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STATISTICAL ASSESSMENT OF ESSENTIAL TRACE ELEMENTS IN BILBERRY AND ROSEHIP FRUITS

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Abstract

The total mineral concentration in foods does not always reflect the actual nutritional value, as only the fraction released from the food matrix during digestion becomes available for intestinal absorption. The study aimed to evaluate the total concentration, bioaccessible concentration, and bioaccessible fraction of four essential microelements - iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) - in bilberry (Vaccinium myrtillus L.) and rosehip fruits (Rosa canina L.) harvested from hilly and submontane areas of western Romania. Total concentrations were determined by atomic absorption spectrometry, and bioaccessibility was assessed using a standardized in vitro gastrointestinal digestion model. The results revealed significant differences ($p < 0.05$) between the harvesting sites for the total and bioaccessible concentrations of the analyzed elements. Rosehip fruits showed higher levels of Fe, Mn, and Zn, while bilberries showed comparable or higher levels of Cu. Iron had the lowest bioavailability and copper the highest, while Mn and Zn had intermediate values. The results suggest that rosehip fruits are a more important source of Fe, Mn, and Zn, while bilberries can contribute significantly to dietary Cu intake.

Key words*: in vitro digestion, bioaccessibility, Rosa canina, Vaccinium myrtillus, Duncan test for multiple comparisons.*

INTRODUCTION

Blueberries and raspberries are fruits rich in antioxidants, especially vitamin C and flavonoids, which help protect the body from oxidative stress (Varzaru et al., 2024; Dróżdż et al., 2018; de Souza et al., 2014). Both fruits are a good source of fiber, vitamins (B, C, and K), folic acid, fatty acids, polyphenols (anthocyanins), and minerals such as Cu, Fe, I, K, Mg, which support digestion and contribute to maintaining a healthy cardiovascular system (Pereira et al., 2018). Bilberries and blueberries (fruits of the species *Vaccinium myrtillus* and *Vaccinium corymbosum*) are rich in bioactive compounds (polyphenols, anthocyanins, vitamins, minerals, and fiber) that give them a remarkable nutritional and functional value, which is why these fruits are intensively studied for their potential benefits on human health (Wang et al., 2024). In terms of mineral composition, blueberries contain potassium, calcium, magnesium, phosphorus, iron, manganese, and zinc - essential elements for optimal body functioning (Cabrera et al., 2021). The mineral profile of blueberries (genus Vaccinium), both cultivated (especially *Vaccinium corymbosum*) and wild (*Vaccinium myrtillus*) species, highlights a complex composition of essential macro- and microelements, influenced by genetic, pedoclimatic, and technological factors.

For cultivated blueberries (*V. corymbosum*), Cabrera et al. (2021) reported, in eight varieties in northeastern Argentina, high concentrations of K (417,650-1073,058 mg/100 g), Ca (54,738-206,104 mg/100 g) and Mg (31,527-63,025 mg/100 g), as well as relevant levels of Fe (3,274-7,518 mg/100 g), Zn (1,245-2,761 mg/100 g), Cu (0.470-1.137 mg/100 g) and Mn (0.656-5.163 mg/100 g), concluding that blueberries are an excellent source of Mn, Fe and Cu and a valuable source of Zn, K, Mg and Ca. Pereira et al. (2025) confirmed the

predominance of potassium in the Bluecrisp variety (801 mg/kg K), along with notable contributions of Mg and Mn.

Comparisons between wild and cultivated blueberries generally indicate a higher mineral density in fruits from spontaneous flora. Dróżdż et al. (2018) showed higher concentrations in wild blueberries for Ca (164-203 vs. 112-162 mg/kg), Mg (75.1-96.9 vs. 48.1-51.4 mg/kg), Mn (5.82-29.0 vs. 2.94-4.47 mg/kg) and K (880-1105 vs. 825-1031 mg/kg), as well as trace amounts of Cd, Pb, Ni and Cr, reflecting the influence of the environment. Similarly, Karlsons et al. (2018) reported higher values in *V. myrtillus* compared to *V. corymbosum* for K, Ca, Mg, Mn, and Cu, while Fe and S were slightly higher in cultivated blueberries. Gentscheva et al. (2014) and Donut et al. (2014) confirmed considerable contents of Mg, Fe, Mn, Zn, and Cu in wild blueberries, along with trace elements (Se, Mo, Cr, Ni) in low concentrations. The data provided by the USDA database for raw blueberries indicate mean values of 86 mg/100 g K, 12 mg/100 g Ca, 6.2 mg/100 g Mg, 0.34 mg/100 g Fe, 0.09 mg/100 g Zn, 0.046 mg/100 g Cu, 0.423 mg/100 g Mn, and 13 mg/100 g P, confirming the relevant contribution to K intake, Mn and Mg.

Overall, the literature supports the idea that bilberries are an important source of macroelements (especially K, Ca, Mg) and essential microelements (Mn, Fe, Zn, Cu), with a general tendency to accumulate more in wild blueberries. The variability in mineral content depends on species, variety, and environmental conditions, underscoring the need to standardize analytical methodologies and reporting units for adequate inter-study comparability. From a nutritional perspective, bilberries can be considered foods with a high mineral density, helping maintain metabolic homeostasis.

Rosehips, the fruits of the *Rosa canina* shrub (Rosaceae family), have a complex chemical composition that gives them high nutritional and functional value (Paunović et al., 2018; Kulaitiene et al., 2021). Through the diversity of classes of nutritional compounds (vitamins, carbohydrates, minerals, fiber) and bioactive compounds (carotenoids, polyphenols, terpenoids, glycosides), rosehip fruits from Rosa canina are distinguished as a plant raw material with high functional value, with applications in nutrition, phytotherapy, and the food industry (Paunović et al., 2019).

The fruits of wild rosehips (*Rosa canina*) are an important source of macro- and microelements essential for human health, and their mineral content varies significantly depending on the region of origin and environmental conditions. Recent studies have highlighted a varied mineral profile of rosehips, with particular concentrations of calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), manganese (Mn), zinc (Zn), and copper (Cu). According to research by Zlateva et al. (2024), rosehip flour contains the following minerals per 100 g: 169 mg Ca, 1.06 mg Fe, 69 mg Mg, 61 mg P, 429 mg K, 4 mg Na, 0.25 mg Zn, 0.113 mg Cu, and 1.02 mg Mn. These data are supported by Milenković et al. (2024), who report significant concentrations of K (4710-9850 mg/kg), Ca (2650-5140 mg/kg), and P (532-1610 mg/kg) in Rosa fruits. Also, the predominant microelements in these fruits are manganese (Mn), silicon (Si), and iron (Fe), with values of 6.8-64 mg/kg, 15.2-51.6 mg/kg, and 9.9-30 mg/kg, respectively.

Studies by Paunović et al. (2019) on rosehip fruits harvested from Serbia confirmed high mineral contents in both fresh and dried fruits. In dried fruits, 348.12 mg/100 g of Ca, 566.75 mg/100 g of K, and 135.61 mg/100 g of Mg were identified. Also, the comparative analysis carried out by Ivanova et al. (2023) between wild and those cultivated in Bulgaria highlighted the significant differences in the concentrations of P, K, Na, and Mg, with wild rosehips having values higher than P (0.415%), K (1039.56 mg/kg), and Mg (2331.7 mg/kg). The mineral composition of rosehips also varies across genotypes. For example, research by Benković-Lacić et al. (2022) on different genotypes of wild rosehips in Croatia showed variable values of essential minerals such as P (1284-1848 mg/kg), Na (22.9-91.1 mg/kg), Mg (1410-2587 mg/kg), K (9386-18383 mg/kg), and Ca (2856-8934 mg/kg). Similarly, recent studies by (Kulaitiene et al., 2021) and and Igual et al. 2022) on freeze-dried rosehip powders reported significant mineral contents such as K (2630.46 mg/100 g), Ca (590.33 mg/100 g), P (690.81 mg/100 g), Mg (340.66 mg/100 g), Fe (7.52 mg/100 g), Zn (2.55 mg/100 g) and Mn (3.19 mg/100 g), thus strengthening their nutritional

value. Peña et al. (2023) also pointed out that, compared to other berries, rosehips have a higher content of essential minerals, such as Ca (1.69 mg/g), P (0.61 mg/g), K (4.29 mg/g), Mg (0.69 mg/g), Zn (0.25 mg/g), Cu (0.113 mg/g) and Mn (1.02 mg/g), thus emphasizing their importance in the daily diet.

In conclusion, wild rosehips are an important source of minerals, with their mineral content influenced by geographical and genetic factors. These fruits can significantly contribute to meeting daily requirements for macro- and microelements, with a higher nutritional potential than other berries (Pereira et al., 2018). Further studies on the mineral profile of rosehips from different regions of the world are essential for understanding their variability and for their application in human nutrition.

From the above, it can be stated that wild blueberries and rosehips contain important amounts of mineral elements, including iron, manganese, copper, and zinc, essential microelements in the homeostasis of the human body. Acting as cofactors of enzymes involved in fundamental biological processes, such as cellular respiration, antioxidant protection, protein biosynthesis, and the regulation of immune functions (Pereira et al., 2018). Since the total essential/toxic content of a food does not reflect the beneficial/toxic effects after consumption, it is very important to assess its bioaccessible and bioavailable fractions (Pereira et al., 2018; Ramírez-Ojeda et al., 2017).

In this case, the term bioaccessibility refers to the fraction of a given microelement released from the fruit matrix after ingestion and solubilized in the intestinal lumen (Mingroni et al., 2019; Pereira et al., 2018). An accepted definition of bioavailability is the amount of a nutrient available for normal metabolic and physiological processes, i.e., the amount that becomes available for absorption in the small intestine (Affonfere et al., 2023). The bioaccessibility of a given element can be measured through several experimental models, such as in vitro digestion of homogenized foods in a closed system and determination of the soluble nutrient fraction, *in vitro* digestion and dialyzability of soluble nutrients through a semipermeable membrane, or the use of human colorectal adenocarcinoma (Caco-2) cells to mimic many of the characteristics of thin intestinal cells (Mingroni et al., 2019). This study aims to evaluate the bioaccessibility of the microelements Fe, Mn, Zn, and Cu from wild blueberries and rosehips harvested from the spontaneous flora of hilly and submontane areas in the west of the country.

MATERIALS AND METHODS

Materials

The materials used in this experiment are wild fruits, namely rosehips (*Rosa canina*) and bilberries (*Vaccinium myrtillus*), from the spontaneous flora of a hilly and submontane area in western Romania. Approximately 1 kg of fruit was collected from three different areas, each sample originating from a distinct collector (Provider 1, Provider 2, and Provider 3). Homogeneous samples were then prepared from these batches for analysis. Fruits were cleaned of vegetable residues, washed under running water, rinsed with distilled water, and drained of moisture. They were then dried and ground into a powder. The drying operation was performed in an air-drying oven at 50°C until a constant mass was reached, and the dry samples were ground in a kitchen grinder. Until the moment of analysis, the samples were kept in brown glass bottles at cold temperatures.

Total mineral concentration determination

Total concentrations of four essential trace elements - iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) - were determined by atomic absorption spectroscopy (AAS), using the calcination method followed by ash solubilization and measurement of element absorbance in the acidic solution, according to the procedure described by Velciov et al. (2024). Samples were calcined at 500°C in two successive stages of 4 hours each. Measurements were performed using a Varian AA-240 FS (Fast Sequential) atomic absorption spectrometer. All determinations were carried out in triplicate, and results were expressed as the mean ± standard deviation.

Bioaccessible mineral concentration determination

To evaluate the fraction of minerals potentially available for intestinal absorption, the bioaccessible concentrations of Fe, Mn, Zn, and Cu in rosehip and bilberries samples were

determined using an *in vitro* gastrointestinal digestion model described by Souza et al. (2023). Briefly, 300 mg of each sample was subjected to a standardized two-phase *in vitro* digestion procedure simulating gastric and intestinal conditions.

In the gastric phase, 4.5 mL of salivary solution (pH 6.5 ± 0.5) and 6.75 mL of gastric solution (pH 1.1 ± 0.1) were added. The pH was adjusted to 1.20 ± 0.05 with concentrated HCl, and the mixture was incubated for 1 h at 37°C under agitation (100 rpm). For the intestinal phase, 13.5 mL of duodenal solution and 4.5 mL of bile solution were added, and the pH was adjusted to 6.3 ± 0.5 using 1 mol/L NaOH. Incubation continued for 4 h at 37°C under constant shaking (100 rpm). After centrifugation (3000 rpm, 5 min), the supernatant was collected as the bioaccessible fraction.

Concentrations of Fe, Mn, Zn, and Cu were determined by the same AAS method. Bioaccessibility, specifically the bioaccessible fraction (BF, %), was calculated as: BF (%) = (MBF/TMC) × 100, where MBF represents the mineral concentration in the bioaccessible fraction (mg/100 g, dry weight) and TMC is the total mineral content (mg/100 g, dry weight). All analyses were performed in triplicate.

Statistical Analysis

The mathematical rigor and statistical evaluation of the experimental data were conducted to ensure the highest reliability of the results. Before performing the analysis of variance (ANOVA), the normality of the data was confirmed using the Shapiro-Wilk test, and the homogeneity of variances was assessed using Levene's test. Following validation of these premises, a one-way ANOVA was performed to assess differences between harvesting sites (providers). When significant differences were detected ($p < 0.05$), the Duncan multiple-range test was used for post hoc pairwise comparisons. All statistical procedures were performed using the R software environment (R Core Team), specifically utilizing the agricolae package for agricultural and biological research data analysis.

RESULTS AND DISCUSSIONS

Before performing the ANOVA, the normality of the data was confirmed using the Shapiro-Wilk test, and the homogeneity of variances was assessed using Levene's test, thereby ensuring a robust mathematical foundation for the data. The extremely low standard deviations highlight the precision of the measurements.

The results obtained for determining the total and bioaccessible concentrations of microelements, as well as the accessible fractions of these microelements in the analyzed bilberries and rosehips, are presented in Tables 1, 2, and 3.

Table 1. Total and bioaccessible concentration (mg /100g DM) of Fe, Mn, Zn, and Cu in bilberry fruits

Fruit origin	Total concentrations				Bioaccessible concentrations			
	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu
Provider 1	2.1814 ± 0.07d	1.6219 ± 0.08f	0.8609 ± 0.05d	0.8932 ± 0.03a	0.2142 ± 0.02g	0.4155 ± 0.02i	0.2167 ± 0.02f	0.4262 ± 0.02d
Provider 2	1.8062 ± 0.07e	2.0567 ± 0.05d	0.8913 ± 0.04cd	0.5717 ± 0.33c	0.1694 ± 0.02g	0.5457 ± 0.02i	0.2240 ± 0.02f	0.2936 ± 0.02f
Provider 3	2.2289 ± 0.09d	1.8704 ± 0.05e	1.1104 ± 0.03c	0.6329 ± 3.02b	0.2175 ± 0.02g	0.4878 ± 0.02i	0.2783 ± 0.03f	0.3039 ± 0.02f

The distinct letters in each column indicate statistically significant differences between the samples ($p < 0.05$) according to the Duncan test.

Table 2. Total and bioaccessible concentrations (mg/100g DM) of Fe, Mn, Zn, and Cu in wild rosehip fruits

Fruit origin	Total concentrations				Bioaccessible concentrations			
	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu
Provider 1	2.8728 ± 0.09a	3.1155 ±0.08c	2.7934 ± 0.07b	0.3707 ± 0.01e	0.3453 ± 0.03f	0.8759 ± 0.09h	0.5967 ± 0.30e	0.1802 ± 0.02g
Provider 2	3.1158 ± 0.08b	3.8645 ± 0.06a	2.6081 ± 0 19 b	0.4504 ± 0.02d	0.3649 ± 0.04f	1.1157 ± 0.07g	0.5670 ± 0.05e	0.2213 ± 0.03g
Provider 3	3.2426 ± 0.06c	3.7092 ± 0.08b	3.3181 ± 0.19a	0.3629 ± 0.01e	0.3839 ± 0.03f	1.0649 ± 0.09g	0.7313 ± 0.05de	0.1759 ± 0.02g

The distinct letters in each column indicate statistically significant differences between the samples ($p < 0.05$) according to the Duncan test.

Table 3. The bioaccessible fraction of Fe, Mn, Zn, and Cu in bilberry and rosehip fruits

Fruit origin	Bioaccessible fractions (%)							
	Bilberry fruits				Rose hip fruits			
	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu
Provider 1	9.81± 0.11b	25.73± 0.13a	25,31± 0.10a	48.71± 0.09a	12.00± 0.12a	28.20± 0.10a	22.11± 0.11a	47.85± 0.12a
Provider 2	9.39± 0.09b	26.56± 0.11a	25.19± 0.10a	49.10± 0.10a	11.68± 0.10a	28.83± 0.08a	21.85± 0.10a	48.30± 0.11a
Provider 3	9.74± 0.08b	26.09± 0.10a	25.13± 0.11a	48.50± 0.11a	11.83± 0.10a	28.75± 0.12a	21.33± 0.10a	48.04± 0.11a

The distinct letters in each column indicate statistically significant differences between the samples ($p < 0.05$) according to the Duncan test.

The results presented in Table 1 show variations in the total and bioaccessible concentrations of Fe, Mn, Zn, and Cu in analyzed bilberries.

Regarding the total concentrations, significant differences are observed for all the microelements investigated. The total Fe content was higher in the samples from Provider 3 (2.2289 mg/100 g DM) and Provider 1 (2.1814 mg/100 g DM) than in Provider 2 (1.8062 mg/100 g DM), the differences being statistically significant ($p < 0.05$). For Mn, the highest total concentration was recorded in Provider 2 (2.0567 mg/100 g DM), followed by Provider 3 (1.8704 mg/100 g DM) and Provider 1 (1.6219 mg/100 g DM), each value differing significantly from the others. In the case of Zn, the blueberries from Provider 3 showed a significantly higher content (1.1104 mg/100 g DM) compared to the other samples, while for Cu, the highest total concentration was observed in Provider 1 (0.8932 mg/100 g DM); the differences compared to the other suppliers were also significant ($p < 0.05$).

The analysis of bioaccessible concentrations shows considerably lower values than the total concentrations; however, even in this case, statistically significant differences are found between the samples.

For Fe, the bioaccessible fraction was relatively low for all providers (9.39-9.81% of total content), with minor but significant differences ($p < 0.05$). In the case of Mn, the highest bioaccessible value was observed in Provider 2 (0.5457 mg/100 g DM), followed by Providers 3 and 1, with significant differences between samples. Zn showed the highest bioaccessible concentration in blueberries from Provider 3 (0.2783 mg/100 g DM), while for Cu, the bioaccessible values were highest at Provider 1 (0.4262 mg/100 g DM), suggesting a relatively higher proportion of this element available for absorption.

These results show that the origin of bilberries significantly influences both the total content and the bioaccessible fraction of the microelements analyzed ($p < 0.05$). It is also noted that the assessment of the nutritional value of fruits should not be based solely on total mineral concentration, but also on the bioaccessible fraction, which better reflects absorption potential at the gastrointestinal level. By correlating the results for total and bioaccessible concentrations (Table 1) with the bioaccessible fraction values (Table 3), an integrated interpretation of the nutritional potential of the analysed bilberries can be achieved.

The data confirm that although there are statistically significant differences ($p < 0.05$) between suppliers in total and bioaccessible concentrations of micronutrients, the proportion of the potential element available for absorption (the bioaccessible fraction) varies by element.

For Fe, the bioaccessible fraction is relatively small and comparable across samples, at 9.81% (Provider 1), 9.39% (Provider 2), and 9.74% (Provider 3). The statistical calculation indicates the absence of statistically significant differences between providers ($p < 0.05$). These results are consistent with low bioaccessible concentrations (Table 1) and suggest limited Fe availability, probably due to interactions with phenolic compounds or dietary fibres in the fruit matrix.

For Mn, the bioaccessible fraction is considerably higher, ranging from 25.73% to 26.56%, with no significant differences between providers. Although the total concentrations differ significantly (Table 1), the proportion available for absorption remains relatively

constant, indicating a stability of the digestive behavior of this element in the blueberry matrix. A similar profile is observed for Zn, where the bioaccessible fraction varies very little (25.1265–25.31%), with no statistically significant differences ($p < 0.05$). Thus, although Provider 3 showed the highest total and bioaccessible Zn concentrations (Table 1), the proportion of the total that becomes bioaccessible is similar across all samples.

In contrast, Cu has the highest bioaccessible fraction among the microelements analyzed, ranging from 48.50% to 49.10%, with no significant differences between suppliers. These results confirm the observations in Table 1, where Cu recorded relatively high bioaccessible values compared to the total content, suggesting a chemical form more favourable to solubilisation and potential intestinal absorption.

Overall, the data show that although the origin of bilberries significantly influences the total and bioaccessible concentrations of microelements ($p < 0.05$), the bioaccessible fraction is relatively constant for Mn, Zn, and Cu, with no significant differences between suppliers. Iron remains the element with the lowest percentage bioaccessibility (approximate values: 9–10%), while copper has the highest relative availability (approximate values: 48–49%).

These results underline the importance of the simultaneous assessment of the total content, the bioaccessible concentration, and the bioaccessible fraction for a correct assessment of the nutritional value of bilberries, demonstrating that the potential mineral intake depends not only on the total level of the element, but also on the efficiency of its release under simulated gastrointestinal conditions.

The results presented in Table 2 show significant variations in the total and bioaccessible concentrations of Fe, Mn, Zn, and Cu in wild rosehips from the three suppliers analyzed. The statistical scale of the mean values in each column indicates statistically significant differences between the samples ($p < 0.05$), confirming the influence of origin on the mineral composition of the fruits.

Regarding the total concentrations, significant differences are observed for all the microelements investigated. The total Fe content progressively increases from Provider 1 (2.8728 mg/100 g DM) to Provider 2 (3.1158 mg/100 g DM) and Provider 3 (3.2426 mg/100 g DM), with each value being significantly different (letters in distinct colors, $p < 0.05$). For Mn, the highest total concentration was recorded in Provider 2 (3.8645 mg/100 g DM), followed by Provider 3 (3.7092 mg/100 g DM) and Provider 1 (3.1155 mg/100 g DM), with the differences also being statistically significant.

In the case of Zn, the rosehips from Provider 3 presented the highest total content (3.3181 mg/100 g DM), significantly higher than the other samples ($p < 0.05$), while for Cu, the maximum value was recorded in Provider 2 (0.4504 mg/100 g DM), differing significantly from the other two samples, which do not differ from each other (same letter).

The analysis of bioaccessible concentrations also reveals statistically significant differences between providers ($p < 0.05$). For Fe, bioaccessible values increase from Provider 1 (0.3453 mg/100 g DM) to Provider 3 (0.3839 mg/100 g DM), with the difference being significant. In the case of Mn, the highest bioaccessible concentration is found in Provider 2 (1.1157 mg/100 g DM), followed by Provider 3 (1.0649 mg/100 g DM) and Provider 1 (0.8759 mg/100 g DM), all differences being statistically significant.

For Zn, Provider 3 has the highest bioaccessible value (0.7313 mg/100 g DM), significantly higher than the other providers, whereas for Cu, there are no significant differences between the samples, suggesting a relatively constant availability of this element regardless of origin.

Overall, the results demonstrate that the origin of wild rosehips significantly influences the total and bioaccessible concentrations of most microelements analyzed ($p < 0.05$). It is noted that Mn and Zn have relatively high total and bioaccessible levels compared to Fe and Cu, indicating a potentially important contribution of rosehips to the dietary intake of essential microelements. At the same time, the statistical differences highlighted underline the importance of pedoclimatic factors and growing conditions in determining the mineral profile of wild fruits.

The correlation between the results for total and bioaccessible concentrations of trace elements (Table 2) and the bioaccessible fraction values

presented in Table 3 allows a more complete assessment of the nutritional potential of the wild rosehips analyzed.

As previously highlighted, the total and bioaccessible concentrations of Fe, Mn, Zn, and Cu differ significantly between suppliers ($p < 0.05$), as indicated by the distinct letters in each column of Table 2.

The analysis of the bioaccessible fraction (Table 3) indicates that, for all the microelements investigated, there is an absence of statistically significant differences between suppliers ($p < 0.05$).

For iron (Fe), the bioaccessible fraction ranges from 11.68% (Provider 2) to 12.00% (Provider 1), with an intermediate value at Provider 3 (11.83%). Although total and bioaccessible concentrations differ significantly between samples, the proportion of total iron that becomes bioaccessible remains relatively constant, ranging from 11.68% to 12.00%.

For Mn, the bioaccessible fraction is higher than for Fe, ranging from 28.20% to 28.83%. The highest value is recorded in Provider 2 (28.83%), but the differences are not statistically significant ($p < 0.05$). This constancy suggests a similar digestive behavior of Mn in the rosehip matrix, regardless of variations in total content.

For zinc (Zn), the bioaccessible fraction ranges from 21.33% (Provider 3) to 22.11% (Provider 1), with no significant differences between providers. Although Provider 3 showed the highest total and bioaccessible Zn concentrations (Table 2), the proportion available for absorption was comparable across all samples.

Copper has the highest bioaccessible fraction among the analysed microelements, with values ranging from 47.85% to 48.30%. Here, too, the lack of statistically significant differences indicates that almost half of the total Cu content becomes potentially available for uptake, independent of changes in the total concentration.

Overall, the results show that although the origin of rosehips significantly influences the total and bioaccessible levels of microelements ($p < 0.05$), the bioaccessible fraction is relatively constant for all elements analyzed. Iron has the lowest bioaccessible proportion, zinc and manganese have intermediate values, and copper has the highest.

These findings underline that the potential bioavailability of microelements in rosehips is determined not only by the total concentration, but also by the efficiency of their release under simulated gastrointestinal conditions, and the relatively constant proportion of the bioaccessible fraction suggests a stable behavior of these elements in the fruit matrix, regardless of provenance.

The comparative analysis of the total concentrations, bioaccessible concentrations, and bioaccessible fractions of the microelements Fe, Mn, Zn, and Cu highlights relevant differences between bilberries and wild rosehips, both quantitatively and in terms of bioavailability potential. In terms of total concentrations, rosehips stand out for superior values for most of the elements analyzed. Thus, the total Fe content is higher in rosehips (2.8728-3.2426 mg/100 g DM) compared to bilberries (1.8062-2.2289 mg/100 g DM). Similar differences are observed for Mn (3.1155-3.8645 mg/100 g DM in rosehips versus 1.6219-2.0567 mg/100 g DM in bilberries) and Zn (2.6081-3.3181mg/100 g DM in rosehips compared to 0.8609-1.1104 mg/100 g DM in bilberries). On the other hand, for Cu, bilberries show comparable or even higher total values (0.5717-0.8932 mg/100 g DM) compared to rosehips (0.3629-0.4504 mg/100 g DM). In both types of fruit, the distinct letters within each column indicate statistically significant differences between suppliers ($p < 0.05$), highlighting the influence of origin on mineral accumulation.

The trends observed in total concentrations are also reflected in bioaccessible concentrations. Rosehips show higher bioaccessible values for Fe (0.3453-0.3839 mg/100 g DM vs. 0.1694-0.2175 mg/100 g DM in blueberries), Mn (0.8759-1.1157 mg/100 g DM vs. 0.4155-0.5457 mg/100 g DM) and Zn (0.5670-0.7313 mg/100 g DM vs. 0.2167–0.2783 mg/100 g DM). For Cu, the situation is different, with bilberries registering comparable or higher bioaccessible concentration values (0.2936-0.4262 mg/100 g DM) than rosehips (0.1759-0.2213 mg/100 g DM). Again, the differences between suppliers are statistically significant for most elements ($p < 0.05$), unless the same letter indicates no significant difference.

The comparative analysis of the bioaccessibility of the microelements Fe, Mn, Zn, and Cu in bilberry and rosehip fruit powders shows that the specific plant matrix of each fruit influences mineral release under gastrointestinal conditions to a greater extent than variations in sample origin. Both bilberries and rosehips are characterized by a high content of phenolic compounds (anthocyanins, flavonols, condensed tannins, and phenolic acids), as well as a significant intake of dietary fiber and pectins, both of which are known to interact with minerals during in vitro digestion. The low iron bioaccessibility values (9.39-12.00%) can be attributed to the formation of stable complexes between Fe and phenolic compounds, which reduce its solubility in the intestinal phase. Similarly, zinc showed moderate bioaccessibility (21.33-25.31%), consistent with its susceptibility to polyphenolic chelation. Manganese showed intermediate bioaccessibility (25.73-28.83%), possibly influenced mainly by interactions with fibers and the plant matrix rather than by specific inhibitors such as phytate, which is virtually absent in these fruits. In contrast, copper showed the highest bioaccessibility (47.85-49.10%), which can be explained by its ability to form more soluble complexes with organic ligands in the fruit matrix.

In the case of rosehips, the high ascorbic acid content could help maintain iron in a more soluble form, explaining the slightly higher values compared to blueberries; however, the favourable effect of vitamin C is probably partially counterbalanced by the high polyphenol concentrations. Overall, the bioaccessibility profile obtained is consistent with the data reported for other berries and reflects the decisive influence of phytochemical composition on the potential availability of microelements.

As regards the bioaccessible fraction, expressed as a percentage, there is a relatively constant behavior across suppliers for each type of fruit ($p < 0.05$), suggesting that the fruit-specific matrix influences the proportion released to a greater extent than variations in origin. Compared between species, rosehips have a slightly higher fraction for Fe (values between 11.68-12.00%) compared to blueberries (values between 9.39-9.81%) and for Mn (values between 28.20–28.83% compared to 25.73-26.56%). For Zn, blueberries register a slightly higher fraction (values between 25.13-25.31%) compared to rosehips (values between 21.33-22.11%). In the case of Cu, both fruits have the highest bioaccessible fraction (approximate values, between 47.85-49.10%), with no notable differences between them.

Overall, wild rosehips stand out for their superior total and bioaccessible Fe, Mn, and Zn content, suggesting a higher nutritional potential for these microelements. Bilberries, on the other hand, can be an important source of Cu, both in total and bioaccessible concentrations. At the same time, the relative consistency of the bioaccessible fraction for each element indicates that the peculiarities of the plant matrix mainly determine the efficiency of release under gastrointestinal conditions.

Therefore, in order to reflect as accurately as possible the real contribution of bilberries and rosehips to dietary mineral intake, it is necessary to comparatively assess the value of both the total level of trace elements and the concentration and bioaccessible fraction.

The results obtained are consistent with the literature, which reports variability in the mineral content of wild fruits across species and pedoclimatic conditions (Cabrera et al., 2021; Gentscheva et al., 2014). The higher Fe, Mn, and Zn levels in rosehips compared to bilberries confirm the observations of other researchers, who describe rosehips as an important source of essential microelements (Peña et al., 2023). Also, the Cu concentrations in bilberries fall within the previously reported ranges for this type of fruit.

The low bioaccessible fractions for Fe and higher values for Cu are also in agreement with studies showing limited bioavailability of iron in the plant matrix and higher solubility of copper under simulated gastrointestinal conditions (de Lima et al., 2014; Cai et al., 2017). Moderate values for Mn and Zn also support the trends described in the literature (de Lima et al., 2014; Cai et al., 2017)

Overall, wild rosehips stand out for their superior total and bioaccessible Fe, Mn, and Zn content, suggesting a higher nutritional potential for these microelements. Bilberries, on the other hand, can be an important source of Cu, both in total and bioaccessible concentrations.

Therefore, in order to reflect as accurately as possible the real contribution of bilberries and rosehips to the dietary mineral intake, it is necessary to comparatively assess the value of both the total level of trace elements, the concentration, and the bioaccessible fraction.

CONCLUSIONS

The results obtained indicate statistically significant differences ($p < 0.05$) between suppliers in the total and bioaccessible concentrations of the microelements analyzed, both in wild blueberries and in wild rosehips. Overall, rosehips show higher total and bioaccessible concentrations of Fe, Mn, and Zn than blueberries, suggesting a superior nutritional potential for these elements. However, blueberries show comparable or even higher Cu values, both at the total level and in bioaccessible levels.

Bioaccessible concentrations generally follow the same trend as the total ones but represent only a fraction of the original mineral content, underlining the importance of assessing potential bioavailability. The bioaccessible fraction was relatively constant between suppliers for each type of fruit, indicating a determining role of the plant matrix on the release of elements under simulated gastrointestinal conditions. Iron had the lowest bioaccessible fraction, while copper showed the highest release percentages in both types of fruit.

From an applied perspective, these findings suggest that the formulation of dietary supplements or functional foods could strategically combine wild fruits to achieve an optimized, highly bioaccessible mineral profile, harnessing Fe, Mn, and Zn from rosehips and Cu from blueberries. The integration of data on total concentration, bioaccessible concentration, and bioaccessible fraction provides a complete picture of the true nutritional value of these wild fruits.

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