displayed in Table 1.

Ground Coffee Sample Preparation

Ground coffee beans (green and roasted) were prepared by milling of 10 g of the beans for 30 s in a laboratory grinder IKA A10 basic (IKA Works, Wilmington, USA). The

Table 1 Basic parameters of roasting process

Roasting degree	Roasting conditions					
	Time	Temperature (°C)				
Green (G)	_	Room temperature				
City + (C+)	11' 05"	224				
Full City (FC)	11' 30"	229				
Full City ++ (FC++)	12' 15"	240				
Dark (D)	12' 40"	245				

homogenized samples were stored in plastic bags until the next treatment step. For pressure microwave digestion, approximately 0.25 g (with a precision to 4 decimal places) of ground coffee was weighed into PTFE digestion tubes. Consequently, 5 mL of HNO₃ and 1 mL of H₂O₂ were added directly to the PTFE vessels. The digestion procedure was carried out using pressure microwave digestion system ETHOS-One (Milestone, Srl., Italy). The mineralized sample solutions were filtered through a quantitative Munktell filter paper No. 390 (Munktell & Filtrak, Bärenstein, Germany) into 50-mL volumetric flasks and filled with ddH₂O to the final volume. Sample solutions were stored in polyethylene tubes until ICP-OES analysis. Each sample was prepared in three replicates.

Preparation of Hot Water Coffee Infusions

Seven grams of ground coffee samples were weighed into glass beakers, poured with 120 mL of hot (95 °C) ddH₂O, and left under cover. After 5 min of brewing, samples were filtered through a quantitative Munktell filter paper No. 390 (Munktell & Filtrak, Bärenstein, Germany) and transferred into polyethylene tubes until ICP-OES analysis. Infusions were prepared in three replicates from each ground coffee sample and analyzed without any pre-treatment step or dilution. Prior to the ICP analysis, all coffee infusions were filtered through PVDF syringe filter Q-Max (0.22 μ m, diameter: 25 mm) (Frisenette ApS, Knebel, Denmark).

ICP-OES Analysis

Elemental analysis was carried out on Agilent ICP-OES spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) with axial plasma configuration and with auto-sampler SPS-3 (Agilent Technologies, Switzerland). Detailed experimental conditions were set as follows: RF power 1.45 kW; plasma gas flow 16.0 L min⁻¹; auxiliary gas flow 1.50 L min⁻¹ and nebulizer gas flow 0.85 L min⁻¹; and CCD detector temperature -35 °C. Signal accusation time 3 s for three replicates. In total, 150 ground coffee samples (50 samples × 3 replicates) and 150 infusions (50 samples × 3 replicates) were analyzed

for concentration of 15 macro- and micro-elements (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, and Zn). ERM®-CE278k (Mussel tissue; IRMM, Belgium) was used to check the measurement quality. Its recovery values (taking into account the water content) ranged from 85 to 123% for most of the determined elements.

Statistical Analyses and Health Risk Assessment

All the data obtained were analyzed by descriptive statistics for minimum and maximum values, arithmetic average, and standard deviation. The selected variables were tested for normality. In all cases, the variables did not follow the normal distribution according to the Kolmonogov-Smirnov test and to the Shapiro-Wilk test. Therefore, non-parametric procedures were used in the latest analyses. The Kruskal-Wallis test was used to identify significant differences between roasting degrees at significance level 5% using asymptotic p value. Spearman correlation matrix at significance level alpha 0.05, 0.01, and 0.001, respectively, was used to analyze the correlations between the variables. All the statistical evaluation was performed using MS Excel and XLSTAT package program [29].

The recommended daily dose of the studied elements (assuming the consumption of two cups of coffee per day) was evaluated based on RDA (recommended daily allowance). The risk assessment of long-term regular consumption of two cups of coffee per day was performed based on PTWI (provisional tolerable weekly intake) for aluminum (2 mg kg⁻¹ body weight week⁻¹). The RDA and PTWI values are shown in Table 6.

Results and Discussion

Concentration of Macro- and Micro-Elements in Ground Coffee

Data of the elements analyzed in coffee bean samples are displayed in Table 2. The element concentrations in the samples according to different roasting degrees are characterized by arithmetic mean value (AVG), the corresponding standard deviation (SD), and ranges. The macro-element concentration in the analyzed samples quite varied with the highest values recorded for potassium. Concentration of K in 1000 g of coffee bean samples ranged as follows: 9913–12,092 mg (green coffee), 11,416–13,159 mg (C+roasting degree), 11,711–13,226 mg (FC roasting degree), 12,278–14,155 mg (FC++ roasting degree), and 12,322–14,301 mg (D roasting degree). Magnesium concentration ranged from 1315 mg kg⁻¹ in green coffee bean samples to 1950 mg kg⁻¹ in dark roasting degree. The variation in elemental composition could be attributed to the type of

Table 2 Concentration of the	ie
macro- and micro-elements	
coffee bean samples in mg l	cg^{-1}

	G AVG±SD (Range)	C+ AVG ± SD (Range)	FC AVG ± SD (Range)	FC++ AVG ± SD (Range)	D AVG ± SD (Range)
Al	14.3 ± 11.4	26.6 ± 19.8	27.3±15.1	24.9 ± 18.5	18.7±14.3
	(2.55–37.6)	(9.55–65.3)	(10.8–49.8)	(5.75–61.6)	(5.53–45.3)
Ba	3.73 ± 1.58	3.33 ± 1.33	3.48 ± 1.37	3.93 ± 1.56	3.14 ± 1.38
	(0.94–6.03)	(0.83–4.57)	(0.84–5.5)	(0.84–5.86)	(0.85–4.86)
Ca	895 ± 82.4	975 ± 151	1010 ± 169	1005 ± 131	963 ± 80.1
	(796–1029)	(828–1395)	(846–1341)	(858–1347)	(763–1068)
Cd	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.016 ± 0.01	0.01 ± 0.01
	(ND-0.03)	(ND-0.04)	(ND-0.04)	(ND-0.04)	(ND-0.03)
Со	0.12 ± 0.13	0.13 ± 0.15	0.09 ± 0.11	0.14 ± 0.16	0.1 ± 0.12
	(ND-0.34)	(ND-0.34)	(ND-0.30)	(ND-0.4)	(ND-0.31)
Cr	0.12 ± 0.04	0.07 ± 0.02	0.07 ± 0.01	0.05 ± 0.03	0.03 ± 0.02
	(0.07-0.22)	(0.04-0.12)	(0.04–0.09)	(ND-0.1)	(ND-0.07)
Cu	10.3 ± 1.56	12.0 ± 1.74	12.4 ± 1.18	12.9 ± 1.2	12.7 ± 1.18
	(7.77–12.8)	(8.54–14.3)	(10.3–14.2)	(11.1–14.8)	(9.70–14.1)
Fe	23.6 ± 3.28	32.9 ± 18.7	27.9 ± 4.69	27.2 ± 2.67	30.5 ± 3.89
	(17.6–28.2)	(24.4-88.0)	(20.7-37.1)	(21.5-30.6)	(26.2–39.8)
Κ	$10,785\pm688$	$12,147 \pm 551$	$12,411 \pm 388$	$13,064 \pm 653$	$13,\!095\pm547$
	(9912-12,092)	(11416–13,159)	(11771–13,226)	(12278–14,155)	(12322–14,301)
Mg	1435 ± 106	1693 ± 108	1726 ± 110	1784 ± 88.0	1792 ± 83.0
	(1315–1618)	(1538–1905)	(1614–1921)	(1660–1938)	(1680–1950)
Mn	21.3 ± 8.60	23.8 ± 8.75	24.8 ± 12.9	25.9 ± 10.4	23.9 ± 9.89
	(11.3–34.6)	(12.3–36.4)	(12-57.2)	(12.7–44.1)	(13.2–45.8)
Na	25.7 ± 15.3	22.7 ± 26.8	33.5 ± 44.0	26.1 ± 23.2	20.5 ± 7.31
	(10.1–64.4)	(5.73–101)	(5.78–130)	(5.98-88.2)	(13.6–39.8)
Ni	0.34 ± 0.30	0.45 ± 0.37	0.44 ± 0.40	0.53 ± 0.47	0.43 ± 0.40
	(ND-1.05)	(ND-1.37)	(ND-1.51)	(ND-1.6)	(ND-1.4)
Sr	4.48 ± 1.61	5.08 ± 2.19	5.77 ± 2.95	5.36 ± 2.14	4.61 ± 2.23
	(1.12-6.76)	(1.02-8.48)	(0.96–9.96)	(1.01-8.56)	(1.01-8.77)
Zn	4.50 ± 0.73	4.96 ± 0.57	5.32 ± 0.96	5.68 ± 0.85	5.09 ± 0.53
	(3.4–6.08)	(3.81–5.91)	(4.02–7.73)	(4–7.25.0)	(4.12–5.86)

AVG arithmetic mean value, SD standard deviation, ND not detected

soil where the coffee was cultivated. Flowering, harvesting periods, and climatic conditions may also have an impact on the elemental composition [22]. The highest average Ca level was obtained for FC roasting degree (1010 mg kg⁻¹), while the lowest for green coffee beans (895 mg kg⁻¹). The highest average Na level was obtained for FC roasting degree (33.5 mg kg⁻¹), while the lowest for D roasting degree (20.5 mg kg⁻¹). These findings are in agreement with Grembecka et al. [19] and Souci et al. [30]. Much higher levels for K, Mg, and Na were reported by Anderson and Smith [31]. Santos and de Oliveira [22] reported higher levels of all tested macro-elements in Brasilian soluble coffees. The general trend of the macroelement concentration (K > Mg > Ca > Na) is in good agreement with Martin et al. [11] and Grembecka et al. [19]. There were significant differences (p < 0.05) observed in Ca, K, and Mg between green coffee beans and all roasting degrees. However, it is necessary to keep in mind the fact that increasing level of roasting results in the evaporation of water and/or combustible mass in the coffee grain and that leads to concentration of the studied elements. The concentration of Zn in the samples ranged between 4.50 mg kg⁻¹ (green coffee) and 5.68 mg kg⁻¹ (FC++ roasting degree). Similar concentrations as in Zn were recorded in Sr levels. The highest Fe concentration was obtained for C+ roasting degree samples $(32.9 \text{ mg kg}^{-1})$. The lowest Fe concentration was obtained in green coffee (23.6 mg kg^{-1}). The concentration of Mn ranged from 21.3 mg kg⁻¹ (green coffee) to 25.9 mg kg⁻¹ (FC++ roasting degree). The Ni concentration ranged between 0.34 mg kg⁻¹ (green coffee) and 0.53 mg kg⁻¹ (FC++ roasting degree). The Cu concentration varied from

10.3 mg kg⁻¹ (green coffee) to 12.9 mg kg⁻¹ (FC++ roasting degree). The highest level of Cd was obtained in C+ and FC roasting degrees $(0.02 \text{ mg kg}^{-1})$ and the lowest level of Cd was obtained in green coffee (0.01 mg kg⁻¹). The Cr concentration decreased from 0.12 mg kg^{-1} (green coffee) to 0.03 mg kg⁻¹ (D roasting degree). The Ba concentration ranged from 3.73 mg kg^{-1} (green coffee) to 3.14 mg kg⁻¹ (D roasting degree). The Al concentration ranged from 14.3 mg kg⁻¹ (green coffee beans) to 27.3 mg kg⁻¹ (FC roasting degree). The average Co concentration ranged from 0.09 mg kg^{-1} (FC roasting degree) to 0.14 mg kg⁻¹ (FC++ roasting degree). The results of Zn, Cu, and Mn are comparable to the findings of Grembecka et al. [19], Santos and de Oliveira [22], and Souci et al. [30] who reported higher Fe values in ground and instant coffees. In general, the infusions containing soluble components in hot water had lower concentrations of each elements than the coffee bean samples. There were significant differences (p < 0.05) in Al, Cr, Cu, Fe, and Zn between green coffee beans and all roasting degrees. In the case of Cr, significant differences (p < 0.05) were observed among G-C+-FC-FC++-D; C+-FC++-D; FC-FC++-D roasting degrees. Micro-elemental, similarly to macro-elemental composition of coffee beans, was significantly affected by the roasting process.

Concentration of Macro- and Micro-Elements in Coffee Infusions

The concentration of macro- and micro-elements in hot water infusions is displayed in Table 3. The concentration of K ranged between 284 mg L^{-1} (green coffee infusion) and 341 mg L^{-1} (C+ coffee infusion). The highest concentration of Mg was detected in C+ coffee infusion 68.7 mg L^{-1} , while the lowest concentration of Mg was detected in the infusion prepared from green beans (36.6 mg L^{-1}). The concentration of Na ranged from 0.72 mg L^{-1} (green coffee infusion) to 1.14 mg L^{-1} (FC++ coffee infusion). The highest level of Ca was observed in C+ coffee infusion (21.6 mg L^{-1}) while the lowest level of Ca was observed in the infusion prepared from green beans (12.7 mg L^{-1}). The concentrations of Cd, Co, Cr, and Ni were under the limits of detection. There were very low concentrations of micro-elements leached in the infusions in all tested groups. The percentages of all macro- and microelements leaching to infusions estimated in this study were much lower than those reported by Grembecka et al. [19] and Ashu and Chandravanshi [28]. The highest leaching percentages could be caused by using acidification with HNO₃. Stelmach et al. [25] investigated the concentration of Ca, Cu, Fe, Mg, and Mn in green coffee brews. They used no treatment or acidification with HNO3 at the extraction from coffee brew step. The results of the presented study are comparable to the work of Stelmach et al. [25].

Table 3 Concentration of the macro- and micro-elements in coffee infusions in mg L^{-1}

	G AVG±SD (Range)	C+ AVG ± SD (Range)	FC AVG ± SD (Range)	FC++ AVG ± SD (Range)	D AVG±SD (Range)
Al	0.017 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
	(ND-0.05)	(ND-0.03)	(ND-0.03)	(ND-0.03)	(ND-0.02)
Ва	0.03 ± 0.01	0.06 ± 0.02	0.05 ± 0.03	0.03 ± 0.01	0.02 ± 0.01
	(ND-0.05)	(0.015–0.10)	(0.01–0.09)	(ND-0.05)	(ND-0.03)
Ca	12.68 ± 2.31	21.5 ± 2.43	18.1 ± 3.3	14.1 ± 3.82	12.5 ± 1.28
	(7.86–16.4)	(16.1–25.2)	(11.5–22.2)	(5.59–21.5)	(9.47–14.2)
Cd	ND	ND	ND	ND	ND
Co	ND	ND	ND	ND	ND
Cr	ND	ND	ND	ND	ND
Cu	0.19 ± 0.03	0.02 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.01
	(0.15–0.24)	(0.02–0.02)	(0.02–0.03)	(0.02–0.03)	(0.02–0.04)
Fe	0.16 ± 0.031	0.06 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	0.10 ± 0.02
	(0.10-0.20)	(0.04–0.07)	(0.05–0.09)	(0.04–0.08)	(0.07–0.14)
Κ	284 ± 34.1	340 ± 2.26	341 ± 3.32	340 ± 4.62	338 ± 2.88
	(218–330)	(336–345)	(334–344)	(324–350)	(332–348)
Mg	36.6 ± 6.66	68.7 ± 7.24	65.8 ± 8.43	57.9 ± 7.75	53.9 ± 5.41
	(24.2–45.8)	(58.2–82.1)	(51–81.9)	(37.9–69.6)	(45.4–63.9)
Mn	0.3 ± 0.12	0.57 ± 0.23	0.49 ± 0.32	0.32 ± 0.13	0.21 ± 0.10
	(0.15–0.47)	(0.26–0.95)	(0.16–1.30)	(0.08–0.55)	(0.10-0.39)
Na	0.72 ± 0.25	0.99 ± 0.47	1.01 ± 0.60	1.14 ± 0.60	1.09 ± 0.50
	(0.32–1.10)	(0.43–1.79)	(0.38–2.28)	(0.43–2.19)	(0.5–2.22)
Ni	ND	ND	ND	ND	ND
Sr	0.05 ± 0.02	0.12 ± 0.06	0.11 ± 0.07	0.07 ± 0.04	0.06 ± 0.03
	(0.01–0.08)	(0.03–0.23)	(0.02–0.27)	(0.02–0.15)	(0.01–0.12)
Zn	0.06 ± 0.01	0.06 ± 0.02	0.04 ± 0.02	0.02 ± 0.01	0.02 ± 0.00
	(0.05–0.08)	(0.03–0.09)	(0.02–0.07)	(0.01–0.04)	(0.01–0.02)

AVG arithmetic mean value, SD standard deviation, ND not detected

Correlation Analyses

The Spearman correlation coefficients are presented in Table 4 (ground coffee) and Table 5 (coffee infusions). Most of the elements exhibited significant positive and negative correlations. Table 4 shows that a strong significant positive relationship was observed between concentrations of Co-Ni, Co-Mn, Ba-Mn, and Mg-Cu. A moderate positive significant relationship was observed between Co-Ba, Co-Cu, Co-Zn, Ca-K, Ca-Fe, K-Mg, K-Cu, K-Fe, Mg-Mn, Mg-Zn, Ba-Cu, Ba-Ni, Ba-Sr, Ba-Zn, Cu-Mn, Cu-Zn, Mn-Ni, Mn-Sr, Ni-Zn, and Sr-Zn. There were no strong negative relationships observed between the investigated elements. Moderate negative significant relationships were found between K-Cr and Mg-Cr. Table 5 shows strong significant positive relationships between Ca-Mg, Ba-Mn, Ba-Sr, Cu-Fe, and Mn-Sr. There were also moderate significant positive relationships observed

	Spean	nun conciu		indero di	a miero erei		iee beam sai	npies					
	Co	Ca	Na	К	Mg	Al	Ba	Cr	Cu	Fe	Mn	Ni	Sr
Са	0.068												
Na	0.163 ^a	0.190 ^c											
K	0.244 ^c	0.510 ^c	0.159										
Mg	0.298 ^b	0.294 ^b	-0.226^{b}	0.583 ^c									
Al	-0.356 ^c	0.304	-0.286 ^c	0.209 ^a	-0.071								
Ba	0.669 ^c	-0.048	0.027	0.082	0.396 ^c	-0.355°							
Cr	- 0.049	-0.015	0.066	-0.565°	-0.546°	0.012	0.011						
Cu	0.570 ^c	0.466 ^c	-0.190^{a}	0.581 ^c	0.746 ^c	-0.037	0.535 ^c	-0.380°					
Fe	-0.008	0.564 ^c	-0.156	0.517 ^c	0.413 ^c	0.463 ^c	-0.121	-0.082	0.417 ^c				
Mn	0.799 ^c	-0.050	-0.011	0.202^{a}	0.585 ^c	-0.411°	0.755 ^c	-0.181^{a}	0.537 ^c	-0.015			
Ni	0.715 ^b	0.107	0.251 ^b	0.177^{a}	0.279 ^c	-0.285°	0.580 ^c	-0.135	0.442 ^c	-0.017	0.669 ^c		
Sr	0.242 ^c	0.113	0.003	0.056	0.415 ^c	-0.241^{b}	0.567 ^c	0.139	0.261 ^c	0.066	0.536 ^c	0.151	
Zn	0.556 ^c	0.167 ^a	0.124	0.391 ^c	0.639 ^c	-0.128	0.674 ^c	-0.201^{b}	0.523 ^c	0.207 ^b	0.745 ^c	0.549 ^c	0.546°

 Table 4
 Spearman correlation matrix of macro- and micro-elements in coffee bean samples

 $a^{a} p < 0.05$

 $^{b}p < 0.01$

 $^{c} p < 0.001$

between Ca-Ba, Ca-Mn, Ca-Sr, Ca-Zn, Mg-Ba, Mg-Mn, Mg-Sr, Ba-Zn, and Mn-Zn. There were moderate significant negative relationships between Ca-Cu, Ca-Fe, K-Cu, K-Fe, Mg-Cu, and Mg-Mn. Grembecka et al. [19] found significant positive relationships between concentrations of Mg-Na, Ca-P, Ca-Zn, Ni-Co, P-Cr, P-Zn, and Fe-Ni in ground coffee samples. They found significant negative correlations between the concentrations of Mg-P, Mg-Cr, P-Na, Zn-Na, Zn-Mg, and Mn-Na in ground coffee samples. Growing process of coffee plants, including the use of inorganic fertilizers, organic manures, pesticides, and also environmental pollutions, may be the cause of positive correlations between P-Zn, K-Cu, Mn-Ni, B-Cu, Mg-Cu, and As-Hg pairs in the coffee beans [22, 23].

Estimation of Dietary Element Intake

The dietary intakes of elements were estimated for consumption of two cups of coffee (prepared from 2×7 g of coffee) per day according to Şemen et al. [23]. Daily mineral intakes (DMI, %) were calculated as follows:

$$DMI = C \times 100/RDA \tag{1}$$

where: C = element concentration (in mg) in 2×120 mL coffee infusion, RDA = recommended daily allowance [32]. Estimated dietary intakes (%) according to the reference values are presented in detail in Table 6. For Sr and Ba as trace elements, no RDA values have been established yet

 Table 5
 Spearman correlation matrix of macro- and micro-elements in coffee infusions

	Ca	Na	Κ	Mg	Al	Ba	Cu	Fe	Mn	Sr
Na	-0.160									
Κ	0.370 ^c	0.070								
Mg	0.790 ^c	-0.130	0.470 ^c							
Al	0.060	-0.020	-0.050	-0.300°						
Ba	0.600 ^c	-0.170^{a}	-0.070	0.580 ^c	-0.220^{b}					
Cu	-0.640°	-0.320°	-0.550°	-0.690°	0.120	-0.350°				
Fe	-0.510°	-0.180^{a}	-0.540°	-0.590 ^c	0.190 ^a	-0.420°	0.800°			
Mn	0.640 ^c	-0.190^{a}	0.030	0.620 ^c	-0.080	0.800°	-0.370°	-0.360°		
Sr	0.520 ^c	-0.260°	0.150	0.670 ^c	-0.190^{a}	0.760 ^c	-0.420°	-0.490°	0.710 ^c	
Zn	0.550 ^c	-0.280°	-0.280°	0.170^{a}	0.280^{c}	0.560 ^c	-0.120	-0.090	0.640 ^c	0.290

 $^{a}p < 0.05$

^b p < 0.01

 $^{c}p < 0.001$

Table 6Estimated dietary intakes (%) according to reference values of
each element for the consumption of 2 cups day $^{-1}$

	RDA (EEC, 2008)	Roasting degree						
		G	C+	FC	FC++	D		
Са	800 (mg day ⁻¹)	0.40	0.62	0.50	0.48	0.43		
Κ	2000 (mg day ⁻¹)	3.40	4.11	4.15	4.19	4.14		
Mg	$375 (mg day^{-1})$	2.30	4.43	4.23	3.77	3.40		
Cu	$1 (\text{mg day}^{-1})$	4.80	0.56	0.60	0.61	0.82		
Fe	$14 (mg ~ day^{-1})$	0.30	0.17	0.18	0.17	0.20		
Mn	$2 (\text{mg day}^{-1})$	3.60	6.98	5.95	3.83	2.57		
Zn	$10 (mg ~ day^{-1})$	0.10	0.15	0.14	0.15	0.01		
	Daily intake (mg day ⁻¹)							
Sr	_	0.01	0.03	0.03	0.02	0.01		
Ba	_	0.01	0.01	0.01	0.01	0.01		
	PTWI (CAC, 2011)							
Al	$2 (\text{mg kg}^{-1} \text{ bw week}^{-1})$	0.015	0.01	0.01	0.01	0.02		

RDA recommended daily allowance, *PTWI* provisional tolerable weekly intake, C+ City + roasting degree, *FC* full city roasting degree, *FC*++ Full city ++ roasting degree, *D* dark roasting degree

[32]. Provisional tolerable weekly intake (PTWI) was calculated for Al [33]. The values ranged from 0.01 to 0.02% (Table 6). Therefore, the amounts of Al consumed via coffee infusions of different roasting degrees were considered nonhazardous. Based on RDA, consumption of two cups of coffee supplies to human body 0.43–0.62% Ca, 4.11–4.19% K, 3.40–4.43% Mg, 0.56–0.82% Cu, 0.17–0.20% Fe, 2.57–6.98% Mn, 0.01–0.15% Zn (Table 6). Estimated dietary intakes of Sr and Ba through consumption of two cups of coffee were 0.01–0.03 mg day⁻¹ and 0.01 mg day⁻¹ of Sr and Ba, respectively. The exposure amounts are low and no element can be referred as significant since none reaches 15% [24, 34].

Semen et al. [24] reported that consumption of two cups of ground coffee (6×2 g of green coffee) per day contribute on average to 5.94 $\mu g \ day^{-1}$ of Sr, 2.70 $\mu g \ day^{-1}$ of Ba in green coffee, 15.2 μ g day⁻¹ of Sr, 7.41 μ g day⁻¹ of Ba in mud coffee, 15.2 μ g day⁻¹ of Sr, and 7.41 μ g day⁻¹ of Ba for Turkish coffee. PTWI for Al was 0.005-0.01%. Few studies showed that the mineral intake related to roasted and grounded coffee consumption [24, 25]. Based on the RDA, Grembecka et al. [19] reported that consumption of two cups of ground coffee (300 mL prepared from 6×2 g coffee) contributes, on average, to 4.72% of RDA for Mg, 0.14% for Ca, 3.52% for K, 1.95% for P, 0.13% for Zn, 0.32% for Cu, 3.41% for Mn, 38.9% for Co, and 15.6% for Ni. Semen et al. [24] have noticed that regular consumption (12 g) supplies mean intakes less than 1% for most of the elements, except for Mg, P, K, Mn, Co, and Cu that represent 2.62%, 1.10%, 2.80%, 1.78%, 54.3%, and 7.28% of the RDA values, respectively. According to the presented dietary intakes based on the RDA values for macro- and micro-elements, it can be concluded that coffee

infusions prepared from ground coffee in different roasting degrees are not an important source of elements in nutrition.

Conclusion

Coffee is very popular and widely consumed non-alcoholic beverage in the world. Several research studies were analyzed in the literature in order to determine the characteristics of the coffees and positive or negative effects of its consumption. In this study, 15 macro- and micro-elements were determined in coffee samples, and correlation between the elements was compared for coffee bean samples as well as coffee infusions. There were significant differences (p < 0.05) observed in Ca, K, and Mg between green coffee beans and all roasting degrees. Similarly, significant differences (p < 0.05) were found in Al, Cr, Cu, Fe, and Zn between green coffee beans and all roasting degrees. In the case of Cr, significant differences (p < 0.05) were observed among G-C+-FC-FC++-D; C+-FC++-D; FC-FC++-D roasting degrees. Micro-elemental composition, similarly to macro-elemental composition of coffee beans, was significantly affected by the roasting process. The results showed that roasting degrees affected the concentration of elements in resulting infusions. Dietary intakes for macro- and micro-elements based on RDA and Al based on the PTWI were calculated. Based on the RDA values for macro- and micro-elements, it can be concluded that coffee infusions are not an important source of elements in nutrition. In the case of Al, the amounts determined in coffee infusions were considered non-hazardous based on the PTWI value.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflicts of interest.

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