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Elemental composition of ginger (*Zingiber officinale* L.) – Analytical approach and assessment of 29 analytes according to classification approaches

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ABSTRACT

Ginger (*Zingiber officinale* L.) is a widely used spice which beyond nutritional properties exhibit therapeutic properties. It is sold fresh or dried. In order to characterize this food more in detail, the content of 29 elements in ginger was determined by inductively coupled plasma mass spectrometry (ICP-MS). The either fresh or dry powdered products, were bought in (super)markets in Zagreb (Croatia) and Örebro (Sweden) in either loose form or packaged in plastic or glass. For analysis, all samples were dried and homogenised prior to digestion using nitric acid and hydrogen peroxide. The content of metals and metalloids, grouped according to their orbitals ("block") and definitions as "toxic", bioavailability, and Geochem, was assessed. Most abundant element found in all samples was K (2940 mg/kg – 50500 mg/kg), followed by Mg (1080 mg/kg – 3680 mg/kg), Ca (786 mg/kg – 2240 mg/kg), Mn (18.6 mg/kg – 789 mg/kg), Na (52 mg/kg – 987 mg/kg), Al (6.09 mg/kg – 1070 mg/kg), and Fe (32.1 mg/kg – 779 mg/kg). Metals founds in the earth-crust are correlated in the ginger products, which suggests similar uptake pattern. Statistical analysis showed that the origin of the samples as well processing method (drying, grinding) have an impact on the elemental pattern in ginger, whilst no correlation between packaging material (none, glass, plastic) and elemental contents in the products was found.

1. Introduction

Ginger (*Zingiber officinale* L.) is a perennial tropical plant from the *Zingiberaceae* family. Known for its aromatic underground root, ginger is used both raw and processed as a spice. Native to Southeast Asia, it has been utilized for medicinal purposes since ancient times in India and China. Major producers of ginger include India, China, Nigeria, Sierra Leone, Indonesia, Bangladesh, Jamaica, Australia, and Nepal, with the highest quality ginger often coming from Jamaica and India. The plant grows from a gnarled rootstock, producing stems and leaves that can reach heights of 30 cm to 100 cm [1,2]. Ginger leaves are lanceolate and green, while its yellow flowers are densely arranged in spikes at the top of the stem. The plant is propagated through rootstock division and thrives in moist soil. Ginger is ready for harvest once the leaves die back [3–6].

The primary ginger products are fresh, dried, and preserved ginger, while secondary products include ginger powder, oil, and oleoresin. Fresh ginger pods have a distinctive taste with full spiciness, low fiber, and rich aroma. Preserved ginger is made from unripe, juicy pods that are peeled, syrup-impregnated, dried, and sugar-coated. Dried ginger, which can be peeled or unpeeled, is used for ground ginger and oleoresin and oil extraction. It is made from ripe rootstocks by washing, peeling, slicing, and sun-drying. Ground ginger is produced by crushing dried ginger, while ginger oil is obtained through steam distillation of dried ground ginger. Oleoresin is extracted using solvents like acetone and ethylene dichloride. [3] Drying is an important step in food preserving. Microwave drying is reported to be the most effective method for drying Chinese ginger, resulting in increased volatiles and novel compounds, followed by air drying at 60 °C, vacuum drying, and freezing drying [7]. Another comparative study investigated different drying methods on ginger rhizome slices, namely ginger rhizome slices were subjected to air-drying, freeze drying, infrared drying, microwave drying and intermittent microwave & convective drying, whereby the latest has shown to be a promising method for preserving ginger rhizome quality and

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reducing energy consumption, while maintaining antioxidant properties [8]. Dried ginger is often ground, liquid nitrogen pulverization, ultramicro grinding, and mortar grinding being common methods, which influence the quality of the obtained ginger products when assessing organic compounds [9]. Superfine grinding technology is an innovative method also used in food industry for producing superfine powder with excellent surface properties, such as enhanced dispersibility and solubility. Regarding ginger powder this leads to increased surface area, greater water absorption, higher water solubility, and higher protein content [10]. Grinding ginger is not only relevant to produce powder for the market, but also to improve extraction efficiency [11]. Even if already known and used for long time, ginger processing is still investigated aiming reduce the pungent taste, extend shelf-life, increase health-functional compound content, and improve safety, potentially increasing its consumption and applications in food, cosmetics, and pharmaceutical industries [12].

Ginger contains over 400 compounds, primarily carbohydrates (70 %), lipids (8 %), volatile oils (3 %), crude fiber, minerals, and vitamins B1, B2, B3, and C. Its composition varies based on growing, drying, grinding and storage conditions.[4,6,13]. Ginger is a valuable source of essential elements for both plant growth and human health. Various research groups have analyzed ginger, identifying macronutrients like K, Ca, Mg, and Na, which are crucial cofactors in many biochemical processes [14]. Additionally, micronutrients have been studied [15]. Research has also focused on detecting toxic elements in ginger, with studies conducted by Ansari et al. [16] and Nguyen et al. [17]. Regarding risk assessments, the investigation of the uptake of harmful elements from soil is of importance, as shown by working groups studying the soil-ginger system [18,19]. All these studies are limited by the small number of analytes, which was overcome in the present study by including 29 elements, as well as focusing on products deriving from the same geographic area. Furthermore, it is important when trying to evaluate and identify correlations between elements in plant-derived products, to classify them according to their biological significance. Duffus [20,21] suggests emphasizing electron configuration and the positions of the elements in the periodic table. Accordingly, elements are classified as macro element: Al, Ca, Fe, K, Mg, and Na; as micro elements: Ba, Cr, Cu, Mn, Ni, and Zn; followed by trace elements, namely Co, Ga, Li, Se, and V. Finally, As, Cd, Mo, Pb, and Tl are considered toxic elements.

Beyond nutritional and safety concerns, the metal content in plant-derived food products aids in identification and has applications in plant ecology, environmental pollution research, bioremediation, and food authentication [22]. To evaluate and compare elemental patterns in these products, it is important to consider factors influencing metal uptake and accumulation. These factors include soil composition, metal availability, plant species, age, growth stage, and environmental conditions such as climate, temperature, and humidity [23–26].

This investigation aims to determine the presence of 29 elements—Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, Te, Tl, U, V, and Zn using commonly used methods for elemental analysis, as ICP-MS (inductively coupled plasma mass spectrometry) after acidic sample digestion. The quantitative results are assessed according to analytes' atomic structure and classifying criteria, such as bioavailability or geochemical properties. These criteria may influence the content of these elements in the ginger since they have an impact on occurrence or transport. The study did focus on commercially available ginger and included fresh ginger roots and dried ginger powder, packaged in glass sprinklers or plastic bags. The products sourced from Africa and Asia but were purchased in two European countries from different companies. Detailed information on influencing parameters such as exact growing area, soil composition, climatic conditions, and processing methods is lacking. Some products do not even specify the country of origin.

2. Materials and methods

2.1. Origin of samples

In total, 11 products of ginger were bought from local markets or supermarkets in Zagreb (2), Croatia (companies indexed as HR) or Örebro (9), Sweden (companies indexed as "SE"). They were either fresh tubers, mass between 10 g and 30 g per tuber, or dry and grinded, mass 49 g–45 g. The latter are referred to as "powder". The samples (A-K) and their characteristics are shown in Table 1. Samples A and B were bought in Croatia, but the ginger originated from India. Of the 11 samples, 7 were powder, and four were fresh. The fresh samples consisted of two tubers, referred to as "batch 1 (b1)" and "batch 2 (b2)". For the powder samples, two different packages were purchased and designed as b1 and b2. Samples H, J, and K consisted of only one batch due to limited access to the product. The three fresh products (F, G, and H) were from China (bought in Sweden), loose and did not have any packaging whereas the bulb product I was dried and packaged in a plastic bag; its origin is not known (UKN).

All batches bought in Sweden were digested in triplicate (r1, r2, r3) and a mean value was calculated for each batch (referred to as "_mean"). For the two Croatian samples (A, B), only pooled samples were analyzed. With all the replicates, including mean values, and batches, a total of 64 analytical results were generated (Table 1).

2.2. Sample preparation

The general sample preparation procedure is based on previous studies analysing similar matrices [27,28]. The fresh samples were cut in small pieces (3 mm – 4 mm) with a ceramic knife, precleaned with diluted nitric acid, prior to further treatment. All samples were dried at 105 °C for 24 h in a laboratory oven, then homogenized in a metal-free mortar. Three aliquots of each dried sample batch were weighed on an analytical balance in the range from 0.15 g to 0.2 g and transferred into the digestion vessels. Then 6 mL semi-concentrated nitric acid (suprapure, Merck, Darmstadt, Germany) and 6 mL hydrogen peroxide (30 % *w/w*, Merck; Darmstadt, Germany) were added. All mixtures were left to react for approx. 1 h at room temperature. Complete digestion of the organic matrix took place in a microwave digestion unit (MWS-2 Speedwave Berghof; Germany), applying the following temperature program: 30 min at 120 °C (500 W), 30 min at 170 °C (700 W), and 30 min at 130 °C (400 W). Blank solutions were prepared in the same way. The obtained clear solutions were made up to 25.0 mL using ultrapure water from the in-house production unit. Before measuring the solutions, they were diluted 1:10 using ultrapure water, and the internal standard Rh (single element stock solution purchased from Merck, Darmstadt) was added to a final concentration of 10 μg/L.

2.3. Analytical method for quantification of elements

All digest solutions (samples, CRM, blanks) were analysed inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500cx, Tokyo, Japan). The operational conditions are listed in Table 2. The quantification of all analytes was made via external five-point calibrations based on multi-elemental standards solutions obtained by appropriate dilution from a multielement stock solution (ICP Multielement Standard IV, Merck, Darmstadt, Germany).

The used analytical procedure has been validated and proven to be applicable for plant derived food products in previous investigations [27,28]. Four different plant-derived standard reference materials, namely algae (IAEA 392), apple leaves (NIST SRM 1515), peach leaves (NIST SRM1547) and tomato leaves (NIST SRM1573a), underwent the above given digestion procedure and were analysed using the same instrumental settings. Limits of quantitation expressed as mass fraction in the dried sample were calculated based on 10 *s* (standard deviation of digestion blank) and are listed in Table 3 (column 6).

Table 1
Information for each sample (A-K).

	A (N = 2)	B (N = 2)	C (N = 8)	D (N = 8)	E (N = 8)	F (N = 8)	G (N = 8)	H (N = 4)	I (N = 8)	J (N = 4)	K (N = 4)	Overall (N = 64)
Company	HR1	HR2	SE1	SE2	SE3	SE4	SE5	SE6	SE7	SE7	SE5	9
Form	powder	powder	powder	powder	powder	fresh	fresh	fresh	fresh	powder	powder	
Country of origin	IND	IND	NGA	UKN	UKN	CHN	CHN	CHN	UKN	UKN	UKN	
Packaging	glass	plastic	glass	plastic	plastic	no	no	no	plastic	glass	glass	
No batches	2	2	2	2	2	2	2	1	2	1	1	
Replicates												
r1	0	0	2	2	2	2	2	1	2	1	1	15
r2	0	0	2	2	2	2	2	1	2	1	1	15
r3	0	0	2	2	2	2	2	1	2	1	1	15
mean	2	2	2	2	2	2	2	1	2	1	1	19

Table 2
Instrumental conditions of the ICP-MS used.

Parameter	Settings
Output power	1500 W
Argon flows	Plasma:15 L/min Auxiliary: 0.9 L/min Nebulizer: 0.2 L/min
Collison cell	activated for K, V, Cr, Fe, Cu, As, and Se, with a helium flow rate of 5 mL/min
Nebulizer	MicroMist
Spray chamber	Scott double pass
Sample flow	0.3 mL/min
Isotopes	^{7}Li, ^{9}Be, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{51}V, ^{53}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{69}Ga, ^{75}As, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{125}Te, ^{137}Ba, ^{205}Tl, $^{204+206+207+208}$Pb, ^{209}Bi, ^{238}U.

2.4. *Data treatment and statistical methods*

All data were stored in Microsoft Office 365 Excel® (Microsoft 365, version 2305, Microsoft Corporation, Redmond, WA, United States of America). To perform statistical evaluations and visualization, R packages (R 4.3.2) along with R-Studio (version 2023.09.1 Build 494, Posit Software, PBC, Boston, MA, United States of America) were employed.

Multivariate methods, specifically hierarchical cluster analysis (HCA) and principal component analysis (PCA), were used to examine the similarities, differences, and correlations between datasets and meta-data.

For clustering, Euclidean distances and the Ward method (ward.02 in R) were utilized, which grouped the data into clusters of higher similarity, resulting in a dendrogram and heatmap. PCA was employed to extract and project systematic variations in a data matrix.

In all quantitative assessments, values below the limit of quantification (LOQ) were treated as zero.

To determine statistically significant differences between the independent and dependent variables, non-parametric testing was conducted using the Kruskal-Wallis H test. Post hoc analysis was performed using the pairwise Wilcoxon test. Adjustment of values was done using the Benjamini-Hochberg method, and the significance level was set at $p = 0.05$. Additionally, the Pearson method was used to assess the correlation between variables.

These methods have been successfully applied to similar sample types [29,30].

3. Results and discussion

This paper presents the analytical approach from the results of 29 metals and metalloids starting with the assessment of all subsamples ($N = 64$), the individual replicates, the batches to conclude with the merged results with one content for any of the 29 elements in each sample.

Regarding the method validation, the recoveries were between 82 % and 115 %, the precision ranging from 0.5 % to 3.9 %. The LOQ values are given in Table 3 below (column 6).

The summary including the grouping into the characteristic groups according to common determination such as macro, micro, trace, toxic elements, into bioavailability and geochemical parameters, or chemical parameters as block is shown in Table 3. More detailed information, allowing a comparison between the batches, is shown in Table S1 in the Supplementary information.

The major cationic osmoticum in plant, potassium, is found in highest contents, followed by the other major elements Mg, Ca, Na and plant micronutrients manganese, iron, zinc alongside the non-essential element Ba. Low contents were found for essential trace elements, like copper, and molybdenum as well as for potentially toxic elements (Cd, Pb, As). Aluminum content differs a lot between the samples, which can be explained by varying soil composition and thus relation to provenience of the product.

3.1. *Assessment of all sub-samples ($N = 64$)*

Fig. 1 shows the graphic representation of the chemical analysis for the sum of the 29 elements in each replicate and mean value. With respect to the sum parameters, it can be seen that there is quite a large difference between batches for samples F and G, whereby batch 2 has the larger scale. The results of the replicates of sample I showed a large variation, also between batches. F, G as well as I were samples purchased as bulbs, which were then peeled, cut and homogenized in the laboratory. This highlights the variation of elements in biological samples. In contrast to samples F and G, the bulbs of sample I were sold in dried form. Even if all samples in the laboratory underwent the same drying step prior to homogenization, the pre-dried bulb was harder to pulverize. This explains the bigger variation not only between the two batches, but also between the three replicates. All powdered samples, however, are well homogenized and thus show less variation even between different batches. Furthermore, it is evident that sample I (pre-dried bulb) has a larger proportion of Ca (skyblue color) than all other samples. A more detailed look at the elemental distribution reveals that the values for Mg in sample F stretches across a large range. Se was quantified only in two subsamples, A (b2) and B (b2) (see also Table S1 in the supplementary information).

The quantitative information for each element in the 64 sub-samples is displayed in Fig. 2. This overview allows an ease comparison with literature data which is shown in Fig. S1 in the supplementary information. Regarding essential macro elements for humans, such as Na (52 mg/kg–987 mg/kg), K (2940 mg/kg–50500 mg/kg), Ca (786 mg/kg–2240 mg/kg), and Mg (1080 mg/kg–3580 mg/kg) the results from all studies are within the same order of magnitude and reflect the importance of these elements in plants. Exceptions with significantly lower values are found in the publications by Saod et al. (Mg: 12.26 mg/kg; Ca: 8.28 mg/kg; Na: 2.52 mg/kg; K: 67.72 mg/kg) [14] as well as by Savić and colleagues (Mg: 11.01 mg/kg; K:97.51 mg/kg) [15]. The generally high contents of these major elements underline the

Table 3

Compilation of assessment parameters for 29 elements and summary of results for 11 samples All values in mg/kg. Cells with values < LOQ are highlighted in red colour.

Element	Block	Group	Geochem	Bioavail.	LOQ	A	B	C	D	E	F	G	H	I	J	K
Ag	d	NC	chalco	NC	0.010	0.011	0.12	0.26	0.16	0.45	0.14	0.21	0.07	0.038	0.12	0.33
Al	p	macro	litho	NC	0.056	1 070	646	275	164	174	39.4	28.8	6.09	65.2	72.4	333
As	p	toxic	chalco	High	0.0020	0.10	0.08	0.014	0.019	0.009	<LOQ	0.059	0.010	0.19	0.16	0.059
Ba	s	micro	litho	NC	0.011	29.0	31.5	42.0	32.5	36.6	0.93	20.8	18.2	11.8	6.84	25.0
Be	s	NC	litho	NC	0.00031	0.023	0.014	0.013	0.011	0.0008	0.002	<LOQ	<LOQ	0.015	0.015	0.010
Bi	p	NC	chalco	NC	0.0033	<LOQ	0.004	3.29	0.20	0.008	0.13	0.30	0.21	0.042	0.094	1.05
Ca	s	macro	litho	NC	0.50	1 070	1 180	1 680	1 310	1 420	786	1 320	791	2 240	1 280	1 950
Cd	d	toxic	chalco	High	0.0023	0.026	0.040	0.039	0.039	0.033	0.002	0.019	0.073	0.16	0.46	0.070
Co	d	trace	litho_chalco	NC	0.014	0.29	0.27	0.38	0.26	0.23	0.003	0.069	0.063	0.072	0.29	0.73
Cr	d	micro	litho	Low	0.0050	3.55	3.03	0.52	0.49	0.34	0.39	0.13	0.14	0.094	0.26	2.04
Cu	d	micro	litho_chalco	High	0.028	4.95	6.62	7.67	6.83	6.60	4.07	5.18	5.83	2.82	4.88	6.01
Fe	d	macro	litho_chalco	Moderate	0.20	779	368	314	188	211	32.1	50.8	42.3	88.4	148	595
Ga	p	trace	litho_chalco	NC	0.023	1.98	2.03	1.47	1.10	1.22	0.041	0.69	0.59	0.40	0.24	0.92
K	s	macro	litho	NC	6.3	20 700	25 900	21 200	20 300	21 400	20 700	50 500	22 400	2 940	16 600	22 900
Li	s	trace	litho	NC	0.0050	0.26	0.15	0.17	0.087	0.076	0.005	0.19	0.045	0.031	0.019	0.12
Mg	s	macro	litho	NC	0.40	2 370	2 860	3 010	2 530	2 730	1 960	3 390	3 680	1 080	2 450	3 250
Mn	d	micro	litho	Moderate	0.011	263	340	465	358	347	18.6	432	789	153	390	241
Mo	d	toxic	NC	NC	0.024	0.40	0.25	0.44	0.39	0.39	0.49	0.44	0.31	0.044	0.13	0.27
Na	s	macro	litho	NC	6.3	331	358	78.6	72.0	54.0	168	719	657	116	52.0	987
Ni	d	micro	litho_chalco	High	0.0080	1.7	1.32	1.01	0.78	0.76	0.22	1.20	1.07	0.15	1.20	3.62
Pb	p	toxic	chalco	Low	0.0053	1.02	1.05	0.88	0.706	0.72	0.077	0.084	0.056	0.29	0.51	0.33
Rb	s	NC	litho	NC	0.0073	36.9	46.1	51.4	44.9	48.4	32.2	2.36	0.709	0.98	6.16	7.93
Se	p	trace	chalco	High	0.16	0.042	0.034	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sr	s	NC	litho	NC	0.012	12.4	13.0	15.3	12.1	13.3	6.85	9.42	6.95	11.3	3.03	13.6
Te	p	NC	chalco	NC	0.0004	0.006	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	p	toxic	chalco	NC	0.002	<LOQ	<LOQ	0.034	0.028	0.023	<LOQ	<LOQ	<LOQ	0.002	0.016	0.015
U	f	NC	litho	Low	0.0002	0.068	0.035	0.042	0.021	0.018	0.0002	0.002	<LOQ	0.016	0.013	0.048
V	d	trace	litho	NC	0.0091	1.26	0.71	0.60	0.31	0.35	0.04	0.02	0.009	0.19	0.29	1.32
Zn	d	micro	litho_chalco	High	0.037	23.1	23.5	28.4	24.7	24.8	8.83	7.79	13.5	4.90	16.6	14.0

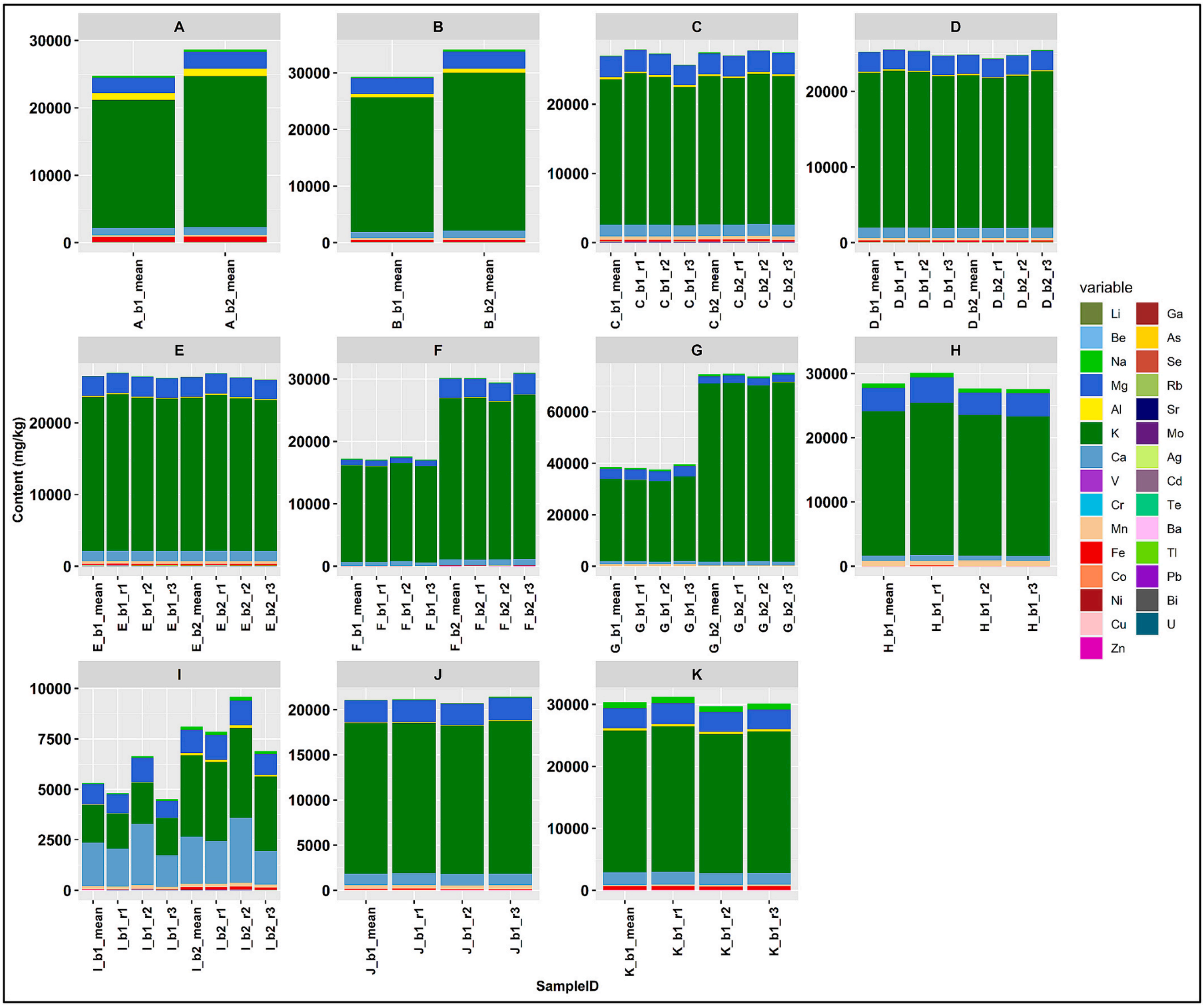

Fig. 1. Stacked bars for the sum of 29 elements in 11 samples by replicate and with mean values (N = 64).

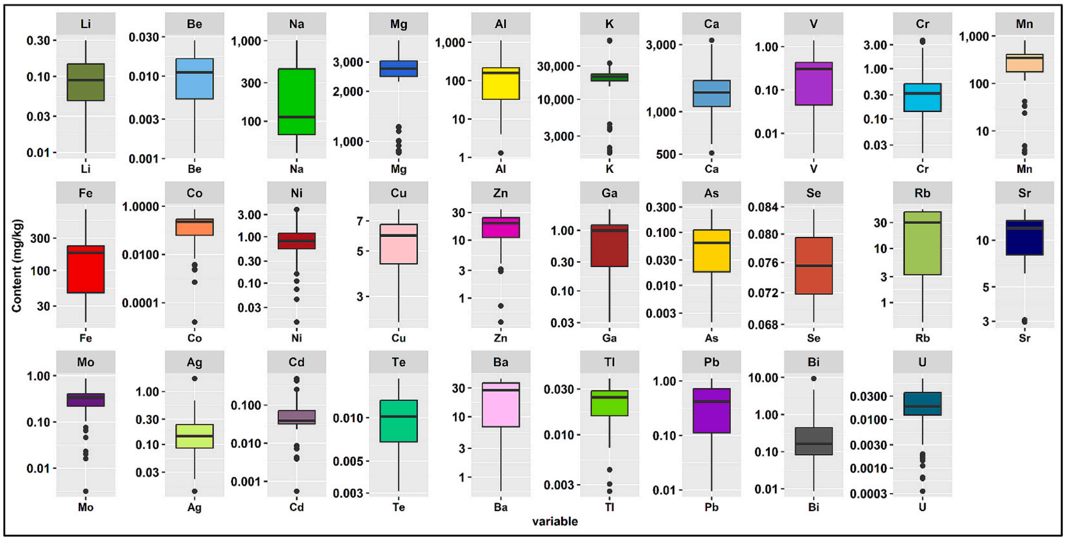

Fig. 2. Summary statistics for the elements as box whisker plots of elements.

nutritional value of ginger besides its flavouring properties. A fact that is generally stated for commonly consumed spices including ginger, cinnamon, black seed, fenugreek, cardamom, cloves and saffron [31].

When looking at the trace elements, especially those that are harmful to plants and/or humans, bigger differences between varieties and provenience are to be mentioned. In this respect the composition and pollution status of the soil where the plants grow are of importance. Alternative growing conditions, like in Agra polybags also seem to have an impact on metal contents in plants, as reported by Daran and co-workers who found elevated Cd levels in ginger grown in polybags compared to wild plants [32]. These harmful elements are the basis for evaluating the potential application of the plants, since the mass fraction of harmful elements, like As, Cd, and Pb is regulated in many countries, an overview is given in the paper by Gupta et al. [33]. This also explains why certain studies are limited only to trace elements and/or potentially toxic metals and metalloids [33,34]. Referring to the World Health Organization [35], the following maximum permissible values are given for As, Cd and Pb in raw (medical) plant material: 1.0 mg/kg, 0.3 mg/kg and 10 mg/kg, respectively. Considering these limits, all the analysed ginger samples, except for sample J (dried powder) which contains more than 0.3 mg/kg Cd, fulfil the requirements for safe use. Ginger samples collected in Ethiopia all showed Cd above the WHO-limit, nevertheless the authors state this as negligible amount, since the daily intake based on 5 g fresh ginger per day does not exceed the tolerable upper limit for this metal [36].

Assessing food safety concerning potentially toxic elements also involves considering the packaging materials. The analyzed samples were either packed in glass or plastic, while some fresh samples were even unpackaged. The European Union regulates the migration of Pb, Cd, Cr, Hg, and Sb from plastic food contact packaging [37]. A working group in Bangladesh analyzed plastic food packaging materials—polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polycarbonate (PC)—for these five elements, finding only Sb exceeded the limit [38]. Since no statistically significant differences in the content of these elements were found in the analyzed ginger samples, it can be assumed that harmful element migration into ginger is negligible. However, further processing appears to impact the elemental pattern in this spice. Fresh and powdered ginger form distinct groups, and samples from the same company also cluster together (see Fig. 3).

The whiskers represent the minimum and maximum amounts without outliers. The lower border of the box represents the first quartile (25 %), the line inside the box is the median and the upper border is the third quartile (75 %). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller than the interquartile range multiplied by 1.5.

3.2. *Assessment of replicates (N = 49)*

Table S1 in the Supplementary information shows the mean and median values together with the standard deviation (SD) and minimum and maximum values (in mg/kg) for each batch, corresponding to the aggregated replicates r1, r,2, r3. The low SDs within the three instrumental replicates (not given) indicate the repeatability of the measurements. The SDs of the digestion replicates is furthermore an indication of the homogeneity of the sample, especially when referring to pre-dried and powdered samples. Larger values of SDs may be caused by inhomogeneity of the samples as discussed above. Based on these findings, it was justified to analyse the Croatian samples only as pooled samples, considering them the same well homogenized powdered products sold on the market.

Multivariate analysis showed that chemical analysis gave very similar results for the replicates as can be seen in the dendrogram (Fig. 3). Also, the batches are located closely together. The dendrogram has two large clusters and it must be noted that all powder samples are

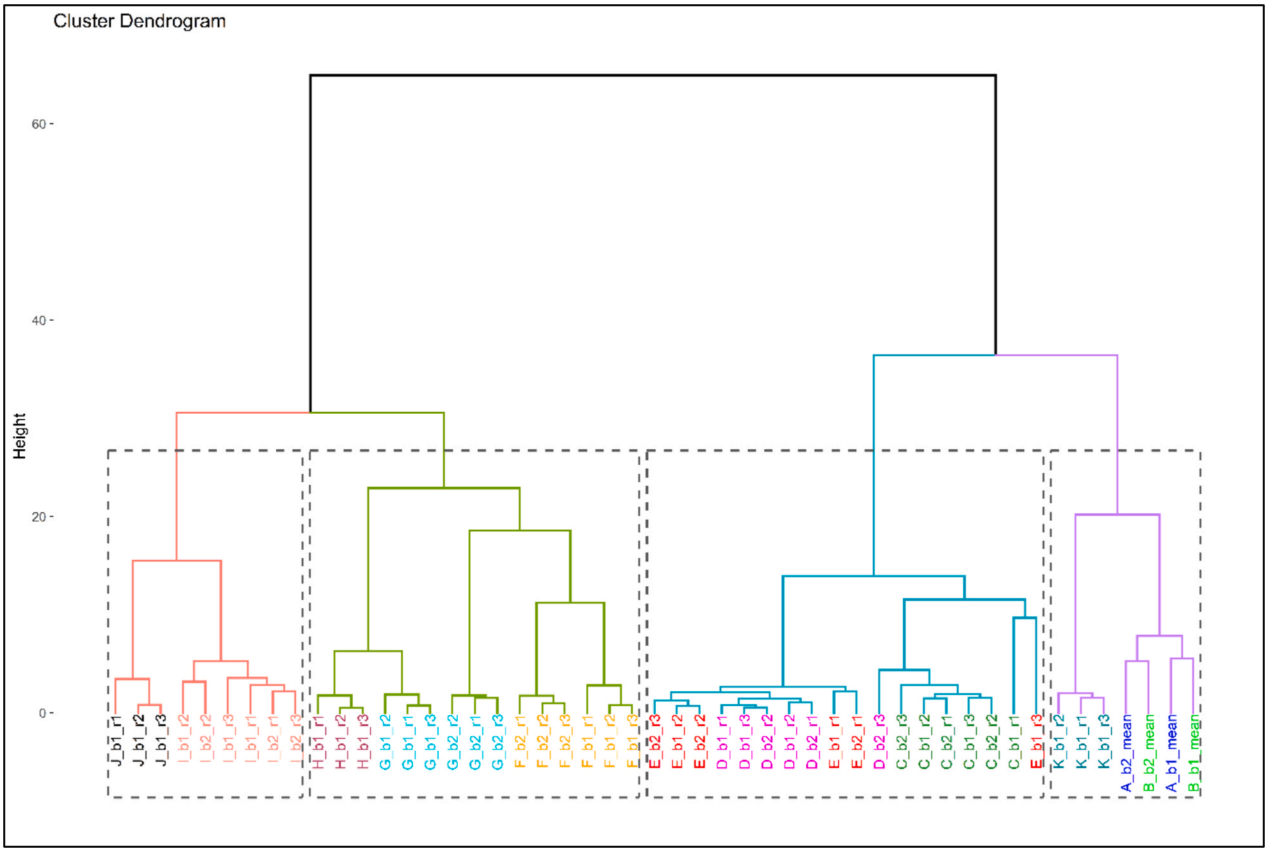

Fig. 3. HCA dendrogram displaying replicates by sample and batch/replicate. Sub-samples of the same sample (A-K) have the same color.

located in the 2nd main cluster at right (having two sub-clusters) whereas the fresh samples (F, G, H, and I) are clustered together at left in the first large cluster. Nevertheless, in the first sub-cluster (left), the three replicates from the powder sample J (black color, only one batch) are included. Samples I and J derive from the same company, even if they are sold in different, but always dried forms, their origin as well as drying and pre-grinding processing seem to be the same. As documented, the drying step has an influence on the organic composition of ginger [9], however it does not seem to have an impact on the metal content. Metals are bound to proteins in food; thus, the elemental composition may be correlated to a change in the protein content such as by superfine grinding [10].

The Kruskal Wallis assessment (not included) shows that with respect to company, SE4 is significantly different from all other companies and that sample F is significantly different from other samples. From Table 1, it can be seen that SE4 corresponds to sample F, fresh (loose) ginger from China.

3.3. Aggregation to mean values by batch ($N = 19$)

Based on the robustness of the analytical procedure and the homogeneity of the samples, further considerations are grounded on the mean values of the nineteen analysed ginger batches. An overview of the elemental composition is depicted in Fig. S2, but also see Table S1 in Supplementary information for more details. Differences in the y-axis scale for samples F, G, and I need to be noted. Sample I is different from other samples due to the larger share of Mg, but also higher content of Ca. All samples are dominated by K, a monovalent cation from group I of the periodical table, which acts as a major cationic osmoticum in plants. Whilst the absolute values differ for the fresh samples, i.e. the analysed tubers, their relative composition show the same pattern. Looking at the box-and-whisker-plots it can be seen that the distribution of K is very narrow, only with two samples showing very low or high content, namely G and I. The high values for K are also reported by other working groups, such as by Nandi and co-workers (China: 16970 mg/kg; Bangladesh: 27860 mg/kg) [39] and Manousi et al. (2863 mg/kg) [40].

Applying Pearson's approach (see Fig. 4), a strong correlation can be seen between Fe, Al, and Cr, all three-valent cations. Fe and Al are elements abundant in the earth crust and their contents correlated [41]. Furthermore, Fe is highly correlated with U and V, both naturally occurring as trace element in soils and sediments. Correlations of these elements in soil have been reported [42,43] which are also reflected in the analysed ginger samples.

3.4. Assessment based on element classification

Fig. 5 shows the sum of relevant elements for the classification or grouping according to Block, Group, Geochem, Bioavailability. In each graph, the top row shows the total contents (in mg/kg) and the lower row the contribution to 100 %.

To assess and establish correlations between elements in plant-derived products, a classification based on their biological significance is useful. Duffus [20,21] recommends focusing on electron configuration and the elements' positions in the periodic table, specifically s-, p-, d-, and f-block elements (referred to as "Block") (see Fig. 5). Additionally, a geochemical classification distinguishes elements as lithophile or

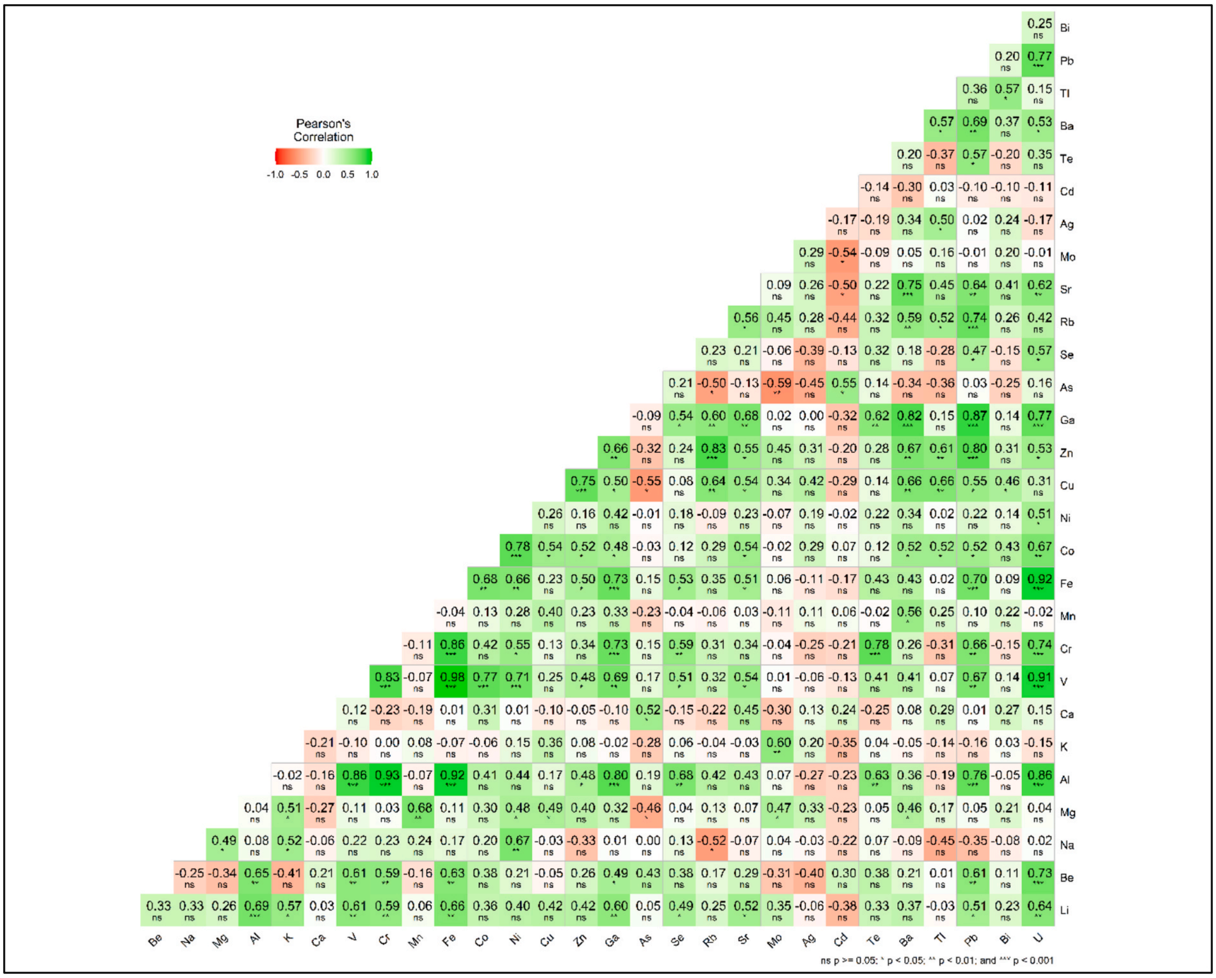

Fig. 4. Plot of Pearson correlation coefficients and significance using mean values for samples, divided into two batches each.

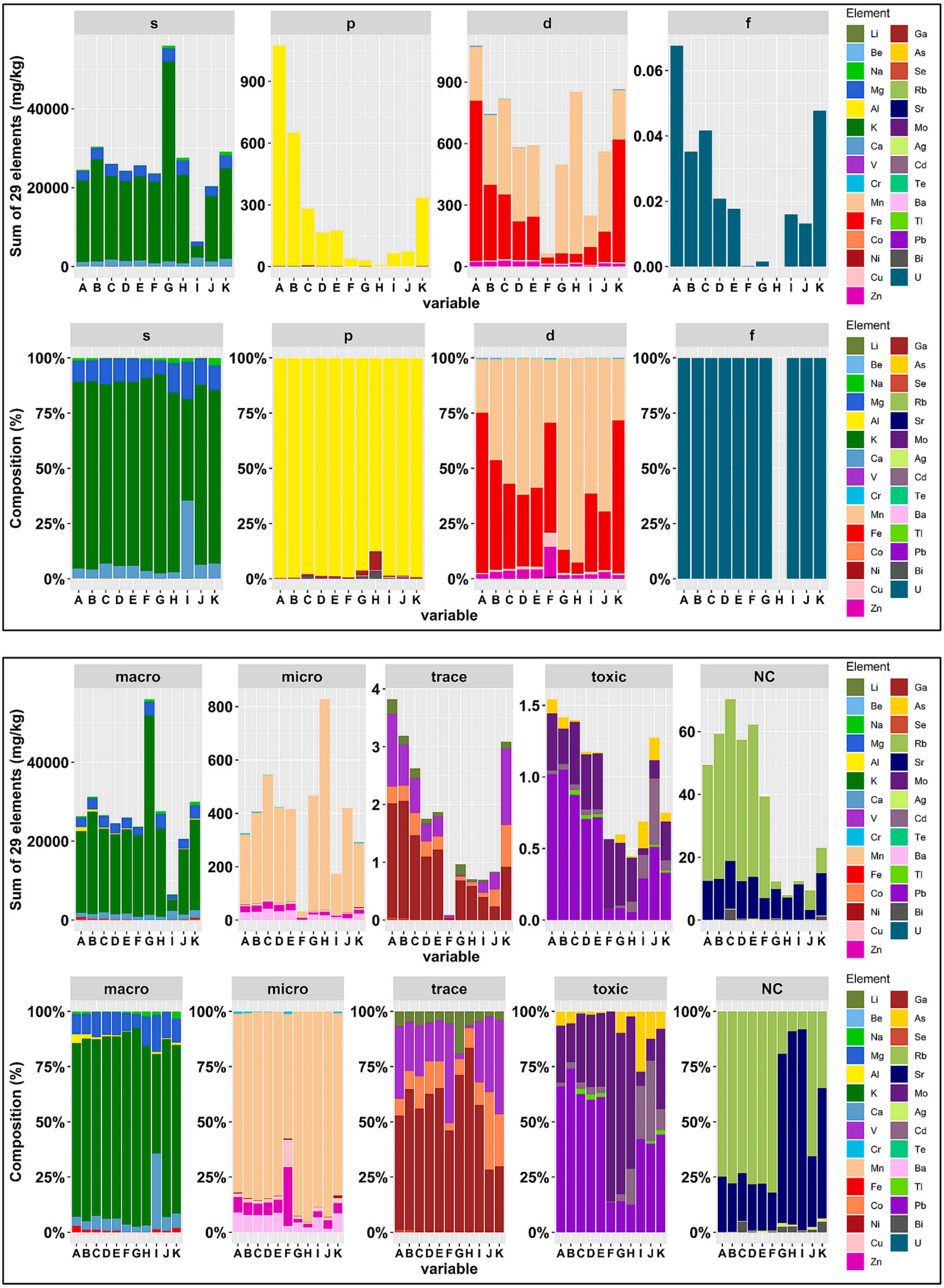

Fig. 5. Stacked bar graphs and pattern using mean values of 29 elements for each sample (n = 11) grouped by block, bioavailability, group, and Geochem.

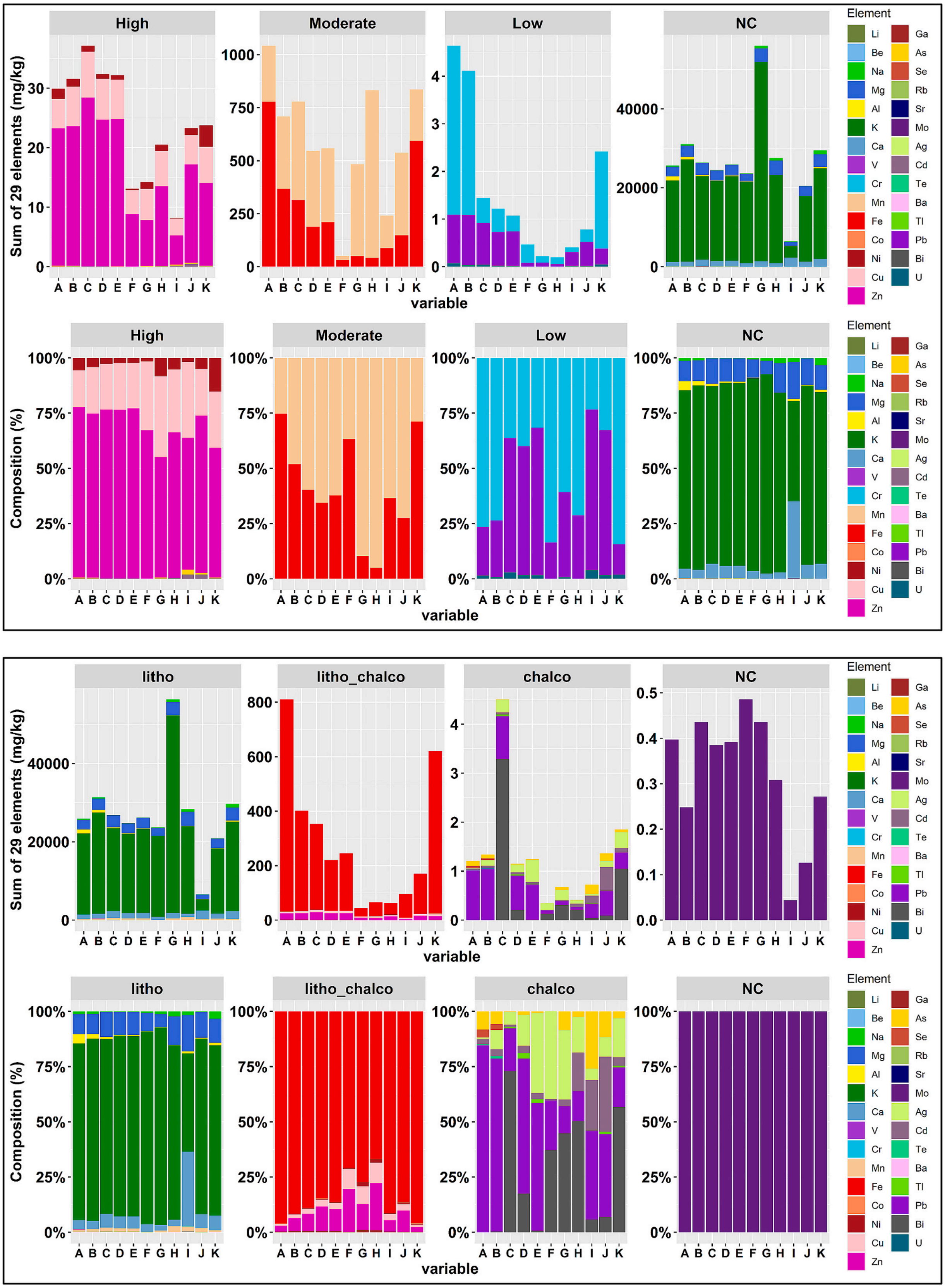

Fig. 5. (*continued*).

chalcophile (referred to as “Geochem”). It is important to consider that for plants, the chemical forms in which metals exist in the soil or plant influence their bioavailability, and thus their uptake and transport [44]. Certain metal species are more accessible to plants than others. However, not all elements analyzed are including in either of these classifications regarding their significance in plant sciences. Another parameter used to classify elements for plants is their bioavailability [45]. The classifications used in this study are summarized in Table 3.

Considering "block" classification, it can be seen that elements of the s-block have by far the highest values (in scale); they contribute 97 % to the sum of the 29 elements. Next are the d elements with 2.2 % followed by the p elements (1.02 %); whereas there is only one f element, U, which is 0.001 % of the sum of all elements.

Within the s elements, K is dominating (84 %), followed by Mg (9.7 %), Ca (5.1 %), and Na (1.1 %). Al is the dominant p element (99.3 %); Fe (54 %) and Mn (42 %) are the most abundant of the d elements.

Regarding bioavailability, it is interesting to notice that main elements, such as K, Na, Mg and Ca are not allocated to one of given groups (high–moderate–low). Studies on the soil-ginger systems also limiting to potentially toxic elements show the following order of bioavailability for selected analytes for ginger originating from China: Cr > Zn > Pb > Ni > Cu > As > Cd > Hg [19]. The leading element Cr is according to Shilpa [45] only classified as element with low bioavailability. Based on results of this study Cr contributes most to this "low" class, whilst Zn most to the "high" class. Direct comparison between mass fractions in ginger and bioavailability is not possible without respective information on the growing soil. Furthermore, metal uptake has found to be species-dependent [46,47], thus such interpretations need to be referenced to specific soil–plant systems.

The classification and correlation of elements, and consequently their presence and content in foodstuffs, enable the geographical authentication of food products through trace elements to determine their origin. This process relies on the fact that the elemental composition of soil, water, and air varies by geographic location, influencing the elemental composition of plants grown in those regions. Although this approach has been reported in the literature for decades, it remains undocumented for many spices and plant-derived food products [48,49]. Establishing a reliable database requires analyzing a large number of samples, as suggested by [50]. However, preliminary conclusions can still be drawn from a smaller sample size as shown in certain pilot studies [51,52]. This pilot study investigated ginger samples from three countries—China (CHN), Nigeria (NGA), and India (IND)—as well as samples with unknown origin (UKN). The respective PCA biplot is shown in Fig. S3 in the supplementary information. The samples from India appear to differ the most, while Nigerian and Chinese samples have ellipses in the same orientation. Samples with no specified country of origin are more similar to those from Nigeria and China than to those from India.

4. Conclusions

To obtain reliable information about the elemental composition of ginger, a validated analytical procedure including acid sample digestion followed by analysis through inductively coupled plasma mass spectrometry (ICP-MS) was used and major, minor, and trace elements were quantified in the spice samples.

Biological samples are well known for high variation of composition, which makes it necessary to analyse a high number of samples and various replicates per sample. However, well homogenized pooled samples like powdered spices give similar results throughout batches and replicates. This means that experimental work can be reduced, and the obtained average value used for further assessment.

The present study revealed that the elemental composition of ginger varies based on geographic location, influenced by soil composition and growing conditions. Generally, ginger contains a variety of elements, with potassium (K), calcium (Ca), and magnesium (Mg) being the most abundant. Trace elements, which are essential for various physiological functions in plants, also contribute to the nutritional profile of ginger. Certain elements such as iron (Fe), aluminum (Al), chromium (Cr), uranium (U), and vanadium (V) were found to be highly correlated and appear to be influenced by the geographical origin. Since bioavailability depends on plant species, a general classification of elements on this parameter is questionable.

The consumption of the investigated ginger samples poses no harmful effects on human health, as arsenic (As), cadmium (Cd), and lead (Pb) levels were below the limits set by the WHO for medicinal plants. Additionally, no significant migration of potentially toxic elements from the packaging materials was observed.

The processing of the ginger samples, especially the drying step, seems to be of importance for the metals and metalloids found in the final product. Conversely, the packaging has no measurable impact on the elemental composition.

These findings are based on a limited number of samples and geographical origins. Furthermore, commercially available products lack detailed background information. A higher number of samples, especially with more detailed information on provenience and processing would strengthen future studies.

CRediT authorship contribution statement

Michaela Zeiner: Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. **Heidelore Fiedler:** Writing – original draft, Visualization. **Doris Toma:** Methodology. **Ivan Nemet:** Methodology, Investigation. **Iva Juranović Cindrić:** Writing – original draft, Validation, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2025.113333.

Data availability

Data will be made available on request.

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