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Chemical insight into pros and cons of coffees from different regions

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The main aim of this work was to study the chemical composition of eighteen ground coffees from different countries and continents with regard to the content of hazardous substances as radioactive elements (^{40}K, ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U and ^{137}Cs), metals, including heavy metals, aluminum and some microelements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn) as well as substances that have a positive effect on human health and well-being (polyphenols, proteins, fats and caffeine). The tests were carried out before and after the brewing process using the following techniques: gamma and beta spectrometry, a microwave-induced plasma optical emission spectrometer (MIP-OES), gravimetric method, UV–Vis spectrophotometry as well as thin-layer chromatography. The leaching percentage of certain elements/compounds in coffee infusions was also measured. The research showed clear differences between Arabica and Robusta coffees, and also allowed for identifying some differences between Arabica coffees depending on the place of their origin. The results presented can raise consumer awareness and help them make better food choices.

Keywords Coffee, Grinding, Radionuclides, Heavy metals, Microelements, Polyphenols

Most people cannot imagine their morning without a cup of aromatic coffee. This beverage originates from Africa, where the coffee plant is widely cultivated, and owes its name to the Ethiopian province of Kaffa[1]. The average daily coffee consumption in the world is up to three billion cups[2], making coffee one of the most popular beverages. Coffee plants grow mainly in the area known as the coffee belt, which lies between the Tropic of Cancer and the Tropic of Capricorn[3]. The coffee tree is a perennial dicotyledonous plant that only grows in the tropics and belongs to the *Rubiaceae* family. The two most popular coffees are Arabica (*Coffea arabica*)—around 70% of coffee production and Robusta (*Coffea canephora*)—around 30%[4]. Arabica species are more demanding to grow and are generally cultivated at high altitudes (> 1000 m asl). Robusta species accept warmer climates and heavier rainfall. They are usually grown below 800 m asl. Interestingly, Arabica coffee, with its milder and sweeter taste, is much more popular with gourmets, although Robusta coffees produce higher yields than Arabicas and have a stronger and spicier flavour[5].

The chemical substances that make up the main components of coffee beverage are: proteins, carbohydrates, fats and waxes, polyphenols, caffeic acid, quinic acid and chlorogenic acid, minerals and caffeine[6]. The factors that determine the composition of coffee are: coffee variety, the roasting process, degree of grain refinement and the brewing method. All this means that the concentration of soluble ingredients in the coffee brew can vary considerably[7]. There are numerous reports in the literature about the health benefits of this beverage. Among the most important ones are a lower probability of obesity, diabetes, cardiovascular disease and a reduced risk of Parkinson's and Alzheimer's disease[8,9]. However, it should be emphasised that this drink contains not only ingredients that have a positive influence on human health, but can also have potentially harmful effects. High contamination of the soil with metals from fertilisers, pesticides and production processes, among others, can have an impact on the quality of coffee[10]. The influence of metals on human health relies upon both the type of metal and its concentration. Microelements (e.g.: iron, zinc, manganese) and macroelements (e.g.:

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calcium, sodium, potassium) are minerals that are involved in many important metabolic processes and are necessary for the optimal functioning of the body. The requirement for microelements is less than 100 mg per day, while the demand for macroelements is higher and amounts to over 100 mg per day. Nevertheless, some elemental species with a molar mass of 63.5 to 200.6 g/mol are chemical elements that might be harmful to human health even at small amounts due to their ability to accumulate in human tissue and their long half-life[11]. This group includes metals such as: mercury, cadmium, lead and uranium. Therefore, the World Health Organization (WHO) has established guidelines that contain permissible limits for the content of toxic elements in food as well as beverages[12]. Coffee plants can serve as responsive detectors of environmental pollution with radioactive elements, as they have a propensity to assimilate radioactively contaminated compounds. The presence of radioactive substances in soil, and therefore in plants, is a consequence of the existence of radioactive series and anthropogenic pollution. The estimated effective dose resulting from coffee intake is insignificant, especially in comparison to the reference limit set by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), which corresponds to an ingestion dose of 290 μSv/year. Taking into account the average coffee consumption per day there is no significant radiological risk associated with coffee intake. However, it is important to recognize that this contribution may not be completely negligible if other food components are similarly contaminated with radionuclides. Coffee, along with various other beverages, has a large content of polyphenols, the range of which is very wide and whose effect on the body is extremely positive[13]. Phenolic compounds have special antioxidant properties, as they easily trap radicals and the newly formed (free) radical is so stable (delocalization of the radical due to resonance) that it cannot split off a hydrogen atom from the fatty acid molecule[14]. In addition, coffee appears to be desirable in the diet of people predisposed to many diseases of civilization, including atherosclerosis[15]. Another valuable ingredient of coffee is caffeine (1,3,7-trimethylxanthine), a natural methylxanthine derivative and dihydroxy-purine alkaloid. This psychoactive substance can stimulate the central nervous system. Drinking a cup of coffee provides an average of 80–100 mg of this compound[16]. Adults should refrain from ingesting over 400 mg of caffeine daily to avoid dangerous or negative side effects such as headaches, anxiety, tachycardia, insomnia, nausea, diarrhoea, etc., and a single dose of caffeine ought to be lower than 3 mg/kg body weight[17]. Then, it has a positive effect on reaction time, improves concentration and reduces the feeling of drowsiness.

Since many people consume coffee, it is important to determine how the individual ingredients affect our well-being. Our study points to an important issue, namely the content of different elements that are easily found in coffee. The novelty of our study focuses not only on known metals concentrations (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb), but also on radioactive nuclides that pose an invisible danger to human health (^{40}K, ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U and ^{137}Cs). During this thorough analysis, we also determined the content of substances that are considered beneficial to human health and well-being, such as microelements, polyphenols, proteins, fats and caffeine. Comparing the above ingredients before and after the brewing process allowed us to estimate the potential risks and benefits of coffee consumption. In the end, we attempted to establish a correlation between type, origin and chemical composition of each coffee sample analyzed. The results obtained provide a deep insight into one of the most important consumer goods and expand the knowledge of scientists and consumers about coffee. We hypothesize that coffee is a healthy drink that can have a positive impact on human health and well-being, while knowledge of the type of coffee, its origin and related chemical composition may help to supplement nutritional deficits.

Materials and methods

Coffee samples preparation

Coffee samples were purchased at a store that stocks a wide range of coffees and teas from around the world. The research material was subjected from various origins (Table 1) underwent testing before and after the brewing process. The infusion process followed these steps: (1) 1 L of redistilled water (approximately 95 °C) was added to a vessel containing a 60 g coffee sample. The use of redistilled water aimed to eliminate any impurities from tap water. (2) The coffee was brewed for four minutes and thoroughly mixed. (3) After brewing, the infusion was separated by decantation and then filtered. (4) The wet coffee samples were subsequently dried in a laboratory dryer. Initially, they were dried at 70 °C for 24 h, followed by further drying at 50 °C until completely dry (another 24 h).

Radionuclides analysis of coffee samples

The concentration of radium isotopes (^{226}Ra,^{228}Ra), potassium (^{40} K) and caesium (^{137}Cs) in coffee samples was determined using high-resolution gamma-ray spectrometry. The studies were conducted using germanium detectors (BEGe) in the energy range of 40–2000 keV. The following gamma spectral lines were used: (i) ^{226}Ra, determined directly (186.2 keV—including the interference with 185.7 keV of ^{235}U) and via the short-lived radon progeny ^{214}Bi (609, 1120, 1765 keV) and ^{214}Pb (295, 352 keV); (ii) ^{228}Ra, determined via 228Ac (911 keV); (iii) ^{40} K, determined directly (1461 keV); (iv) ^{137}Cs, determined directly (662 keV). For multiple gamma lines, the weighted average was calculated taking into account the gamma emission probability.

The coffee samples were dried to a constant mass and placed in a plastic (HDPP) measuring container (flat cylinder, 7 cm^3). The mass of the analytical samples varied between 3.509 and 5.412 g. An appropriate correction factor for sample density was applied. The acquisition time depended on the counting statistics of the main photopeaks—the uncertainty of the counts had to be less than 5%. It was typically 24–72 h. The efficiency calibration was performed with standard sources consisting of the reference materials RGU-1, RGTh-1 and RGK-1 from the International Atomic Energy Agency IAEA and IRMM-426 Wild Berries from the Joint Research Center of the European Commission. The bulk density of the prepared sources was adjusted to the density of the analyzed samples (mixing with CAB-O-SIL—silicone powder, ultra-low radioactivity, low density).

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Lp	Sample acronym	Place of origin
1	A1-Am-G	Guatemala
2	A2-Am-H	Honduras
3	A3-Am-CR	Costa Rica
4	A4-Am-B	Brazil
5	A5-Am-P	Peru
6	A6-Am-C	Cuba
7	A7-Am-M	Mexico
8	A8-As-I	India
9	A9-As-IB	Indonesia Bali
10	A10-As-S	Sumatra
11	A11-Af-T	Tanzania
12	A12-Af-Et	Ethiopia
13	A13-Af-U	Uganda
14	A14-Af-Ec	Ecuador
15	R1-As-I-EBL	Indonesia ELB
16	R2-As-I	Indonesia
17	R3-As-V	Vietnam
18	R4-Af-C	Cameroon

Table 1. Acronyms used for the coffee samples analyzed with the place of origin of the samples (A-Arabica, R-Robusta, Am-coffee sample from America, As-coffee sample from Asia, Af-coffee sample from Africa).

Alpha spectrometry was used to determine the uranium isotopes. Before measurement, the samples underwent devoted chemical separation. Each sample (the mass for the analysis was approx. 7 g) was incinerated for 24 h at a temperature of 500 °C. The ash was then subjected to wet mineralization in concentrated nitric and hydrochloric acids. The uranium isotopes were separated from interfering radionuclides using Dowex ion exchange resin and UTEVA extraction resin[18]. The radioactive tracer used was ^{232}U. Finally, the alpha source was prepared using an electrodeposition protocol according to Talvitie[19].

Determination of metals in coffee samples

To determine the metal content in the coffee (Cr, Cu, Mn, Zn, Al, Fe, Ni, Pb, Cd, Co, V), the samples were subjected to microwave-assisted digestion in a 67% nitric acid (8 mL acid per 0.3 g sample) using an Anton Paar microwave mineralisation system. model Multiwave GO. The digestion procedure was as follows: (a) preheating to 110 °C for 15 min, (b) temperature stabilisation at 110 °C for seven min, (c) heating to 185 °C for 10 min, (d) holding the temperature at 185 °C for 25 min, (e) temperature cooling to 60 °C.

The mineral-rich samples were thinned to a volume of 10 mL using demineralized water and then strained to eliminate any minute solid remnants. The prepared samples were stored in plastic tubes in the dark until analysis, which included four replicates for each element.

Calibration and determination of metals in coffee samples

The metal content was determined using the MIP-OES technique (MP-AES 4210, Agilent). The calibration solutions were prepared by serial dilution with standard solutions (concentration 1000 mg/dm^3; ICP purity). Measurements were performed four times for each calibration point (at least five points per wavelength). The limits of detection (LOD) and quantification (LOQ) were estimated on the basis of the calibration curve coefficients. The selected validation parameters are listed in Table 1S (Supporting material).

Estimation of uncertainty and data presentation

The combined expanded uncertainty of the measurements was estimated using Eq. (1). The trace element analysis data was presented as mean values with error bars indicating the measurement uncertainty. The degree of leaching as the relative content of the element in the coffee samples after brewing was presented in the form of a box plot.

$$U_C = k \cdot \sqrt{(u_{cal})^2 + (u_{rep})^2} \quad (1)$$

where: U_c—combined expanded uncertainty of the determination of the element content; k—coverage factor (equal to 2); u_{cal}—uncertainty of the calibration (determined from the regression parameters); u_{rep}—standard uncertainty in relation to repeatability (as the quotient of the standard deviation and the square root of the number of repetitions).

Analysis of polyphenols, proteins and fats in coffee samples

To analyze the total polyphenol content (TPC) the studied samples were extracted with 80% methanol[20] and then centrifuged at 5500 rpm for 15 min. 0.1 µL of the sample extracts were added to 25 mL volumetric

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flasks and mixed with 2 mL distilled water, 0.2 µL Folin–Ciocalteu reagent and 1 mL sodium carbonate (20% aqueous solution). The flasks were placed in darkness at room temperature for 1 h (formation of blue complex). Measurements were carried out with a UV/VIS Helios Omega 3 spectrophotometer (Massachusetts, MA, USA) at a wavelength of 765 nm. TPCs were presented in milligrammes of gallic acid equivalents (GAE) per 100 grammes of sample.

The proteins were analysed using the Kjeldahl method (ISO 1871:2009). The Kjeldahl method is a chemical procedure used to determine the nitrogen content in organic compounds. Here are the key steps involved: 1. Digestion: the sample is heated with concentrated sulfuric acid, which breaks down organic nitrogen compounds into carbon dioxide, water, and ammonium sulphate. This step ensures efficient nitrogen recovery; 2. Ammonium Separation: After digestion, the ammonium ion is separated from the solution; 3. Quantitative Determination: The separated ammonium ion is quantitatively determined, and its stoichiometric conversion to nitrogen is calculated.

The fat content was analysed using a Soxtec 8000 instrument (ASN 310 applications). The Soxhlet method involves repeated continuous extraction of the fatty substance from a previously dried comminuted product with an organic solvent, removal of the solvent and determination of the fatty substance using the gravimetric method. The analysis was carried out in accordance with the ISO 659:1998 Genéve Switzerland.

TLC quantification of caffeine in coffee samples

The sample preparation procedure was adopted from Ref.[21]. Deionised water (Millipore DirectQ-UV3, Merck) with a conductance of 0.05 µS/cm or less at 298 K was used. The coffee beans of the origins analysed were finely ground and weighed to an accuracy of approximately 0.25 g using an analytical balance (AS 82/220.R2, Radwag). The samples were infused with 50 mL of boiling deionised water and left until the extracts had cooled to room temperature. Before the next step, they were shaken manually and allowed to stand for 2 min in order to separate solid and liquid phases. The standard stock solution was prepared by diluting accurately weighed 2.87 mg of caffeine (Sigma-Aldrich C0750-5G PRODUCT) in 1.4 mL of deionised water. The standard working solution was prepared by diluting 67.5 µL of the standard stock solution with 922.5 µL of deionised water.

The coffee samples and the working standard solution were applied to chromatography plates with Camag Linomat 5 (Muttenz, Switzerland) on glass-backed TLC SiO2 F254 plates (Merck, Darmstadt, Germany). The application volume was 4 µL (or 2 µL in the case of the Robusta samples from Cameroon, Indonesia and Vietnam) for the samples and 1; 3; 5; and 7 µL for the working standard solution, as 6 mm wide bands, 10 mm from the bottom edge of the plate. The first and last positions on each plate were the blank samples of water from the stock solution and sample extraction, respectively. Different amounts of the working standard were sprayed onto tracks 2, 3, 4 and 5 to create a calibration curve. The solvents analysed were applied to tracks 6–17 and the measurements were repeated three times so that each plate was used to analyze four samples. Chromatograms were developed in an unsaturated horizontal Chromdes DS2 chamber (Lublin, Poland) at a distance of 8 cm using n-hexane/acetone 1/1 (v/v) mobile phase at room temperature. The plates were dried in the air. The results was documented using a Camag Reprostar 3 (Muttenz, Switzerland) device with a Baumer DXA252 digital camera equipped with Computar 12 mm objectives (f = 4.0, time: 30.0 ms, gain: 1.0, $\lambda = 254$ nm)—Fig. 1S (Supporting material).

Detection and confirmation was performed with the Camag TLC Scanner 4 (Muttenz, Switzerland) $\lambda = 275$ nm. Application, documentation, detection and confirmation was carried out under the control of WinCats v. 4.09 software (Camag, Muttenz, Switzerland). Examples of UV/Vis spectra of standards and samples taken from the spots after development are shown in Fig. 2S (Supporting material).

Statistical analysis

Statistical analysis of the results included calculation of the mean and standard deviation (Microsoft Excel 2019) and ANOVA analysis (Statistica 10). Homogeneity of variance was checked with a post-hoc Tukey test ($p \leq 0.05$).

Results and discussion

Radioactivity of coffee samples

Table 2 shows the activity concentration of the gamma-radionuclides found in the coffee samples and measured before and after the brewing process. Four gamma-radionuclides were considered in the analysis, namely: ^{40}K; ^{226}Ra; ^{228}Ra and ^{137}Cs. ^{40}K is categorised as primary isotopes, i.e. an isotope that has existed since the creation of the Earth. ^{40}K ($T_{1/2}$=1.28 billion years) constitutes approximately 0.012% of the total amount of K in the environment[22]. This radionuclide is responsible for the radioactivity of the human body and emits penetrating γ-rays (1.46 MeV). As can be seen, the activity concentration of ^{40}K in the analysed coffee samples varies from 516±67 Bq/kg (A7-Am-M) to 701±67 Bq/kg (R1-As-I-EBL) before brewing and decreases from 97±30 Bq/kg to 178±30 Bq/kg after this process (Table 2). This observation is consistent with the literature, as the ^{40}K activity concentration in coffee beans before brewing was in the range of 484-1265 Bq/kg[23]. The presence of ^{40}K in coffee is a consequence of the ability of plants to take up this element with water from the soil. Considering the widespread use of K-fertilisers and the metabolic processes occurring in plants, the presence of ^{40}K in coffee beans is not surprising. The percentage of ^{40}K released during coffee brewing is similar in all samples (73.9–82.2%). The comparison of the ^{40}K content in Arabica and Robusta coffees shows that the ^{40}K content is higher in Robusta coffees. The reason for this can be found in the structure of the roots of the two species. While Arabica is characterised by a relatively deep nourishing root system, the structure of Robusta roots is shallower and more developed near the surface. Since potassium occurs in the soil as a part of various minerals, one might expect it to be readily available to each plant. However, water-soluble potassium in the form of K^+ ions is more important for plant health. Considering the addition of potassium-containing fertilisers and the fact that potassium is mainly found in the topsoil layer[24], one could therefore conclude that the shallow near-surface root system of

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Sample name b—before brewing a—after brewing	**mass of the sample [g]**	**Ra-226 [mBq/g]**	**Ra-228 [mBq/g]**	**K-40 [mBq/g]**	**Cs-137 [mBq/g]**	**U-238 [mBq/g]**	**U-234 [mBq/g]**
A1-Am-G-b	3.6793	< 15	6.8 ± 5.8	547 ± 55	< 1.6	2.39 ± 0.4	2.59 ± 0.42
A1-Am-G-a	4.636	< 10	< 10	129 ± 22	< 1.1	0.75 ± 0.17	0.74 ± 0.17
A2-Am-H-b	3.8782	< 17	< 11	580 ± 61	< 1.8	0.05 ± 0.02	0.08 ± 0.03
A2-Am-H-a	4.9385	< 11	< 10	108 ± 20	< 1.2	< 0.02	< 0.02
A3-Am-CR-b	3.8246	< 15	< 10	568 ± 59	7.0 ± 2.1	0.07 ± 0.03	0.07 ± 0.03
A3-Am-CR-a	5.0224	< 13	< 10	137 ± 26	4.3 ± 1.6	0.04 ± 0.02	0.04 ± 0.02
A4-Am-B-b	4.027	< 12	6.5 ± 3.4	624 ± 52	< 1.1	< 0.02	< 0.02
A4-Am-B-a	4.9069	< 11	< 10	163 ± 26	< 1.1	< 0.02	< 0.02
A5-Am-P-b	4.1785	< 16	< 10	608 ± 64	< 2.6	0.27 ± 0.06	0.31 ± 0.06
A5-Am-P-a	4.8609	< 14	< 10	126 ± 26	< 1.5	0.12 ± 0.03	0.22 ± 0.05
A6-Am-C-b	4.2091	< 13	< 10	628 ± 61	< 1.4	0.11 ± 0.04	0.12 ± 0.04
A6-Am-C-a	4.7546	< 13	< 10	120 ± 23	< 1.2	0.08 ± 0.03	0.08 ± 0.04
A7-Am-M-b	4.2863	< 16	< 10	516 ± 57	4.9 ± 1.8	0.05 ± 0.02	< 0.02
A7-Am-M-a	5.205	< 15	< 10	108 ± 23	4.9 ± 1.4	< 0.02	< 0.02
A8-As-I-b	4.0621	< 12	< 10	666 ± 61	< 1.3	0.10 ± 0.03	0.18 ± 0.04
A8-As-I-a	4.8402	< 14	< 12	135 ± 25	< 1.2	0.08 ± 0.04	0.08 ± 0.04
A9-As-IB-b	3.9387	< 17	< 10	629 ± 66	< 2.6	0.11 ± 0.03	0.15 ± 0.03
A9-As-IB-a	4.8409	< 11	< 10	109 ± 21	< 1.8	0.09 ± 0.03	0.10 ± 0.03
A10-As-S-b	3.8415	< 17	< 11	600 ± 66	< 1.8	0.16 ± 0.03	0.29 0.05
A10-As-S-a	4.8741	< 10	< 10	142 ± 20	< 1.1	0.13 ± 0.03	0.10 ± 0.03
A11-Af-T-b	3.6623	< 18	< 11	526 ± 61	< 1.8	0.14 0.04	0.19 ± 0.05
A11-Af-T-a	4.7588	< 14	< 10	119 ± 26	< 1.4	0.04 ± 0.02	0.05 ± 0.02
A12-Af-Et-b	3.7616	< 18	< 11	601 ± 65	< 2.8	0.11 ± 0.03	0.18 ± 0.04
A12-Af-Et-a	4.9558	< 13	< 10	138 ± 28	< 1.8	0.06 ± 0.03	0.05 ± 0.03
A13-Af-U-b	3.7564	< 12	< 10	579 ± 47	< 1.1	< 0.02	< 0.02
A13-Af-U-a	3.5087	< 16	< 10	97 ± 30	< 1.6	< 0.02	< 0.02
A14-Af-Ec-b	4.2296	< 17	< 11	623 ± 67	< 1.8	0.34 ± 0.05	0.25 ± 0.04
A14-Af-Ec-a	4.9001	< 11	< 10	147 ± 25	< 1.2	0.11 ± 0.03	0.19 ± 0.04
R1-As-I-EBL-b	3.5757	< 15	< 10	701 ± 67	< 1.6	0.11 ± 0.03	0.23 ± 0.04
R1-As-I-EBL-a	4.9149	< 14	< 10	178 ± 30	< 2.1	0.08 ± 0.02	0.09 ± 0.03
R2-As-I-b	3.9942	< 14	< 10	625 ± 63	7.7 ± 2.7	0.64 ± 0.06	0.73 ± 0.06
R2-As-I-a	4.6363	< 16	< 10	140 ± 31	8.2 ± 2.7	< 0.02	< 0.02
R3-As-V-b	3.9189	< 16	< 10	642 ± 67	13.9 ± 3.6	0.05 ± 0.02	0.07 ± 0.02
R3-As-V-a	4.4693	< 16	< 10	155 ± 43	9.1 ± 2.4	< 0.02	< 0.02
R4-Af-C-b	4.3574	< 15	< 10	628 ± 63	7.2 ± 2.2	0.05 ± 0.02	0.09 ± 0.03
R4-Af-C-a	5.4119	< 13	< 10	156 ± 26	5.5 ± 1.4	< 0.02	< 0.02

Table 2. Activity concentration of radioisotopes in coffee samples before and after the brewing process.

Robusta ensures a higher uptake and content of potassium. When comparing Arabica coffees from different areas, the Asian coffees had the largest ^{40}K content among the samples analysed, while the American and African coffees had lower and similar values. These differences may be the result of different fertilisation intensity and different soil properties.

Radium-226 has a half-life is 1,620 years and is a component of the uranium decay chain. This isotope emits alpha radiation (Ea = 4.6 and 4.78 MeV) and gamma radiation (E = 186.2 keV). ^{226}Ra and its decay products make up the largest part of the dose that humans receive from natural radionuclides. This isotope is transported by plants from the soil to the human body via the food chain[25]. The main route of entry into the human body is therefore the gastrointestinal tract, but it can also be absorbed by inhalation and through the skin[26]. Due to its chemical similarity to calcium, this isotope can be absorbed in the intestine and is deposited first in the soft tissues and then in the bones[27]. The results from Table 2 clearly show that the isotope ^{226}Ra occurs in coffee samples in negligible amounts. ^{228}Ra is a member of the thorium decay chain and is produced by the decay of thorium-232. It is a beta-radioactive isotope with a half-life of 5.75 years. Radium-228 is highly toxic and can cause cell and tissue damage[28]. ^{228}Ra also has a high affinity for bone and can accumulate in the skeleton. According to the data from Table 2 the content of this radionuclide in the coffee samples is so low that no differences can be detected between the coffee varieties or the locations where the coffee plant is grown.

^{137}Cs is an anthropogenic isotope with a half-life of about 30.05 years. Radiocaesium was deposited in the atmosphere by the worldwide radioactive fallout caused by nuclear weapon test explosions in the twentieth

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century and by nuclear accidents (Chernobyl). ^{137}Cs is a radioactive anthropogenic isotope and its presence in the human body is highly undesirable. The presence of radiocaesium in coffee beans results from uptake by the coffee plant together with water from the soil. Therefore, the presence of ^{137}Cs in the analysed samples indicates a contamination of the soil with this radionuclide. It should be emphasised that ^{137}Cs in soil has the form of a monovalent cation that plants can easily absorb[29]. The content of ^{137}Cs was detected in a few coffee samples. The highest level of ^{137}Cs was 13.9 ± 3.6 Bq/kg (R3-As-V). This radionuclide was present in a few Arabica samples and almost in all Robusta samples, which could mean that *Coffea Canephora* absorbs ^{137}Cs better than *Coffea Arabica*. This could be due to the differences in the above-mentioned root system of the coffee plants. *Coffea Canephora* with its extensive and shallow root system can more easily absorb Cs, which is found in the upper soil layers. Analysing the continents where the coffee plants were cultivated, radiocaesium was detected in coffee beans from Costa Rica and Mexico among the American coffee varieties, while it was not found in Asian and African coffee varieties.

Uranium is an element that occurs in nature in the form of several isotopes: ^{238}U (99%), ^{235}U (0.7%) and ^{234}U (0.01%). The isotopes of the natural decay of uranium. Traces of uranium isotopes were present in rocks and soil, water and air. ^{238}U is an isotope with a $T_{1/2} = 4.5$ billion years, which almost corresponds to the predicted age of the Earth. The presence of uranium in plants is a consequence of the uptake of this element by the root system of plants together with water from the soil. The activity concentration of ^{238}U in leafy vegetables is in the range of 6–2200 mBq/kg, while the activity concentration of the other two isotopes is several dozen times lower[30]. According to the literature, the activity concentration of ^{238}U in different types of Arabica coffee powder varies between 9.35 ± 1.81 and 135.11 ± 24.61 mBq/g with a mean value of 44.61 ± 7.95 mBq/g, while the ^{238}U activity concentration in various types of Turkish coffee varies between 10.48 ± 2.14 and 57.16 ± 9.32 with a mean value of 22.55 ± 4.00 mBq/g[31]. Several studies have been conducted to analyze the intake of uranium by an adult male with the consumption of water and food. The authors state that in New York City, the daily intake of ^{234}U and ^{238}U is 18 and 16 mBq, respectively[32]. In most of the coffee samples analysed, the levels of the two uranium isotopes tested were low, often below the detection limit. The highest uranium content was found in sample A1-Am-G ($^{238}U = 2.39 \pm 0.4$ mBq/g; $^{234}U = 2.59 \pm 0.42$ mBq/g), which could mean a higher content of this substance in the soil. On the basis of the results obtained, it is not possible to draw a clear conclusion about which Arabica or Robusta coffee variety favours the presence of uranium or the influence of the place of cultivation on the uranium content.

Chemical composition in relation to metals in the individual coffee samples is shown in Figs. 1, 2. The ranges of metal contents in the tested coffee samples before brewing were: 0.17–0.66 mg/kg for Cr, 14–22 mg/kg for Cu, 12–49 mg/kg for Mn, 8.0–38 mg/kg for Zn, < 5.6–38 mg/kg for Al, 40–128 mg/kg for Fe, < 1.2–3.9 mg/kg for Ni. The content of Cd, Co, V was below the limit of quantification in all samples (Cd: LOQ = 0.72 mg/kg; Co: LOQ = 5.2 mg/kg; V: LOQ = 1.2 mg/kg). The Pb content in almost all samples was below the LOQ (< 0.38 mg/kg), only one sample (A12-Af-Et before brewing) showed Pb concentrations above the LOQ (7.56 ± 0.10 mg/kg). It should be emphasised that the presence of Zn, Mn, Cu, Fe, Cr, Co, which are microelements, is necessary for the proper functioning of internal organs. Currently, many foods are fortified with nutritional components to combat macro- and micronutrient deficiencies. Those deficiencies are one of the more important health risks in developing countries[33]. Natural micronutrient intake is the most effective way to reduce global micronutrient deficiencies. However, inadequate intake can also be due to socioeconomic effects and poor nutrition. Since coffee is consumed worldwide despite the socioeconomic impact and other factors, it is noteworthy that the presence of low doses of metallic micronutrients may be beneficial to the health of coffee consumers as described in this work.

Chromium is a naturally occurring element in volcanic soils. Due to its widespread use in various industries (such as tanning, textiles, mining, and healthcare), chromium contamination in soil can also be observed[34]. It is known that chromium is not a desirable element for plants due to its oxidative nature. However, humans need small doses of chromium(III) in their daily lives. According to the US National Institutes of Health Office of Dietary Supplements, chromium is particularly important due to its regulatory role in glucose intolerance, type II diabetes and dyslipidemia[35]. The prevalence of these diseases of civilisation is increasing rapidly. Therefore, the intake of chromium from natural sources may be a positive factor in maintaining well-being. The average chromium content in the coffee samples tested before brewing was 0.30 mg/kg. The highest amount was in sample A6-Am-C—0.660 ± 0.026 mg/kg. The lowest chromium content was found in the samples A8-As-I and A14-Af-Ec. The crucial aspect is the release of chromium from ground coffee during infusion. There are currently no strict standards for the intake of chromium(III). According to the European Food Safety Authority, chromium supplementation may be beneficial for people with glucose intolerance, but there is no clear data on the benefits for healthy people[36]. In many cases, a limit of 0.025–0.035 mg per kg body weight is considered appropriate for women and men respectively[37]. The average content of chromium in the sample after brewing compared to the sample before brewing was 66% (the degree of leaching was 34%). For this element, there were also samples in which the metal content did not changed after brewing—A14-Af-Ec. The highest release of Cr into the brew was observed in sample A6-Am-C, where the amount corresponded to about 0.5 mg/kg of ground coffee. Considering the aforementioned limits, the contribution of Cr from coffee to the total daily intake is relatively low. However, considering that we also consume other foods and beverages throughout the day, it can still be considered a positive addition to our diet.

Most of the copper contained in the soil is absorbed by complexes or incorporated into the crystal lattice of minerals[38]. Soil contamination by copper originates from various sources, such as mining and the excessive use of fungicides[39]. This element is crucial for plants, used for example in the synthesis of proteins from which the chlorophyll required for photosynthesis is formed[40]. This microelement enters the human body with food, where it takes part in the production of red blood cells and nerve cells and ensures the flawless functioning of the immune system. It also helps with collagen formation, iron absorption and energy production. The WHO

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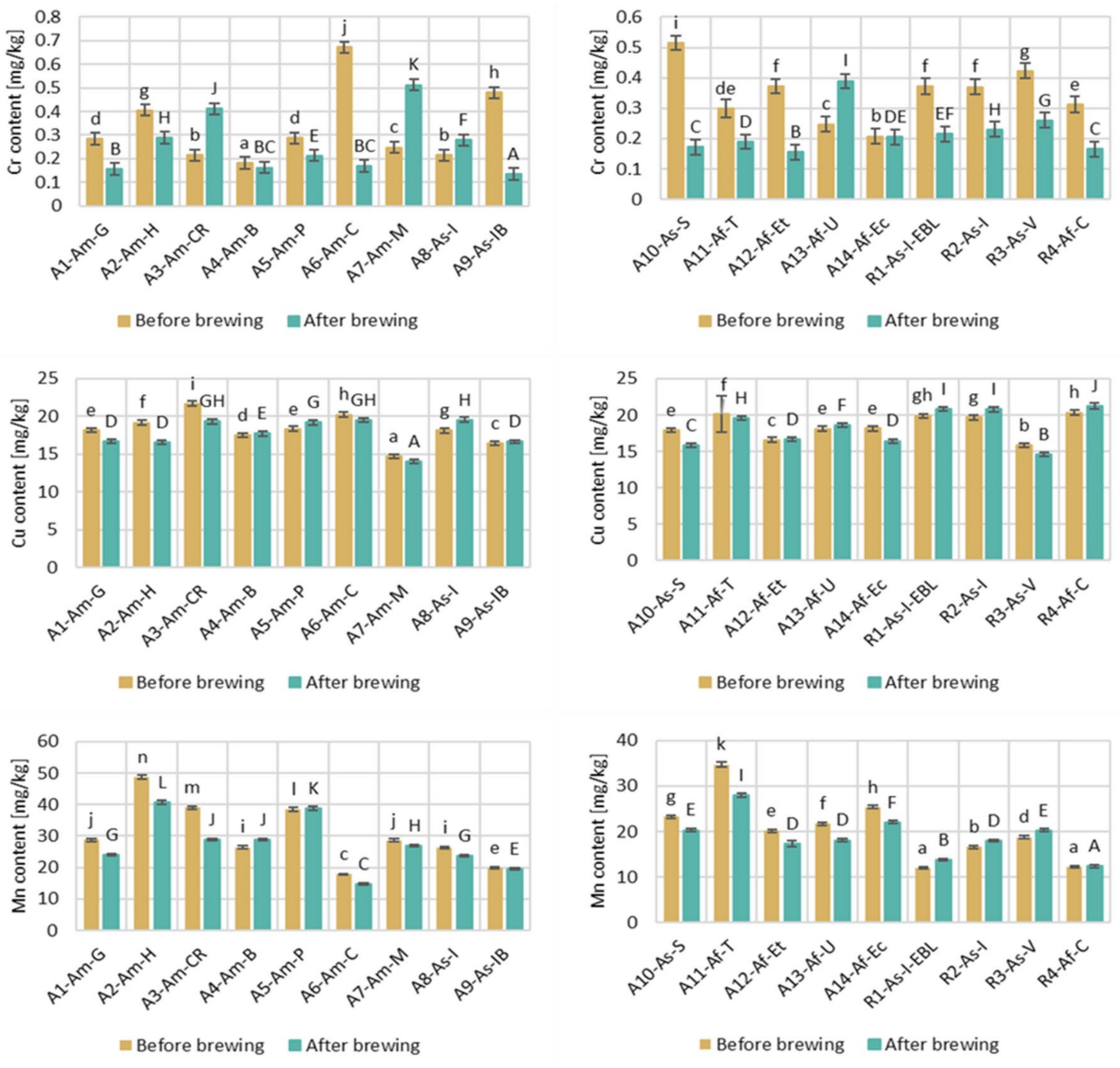

Fig. 1. The content of Cr, Cu and Mn in coffee samples before and after brewing. ^{a,b,c}—Mean values for samples "before brewing" marked with the same small letter are not statistically significantly different ($p < 0.05$). ^{A,B,C}—Mean values for samples "after brewing" marked with the same capital letter are not statistically significantly different ($p < 0.05$).

recommends no more than 30 µg per kg of body weight per day[41]. Before brewing, the tested coffee samples had very similar copper contents. The lowest amount of copper was found in A7-Am-M and the highest in A3-Am-CR, the difference between the extreme values was 6.99 mg/kg. The average copper content in the analysed samples was 18.38 ± 0.44 mg/kg. The leaching rate of this element was highest in A2-Am-H and ranged between almost 0.0% and 13.7%. These results are consistent with the literature[42].

Manganese is one of the microelements that plants absorb in the largest quantities from the soil. Its most important function is its involvement in photosynthesis and nitrogen metabolism in plants and, in the final phase, in the formation of proteins, sugars and fats[43]. In the human body, manganese is involved in flawless work of the nervous system, bones and blood vessels. It takes part in the metabolism of cholesterol, carbohydrates and red blood cells[44]. The analysed coffee samples contained an average of 25.1 mg of manganese per 1 kg of coffee before brewing, which is consistent with the literature reports[45]. The lowest manganese content was determined in R4-Af-C and R1-As-I-EBL samples at 12.29 ± 0.21 and 12.03 ± 0.18 mg/kg respectively. Another sample with a low content of this element was R2-As-I, which contained 16.60 ± 0.27 mg/kg manganese. It was also found that Robusta contains significantly less manganese than Arabica. The sample that contained the largest amount of Mn was A2-Am-H (48.75 ± 0.79 mg/kg). The highest Mn leaching level was found in A3-Am-CR—26%, whereas in R4-Af-C and A5-Am-P the differences were negligible.

Zinc is one of the most important micronutrients for human health, which is undersupplied in the population worldwide. It regulates numerous processes, thus its deficiency can lead to various diseases, including depression, cardiovascular disease and Alzheimer's disease[46]. Zinc is also responsible for the proper growth and reproduction of plants. Its deficiency in plants can pose a significant danger as its distribution in soil is uneven and its bioavailability for fertilisation is less than 1%[47]. Zinc is especially important for coffee plants as it is

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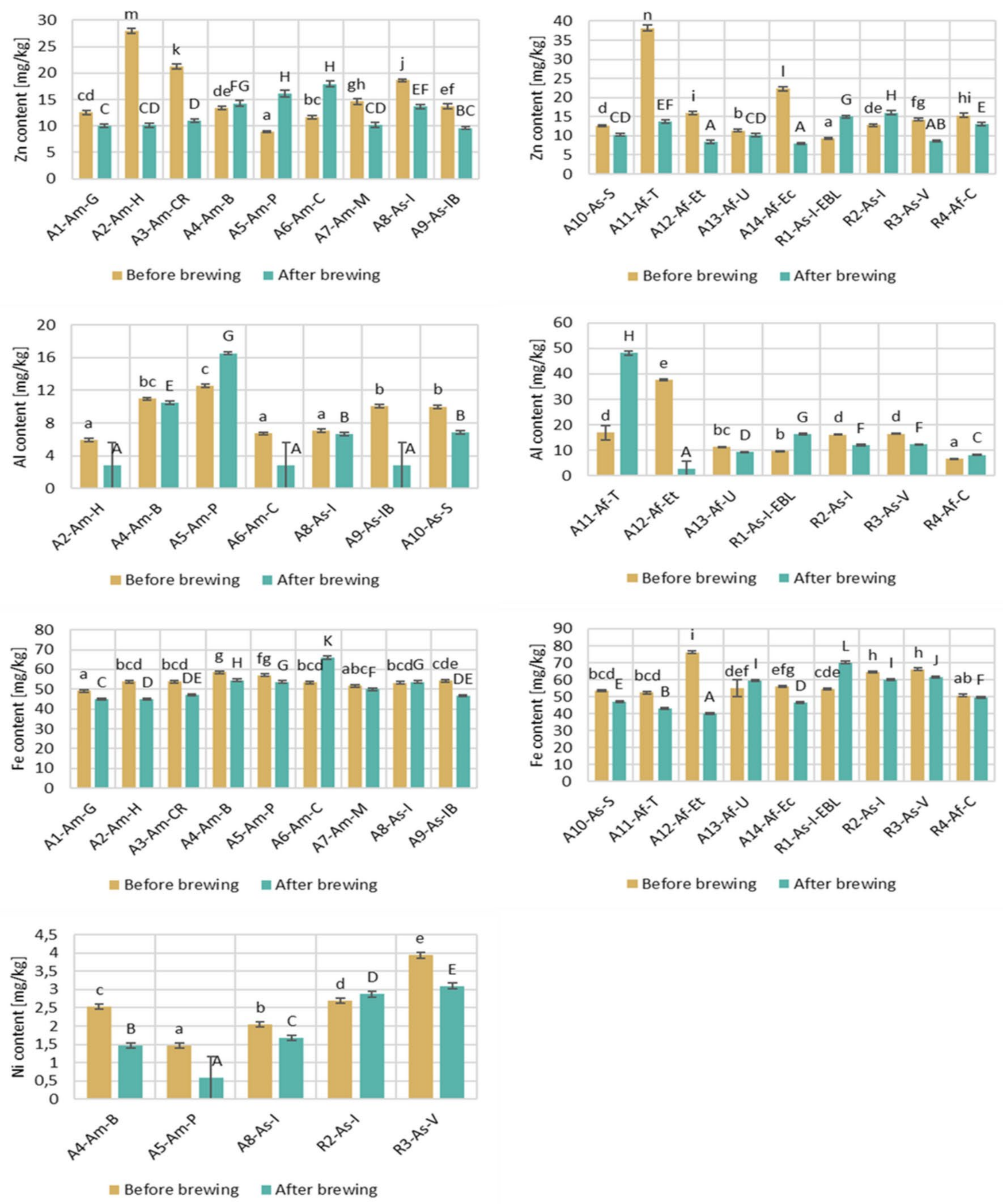

Fig. 2. The content of Zn, Al, Fe and Ni in coffee samples before and after brewing. (In the samples in which the determined content was below LOQ, its value on the figure was presented as half of LOQ, and the uncertainty bar from zero with the LOQ value). ^{a,b,c}—Mean values for samples "before brewing" marked with the same small letter are not statistically significantly different ($p < 0.05$). ^{A,B,C}—Mean values for samples "after brewing" marked with the same capital letter are not statistically significantly different ($p < 0.05$).

needed to obtain high-quality beans and higher levels of positive bioactive compounds[48]. According to the US NIH, the recommended daily intake of zinc increases with age and varies between 8 and 11 mg per day for women and men respectively[49]. The zinc content in the coffee samples before brewing is very wide, ranging from 8.93 ± 0.17 mg/kg in A5-Am-P to 38.20 ± 0.85 mg/kg in A11-Af-T. This sample also stands out clearly from the others, as the average zinc content is 13.68 mg/kg—A11-Af-T contains almost three times as much zinc. Three other samples characterised by a high zinc content are A2-Am-H, A3-Am-CR and A14-Af-Ec. The Robusta samples tested contained zinc in a lower concentration: 9.29–15.38 mg/kg. The median change in zinc content in the ground coffee samples before and after infusion was 21%. In the case of zinc, the greatest changes in the content of this element were observed in three samples. In A2-Am-H the difference in content was 17.9 mg/kg,

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in A11-Af-T—24.4 mg/kg and in A14-Af-Ec—14.4 mg/kg. While this amount may seem significant, considering that most of us use 12 g of coffee per 200 ml of water, this would mean that we consume less than 0.3 mg of Zn per serving. Therefore, it is unlikely that we may overdose on zinc by drinking coffee. Nevertheless, this also shows that a cup of coffee can be a good supplement to our maximum recommended daily intake of zinc.

Aluminum is a common, naturally occurring element in soil. Depending on pH of the soil, its effect on plants can be detrimental or beneficial. If the pH of the soil falls below 5, the aluminum present is dissolved and transported to the roots of the plant, which leads to growth inhibition[50]. In the coffee plant, aluminum stress also causes growth inhibition, but also induces the production of caffeine by the plant[51]. Al can be toxic to humans, but for healthy people, its ingested with food does not cause a serious threat owing to its low biocompatibility. Nonetheless, excessive aluminum intake is toxic to the human body. Its accumulation in various organs, such as the lungs or brain, can lead to conditions like aluminum pneumoconiosis and neurodegenerative diseases[52]. The highest detected aluminum concentration was 37.60 ± 0.43 mg/kg in the A12-Af-Et, and in five samples before brewing (A1-Am-G, A3-Am-CR, A7-Am-M and A14-Af-Ec) the aluminum content was below the LOQ of 5.6 mg/kg. In the majority of samples, the aluminum content was around 10 mg/kg (median 10.66 mg/kg). The largest change in the content of an element in a single sample as a result of brewing was observed in the case of aluminum in the A12-Af-Et, where the content after brewing was below the LOQ of 5.6 mg/kg. This shows that about 35 mg/kg of aluminum was leached from the tested sample. In other samples, leachability was low, which is consistent with literature data[53]. According to the EFSA Panel's recommendations, the tolerable weekly intake (TWI) of this element is around 1 mg/kg body weight[54]. Taking into account an average body weight of 60 kg, the TWI for aluminum corresponds to 60 mg per week. For the A12-Af-Et, which contains the most aluminum, one cup of coffee contains about 0.45 mg of this element (based on 12 g of coffee per serving). This shows that drinking coffee in normal portions alone does not cause a negative impact of aluminum toxicity.

Iron, with an abundance of about 35% in both Earth's inner and outer core, is the fourth most common element in Earth's crust. The presence of iron is necessary for the proper functioning of photosynthesis, cellular respiration, nucleotide metabolism and chlorophyll synthesis[55]. In addition, this element is crucial in the development of growth tips in the roots of plants. In the human body, iron builds haemoglobin, takes part in the formation of red blood cells and protects the cells from free oxygen radicals[56]. Daily iron intake is in the range of 8.3–15.4 mg/day with an estimated median value of 10–11 mg/day[57]. However, a daily intake of about 10–20 mg of iron with food is needed, as normally only small amounts are absorbed by the human body[58]. Of the elements tested, iron concentration in the samples was the largest—an average of 56.45 mg/kg. The sample with the lowest content was A1-Am-G, which contained 49.12 ± 0.60 mg/kg iron. A12-Af-Et had the highest iron content, 76.17 ± 0.84 mg/kg. Two other samples with relatively high iron content were R2-As-I and R3-As-V—64.42 ± 0.61 and 66.16 ± 0.74 mg/kg. The iron content of the remaining samples was between 50 and 60 mg/kg. Although the percentage changes in iron content are among the smallest, considering the high iron content in the coffee seeds, its concentration in the filtrate after brewing is the highest among the elements tested—the average change in the content of this element was 7.7 mg/kg. An extreme value was found in the A12-Af-Et sample, where the difference in content was 35.98 mg/kg, i.e. 47%.

Nickel is a biologically relevant element that occurs naturally and anthropogenically in soil in concentrations of about 80 ppm[59]. Excessively high concentrations of Ni in plants can lead to reduced growth[59]. Studies show that coffee plants are quite tolerant when it comes to nickel[60]. The change in nickel content could only be determined in five samples, as in the others the content of this element in the sample before brewing was below the LOQ of 1.2 mg/kg. R3-As-V had the highest nickel content—3.095 ± 0.077 mg/kg. The coffee sample in which both contents were above the limit of quantification (before and after brewing) and in which the greatest change in nickel content was found was A4-Am-B. This change was 42% and 1.07 mg/kg nickel was released into the coffee filtrate. Attitudes towards nickel have changed over the years, leading to the conclusion that Ni is not an essential nutrient. No daily dose or intake values have been established for Ni. While it should not be harmful to healthy people, people with certain nickel allergies or intolerances should monitor their consumption of foods and beverages rich in this element. The issue of nickel toxicity is becoming increasingly important and is likely to be more widely discussed in the future.

Some additional information about leaching of elements from the coffee during the brewing are presented in Fig. 3S (Supporting materials).

Table 2S and 3S (Supporting material) show the total polyphenol content (TPC), protein and fat content as well as the caffeine in the coffee samples analysed. The results revealed statistically significant differences in the content of these compounds depending on the region of origin ($p \leq 0.05$). Further analysis has been included in the Supporting materials.

In order to summarise the results presented in this manuscript, but also to facilitate the selection of the right coffee based on a possible balance of advantages and disadvantages Fig. 3 has been created. It should be emphasised that all coffees tested are suitable for consumption, and the grading applies to concentration levels that do not exceed the standards. However, according to the UNSCEAR recommendations, the contribution of radionuclides should not be completely neglected and, in the case of potentially toxic elements, the permitted levels of contaminants should be set at the lowest reasonably achievable level (according to the ALARA principle). Figure 3 clearly shows that Arabica coffees differ from Robusta coffees in their chemical composition. The latter contain significantly more protein and caffeine. A large content of fats, polyphenols and radionuclides can be found in most of them, but they contain a low content of aluminum and other metals. It is not an easy task to compare Arabica coffees from different countries. Nevertheless, some global conclusions can be drawn, although it must be emphasised that these only apply to the group of coffees analysed. Arabica coffees from America were characterised by different concentrations of radioisotopes, metals, polyphenols, fats and caffeine, but a low aluminum and protein content. Asian coffees were characterised by a low content of metals, aluminum and proteins. Most of them contained high concentrations of radionuclides and caffeine, while they differed in the

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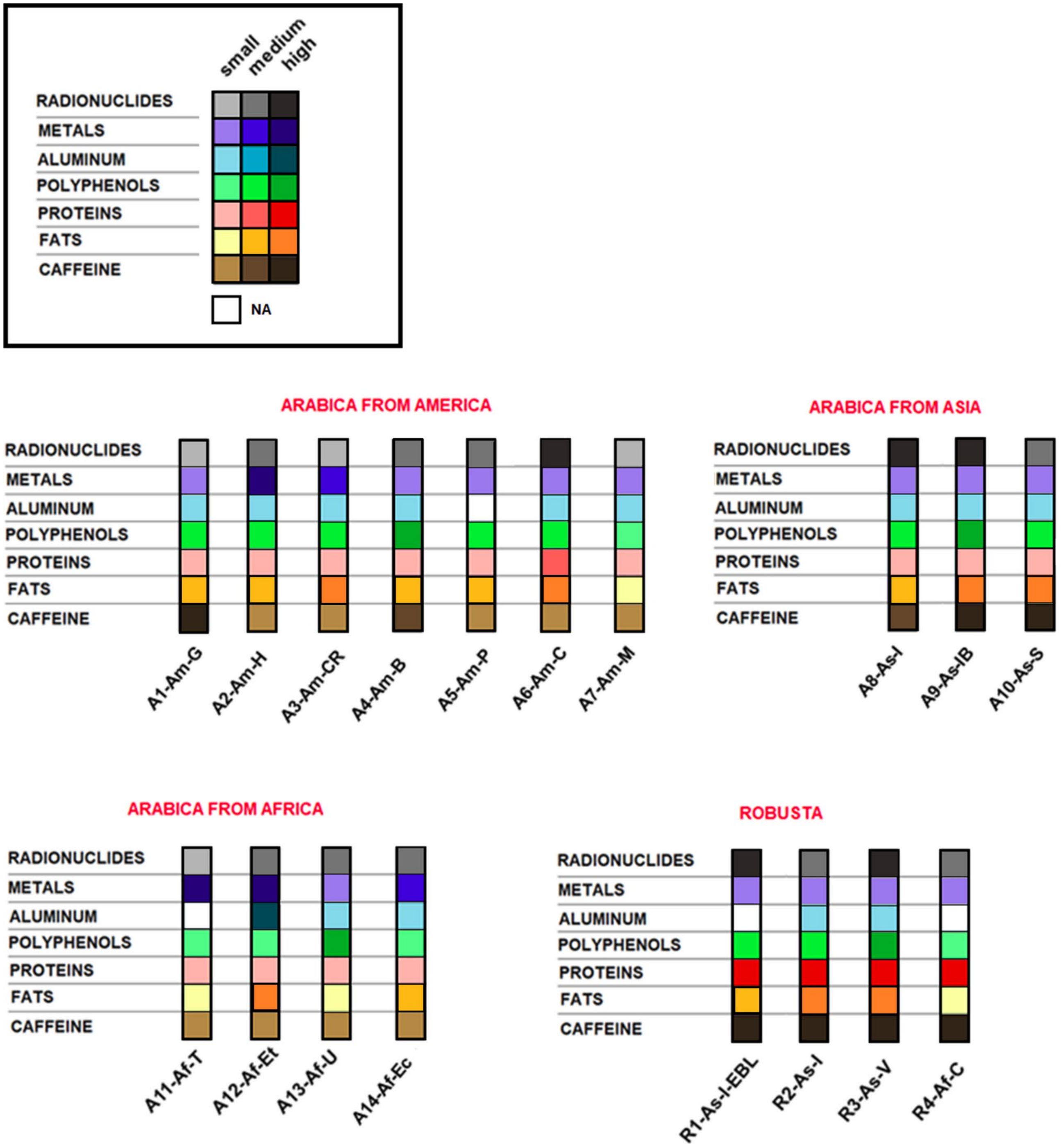

Fig. 3. Graphical summary of the obtained results. The method of estimating individual ranges is presented in the Supporting materials.

concentration of polyphenols. The African coffees were characterised by a low caffeine and protein content, but had different concentrations of fats and polyphenols. In most of the coffees tested, radionuclides were present in medium concentrations, while metals were present in high concentrations. High aluminum concentrations were also found in one of the African coffees.

Conclusions

There is a lot of scientific data on the health-promoting and harmful properties of coffee. Some emphasise its value in combating lifestyle diseases, while others warn against the substances it contains. Scientists rarely bother to take stock of the gains and losses associated with the consumption of this beverage. According to the research, coffee consumption may be associated with benefits related to the absorption of polyphenols, proteins, fats,

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caffeine and microelements into the body, but unfortunately, it is also associated with a certain risk of absorption of potentially toxic elements and radionuclides into the human body. Thus, the question arises: should consumers limit their coffee consumption? As early as the sixteenth century, Paracelsus formulated the definition of poison: ”Everything is poison and nothing is poison. Only the dose makes a substance poisonous”. The authors hope that the research results presented in this will raise consumer awareness and help them make better food choices.

Data availability

The data that support the findings of this study are available on request from the corresponding author A.S.W.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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