

BIOGENIC AND RISK ELEMENTS IN GRAPE POMACE OF DIFFERENT CULTIVARS

Judita Lidiková¹, Natália Čeryová¹*, Janette Musilová¹, Marek Bobko¹, Alica Bobková¹, Alžbeta Demianová¹, Katarína Poláková¹, Olga Grygorieva²

Address(es): Natália Čeryová

¹Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Institute of Food Sciences, Tr. Andreja Hlinku 2, 949 76 Nitra, Slovak Republic. ²M.M. Gryshko National Botanical Garden of the National Academy of Sciences of Ukraine, Department of Fruit Plants Acclimatisation, Timiryazevska 1, Kyiv 04014, Ukraine.

*Corresponding author: xceryova@uniag.sk

https://doi.org/10.55251/jmbfs.11096

ARTICLE INFO	ABSTRACT
Received 3. 4. 2024 Revised 2. 5. 2024 Accepted 22. 5. 2024 Published 1. 8. 2024	The contents of biogenic and risk elements in the pomace of 6 grape cultivars (Blaufränkisch, Cabernet Franc, Cabernet Sauvignon, Devín, Dunaj, and Merlot) were analyzed in this study. Content of K, Ca, P, Mg, and Na was 11 750 – 19 070, 2 400 – 3 908, 1 678 – 2 684, 336 – 760, and 1.43 - 59.3 mg.kg ⁻¹ DM respectively. Content of Fe, Cu, Mn, Zn, Ni, Cr, and Co was 79.5 – 245, 6.18 – 48.4, 10.3 – 22.6, 4.19 – 17.0, 0.66 – 1.36, 0.058 – 2.33, and 0.42 – 0.63 mg.kg ⁻¹ DM respectively. Pb and Cd were detected in the grape pomace of Merlot (0.94 and 0.03 mg.kg ⁻¹ DM, respectively) and Cabernet Sauvignon (0.36 and 0.08 mg.kg ⁻¹ DM, respectively). The total content of Hg ranged from 0.0055 to 0.0080 mg kg ⁻¹ DM. Analysis of variance showed that there are differences in the content of elements among cultivars.
Regular article	Grape pomace of cultivars Blaufränkisch and Cabernet Sauvignon could be characterized by the higher Fe, Mn, Zn, Ni, and Cr content, while grape pomace of cultivar Merlot by higher Mg content. With relatively low content of risk elements, grape pomace can serve as a good source of essential minerals in the human diet.
	Keywords: grape pomace, minerals, lead, cadmium, mercury

INTRODUCTION

Winemaking is one of Slovakia's most important traditional industries, with more than 330 000 hl of wine produced and 11.9 L of wine consumed per capita in 2022 (Ministry of Agriculture and Rural Development of the Slovak Republic, 2023; Statistical Office of the Slovak Republic, 2023). The wine industry also produces a considerable amount of valuable unused waste, including grape pomace, which has not been used in the past. Wine and wine by-products are a rich source of antioxidants and health-promoting bioactive molecules such as flavonoids, phenolic acids, stilbenes, proanthocyanins, and other molecules such as natural colors, vitamins, fibers, and minerals (Chowdhary et al., 2022; Ferrer-Gallego and Silva, 2022; Čeryová et al., 2021; Jara-Palacios, 2019). Due to its content of bioactive substances, grape pomace is a promising raw material for producing nutritional foods, which are of great interest as their consumption can help prevent civilization diseases. Additionally, grape processing by-products are suitable for recovering valuable polyphenolic compounds and reducing environmental waste. The high polyphenol content may lower its pH and increase its resistance to biodegradation (Kalli et al., 2018). With a relatively high content of biogenic elements essential for human health, grape pomace can also be an interesting ingredient for fortifying food and increasing the intake of these elements in the human diet (García-Lomillo and González-SanJosé, 2016). The content of risk elements could limit the possible agricultural as well as food uses of grape pomace. In case there are higher levels of certain essential elements in the plants, they could be classified as risk elements, or heavy metals, which

could limit their use (Vollmannová et al., 2014). These elements can pose longterm risks to human health and harm the environment. Heavy metals are considered priority pollutants due to their potential toxicity if concentrations exceed permitted limits (Dumitriu Gabur et al., 2019). Conventional agriculture is a major contributor to heavy metal contamination in the food chain, posing a risk to environmental health. By-products and wastes may also contain harmful elements and compounds, such as heavy metals and pesticide residues, which can negatively impact human health. Therefore, it is important to prevent contamination of food products that incorporate by-products. (Dumitriu Gabur et al., 2021). Contamination of both the wine and the grape pomace can occur at different stages of the vine-growing process. This is most often caused by applying fertilizers, pesticides, herbicides, and fungicides during crop cultivation (Pérez Cid et al., 2019). According to Herrero-Hernández et al. (2012), the presence of risk elements in the grape pomace can be attributed to treating vines with fertilizers and plant protection products. The accumulation of risk elements in grapes is influenced by various factors such as variety, degree of maturity, geography, and the use of agrochemicals. Additionally, climatic factors such as temperature, humidity, and wind can also have an impact (Fiket *et al.*, 2011).

Although recently, there has been an increased interest in the study of bioactive compounds from grape pomace, studies on the content of biogenic, but especially risk elements, are scarce. Therefore, this study aimed to determine the content of these elements in grape pomace from different grape cultivars and to evaluate the safety of this material as a potential raw material for food production.

MATERIAL AND METHODS

Plant material

Grape pomace of Blaufränkisch (BL), Cabernet Franc (CF), Cabernet Sauvignon (CS), Devín (DE), Dunaj (DU), and Merlot (M) were provided by the Tajna winery. All samples were taken from the same site, in the municipality of Tajná, located in the Nitra wine region of Slovakia. The collected samples were dried at 50 °C for four days using a drying oven Memmert SF 110 (Memmert GmbH, Schwabach, Germany) and then thoroughly homogenized for 60 seconds at 25 000 rpm using batch mill IKA A10 (IKA-Werke GmbH & Co. KG, Staufen, Germany).

Determination of the macroelement contents

Contents of macroelements were determined according to **Musilová** *et al.* (2023). 1 g of the sample was mineralized in 10 ml of concentrated HNO₃ and 5 ml of concentrated HClO using the mineralization device MARS X-press (CEM Corp., Matthews, NC, USA). The mineralized sample was filtered through quantitative filter paper Filtrak 390 (Munktell, GmbH, Bärenstein, Germany). To determine K, Ca, P, and Mg content, 2 ml of filtered sample was diluted with distilled water to the volume of 50 ml and measured against a blank solution using atomic absorption spectrophotometer VARIAN AASpectra DUO 240FS (Varian, Ltd., Mulgrave, VIC, AUS). To determine P content, 1 ml of filtered sample was diluted with 8 ml of solution ($C_6H_8O_6$, H_2SO_4 , (NH_4)₂MoO₄, and $C_4H_4KO_7Sb_0 \times 5H_2O$) and deionized water to the volume of 50 ml and measured against blank solution using a UV/Visible Scanning Spectrophotometer Shimadzu UV- 1800 (Shimadzu, Kyoto, Japan). Analyses were performed in 4 replicates.

Determination of the microelement and risk element contents

Contents of microelements were determined according to $\check{C}eryov\acute{a}$ *et al.* (2023). 1 g of sample was mineralized in 5 ml of concentrated HNO₃ and 5 ml of redistilled

water using mineralization device MARS X-press (CEM Corp., Matthews, NC, USA). The mineralized sample was filtered using filtrating paper Filtra 390 (Munktell, GmbH, Bärenstein, Germany), and diluted with distilled water to the volume of 50 ml. The contents of Fe, Cu, Zn, Mn, Co, Cr, and Ni were determined against a blank solution using an atomic absorption spectrometer Varian 240FS (Varian Inc., Mulgrave, VIC, Australia). The contents of Pb and Cd were determined against a blank solution using an atomic absorption spectrometer Varian 240FS (Varian 240Z (Varian Inc., Mulgrave, VIC, Australia). The content of mercury was determined according to Lidiková *et al.* (2021) by cold-vapor atomic absorption spectroscopy method using selective Hg analyzer AMA254 (Al-tec, Prague, Czech Republic).

Statistical analysis

Statistical analyses were performed using the program XLSTAT (**Lumivero**, **2024**). Shapiro-Wilk test was used to assess the normality of the distribution. Based on the normality tests, analysis of variance (ANOVA with Tukey's multiple pairwise comparison) and non-parametric analysis of variance (Kruskal-Wallis test with Dunn's multiple pairwise comparison with Bonferroni correction) were used

Table 1 Content of macroelements in analyzed samples (mg.kg⁻¹ DM)

to compare the contents of analyzed elements in individual cultivars. Pearson correlation was used to determine the relationships between the analyzed elements.

RESULTS AND DISCUSSION

Content of macroelements in grape pomace

The most abundant macroelement in grape pomace of all analyzed cultivars was K, followed by Ca, P, Mg, and Na. The total content of K ranged from 11 750 (Dunaj) to 19 070 mg.kg-1 (Merlot). Total content of Ca ranged from 2 400 (Devín) to 3 908 mg.kg-1 (Merlot). The total content of P ranged from 1 678 (Devín) to 2 684 mg.kg-1 (Dunaj). Total content of Mg ranged from 336 (Cabernet Sauvignon) to 760 mg.kg-1 (Cabernet Franc). The total content of Na ranged from 1.43 (Blaufränkisch) to 59.3 mg.kg-1 (Devín). Statistical analysis of results showed that there are differences in the content of macronutrients among cultivars. While Devín has the lowest content of Ca and P, it has the highest content of Na. On the other hand, the cultivar Dunaj has the lowest K content but the highest Mg content. Cultivar Merlot had the highest content of K and Ca.

Cultivar	K	Ca	Р	Mg	Na
BL	12 698 ^{ab}	3 257 ^{bc}	1 823 ^{ab}	355 ^{ab}	1.43 ^a
sd	1 358	323	195	30.9	0.15
CF	16 019 ^{ab}	3 803 ^{bc}	1 921 ^{ab}	760 ^c	9.24 ^{abc}
sd	1 399	359	208	82.6	0.95
CS	12 675 ^{ab}	3 017 ^{ab}	1 996 ^{ab}	336 ^a	5.09 ^{ab}
sd	1 156	256	221	29.4	0.54
DE	13 399 ^{ab}	2 400ª	1 678 ^a	572 ^{abc}	59.3°
sd	1 305	185	152	55.5	0.55
DU	11 750 ^a	3 359 ^{bc}	2 684 ^b	754 ^{bc}	13.1 ^{bc}
sd	1 425	339	258	79.4	1.52
М	19 070 ^b	3 908°	2 627 ^{ab}	579 ^{abc}	9.53 ^{abc}
sd	2 181	422	269	61.2	1.11

Legend: BL - Blaufränkisch, DE - Devín, CF- Cabernet Franc, DU - Dunaj, M - Merlot, CS- Cabernet Sauvignon, sd- standard deviation (n=4)

Šimko et al. (2019) reported similar content of K (12 892 - 15 055 mg.kg⁻¹), but higher levels of Ca (4 457 - 5 517 mg.kg⁻¹), P (3 180 - 3 210 mg.kg⁻¹), Mg (1 200 - 1 205 mg.kg⁻¹), and Na (260 - 462 mg.kg⁻¹) in grape pomace of Pinot Blanc from different localities in Slovakia. Tangolar et al. (2018) reported similar content of Ca (2350 - 3460 mg.kg⁻¹), P (1230 - 1910 mg.kg⁻¹), Mg (610 - 850 mg.kg⁻¹), Na $(20 - 70 \text{ mg.kg}^{-1})$, and a wider range of the K (6780 - 17 600 mg.kg⁻¹) in grape pomace of 6 different cultivars. In grape pomace of Cabernet Sauvignon, they reported higher content of K, Mg, and Na (1 110, 530, 50 mg.kg⁻¹ respectively), and lower content of Ca and P (1 110 and 1 190 mg.kg⁻¹ respectively). Chikwhana et al. (2018) reported similar content of Ca (2 390 - 3 730 mg.kg⁻¹), similar and higher content of K (15 000 – 24 200 mg.kg⁻¹), P (2 170 – 3 420 mg.kg⁻¹), and Na $(33.2 - 117 \text{ mg.kg}^{-1})$, and higher content of Mg $(950 - 1.370 \text{ mg.kg}^{-1})$ in grape pomace of three cultivars from South Africa. Ziarati et al. (2017) reported similar content of Mg (321.5 mg.kg⁻¹) and Na (1.36 mg.kg⁻¹), but lower content of K (1348.6 mg.kg⁻¹), Ca (845.6 mg.kg⁻¹), and P (112.0 mg.kg⁻¹) in grape pomace of 5 different cultivars. Sagdic et al. (2014) reported similar average content of Ca (2

400 mg.kg⁻¹), but higher average content of P (3 800 mg.kg⁻¹), and Mg (1000 mg.kg⁻¹) in grape pomace of 5 Turkish grape cultivars. **Hanušovský** *et al.* (2019) reported higher levels of macronutrients (23 825 – 58 550 mg K.kg⁻¹, 2226 – 5367 mg Ca.kg⁻¹, 2260 – 3798 mg P.kg⁻¹, 687 – 1173 mg Mg.kg⁻¹ in, and 341 – 1556 mg Na.kg⁻¹) in grape pomace of different cultivars from Slovakia and Austria, and **Corbin** *et al.* (2015) reported a higher content of macronutrients (27 333 mg K.kg⁻¹, 3867 mg Ca.kg⁻¹, 2 733 mg P.kg⁻¹, 987 mg Mg.kg⁻¹, and 58 mg Na.kg⁻¹) in grape pomace of Cabernet Sauvignon. **Bennemann** *et al.* (2016) determined K, Ca, P, and Mg in grape pomace of 9 different cultivars. They reported similar and higher content of Mg (587 – 1 055 mg.Kg⁻¹; 622 mg.kg⁻¹ in CS, 587 mg.kg⁻¹ in GP of Cabernet Sauvignon, 108 mg.kg⁻¹ in Merlot, and 186.6 mg.kg⁻¹ in CF), and wider range of Ca 1580 – 4295 mg.kg⁻¹ in C342 mg.kg⁻¹ in Cabernet Sauvignon, 1580 mg.kg⁻¹ in Merlot, and 2962 mg.kg⁻¹ in Cabernet Franc).

Table 2 Content	of microeleme	ents and risk	elements in ar	alyzed sam	ples (mg.kg ⁻	¹ DM)

Cultivar	Fe	Cu	Mn	Zn	Ni	Cr	Со	Pb	Cd	Hg
BL	224 ^{bc}	33.2 ^{abc}	22.6 ^b	16.1 ^{bc}	1.05 ^{bc}	1.83 ^{ab}	0.44 ^a	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>	0.0058ª
sd	13.1	1.9	2.47	0.82	0.10	0.20	0.02			0.0006
CF	79.5ª	7.76 ^{ab}	13.1 ^{ab}	4.19 ^a	0.88^{ab}	0.05^{ab}	0.63 ^b	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>	0.0075^{b}
sd	3.55	0.45	1.03	0.22	0.09	0.01	0.04			0.0009
CS	245°	31.6 ^{bc}	22.3 ^b	17.0 ^c	1.36 ^c	2.33 ^b	0.54^{ab}	0.36 ^{ab}	0.084 ^b	0.0068^{ab}
sd	11.8	2.06	1.25	0.80	0.15	0.03	0.03	0.02	0.005	0.0008
DE	133 ^{abc}	6.18 ^a	10.3 ^a	4.29 ^{ab}	0.66^{a}	0.05 ^a	0.42ª	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>	0.0080^{b}
sd	6.58	0.34	0.56	0.22	0.07	0.007	0.02			0.0010
DU	81.6 ^{ab}	11.9 ^{abc}	12.0 ^{ab}	5.34 ^{abc}	0.77 ^a	0.05 ^a	0.63 ^b	<lod<sup>a</lod<sup>	<lod<sup>a</lod<sup>	0.0055ª
sd	3.85	0.58	0.64	0.28	0.07	0.01	0.03			0.0005
М	115 ^{abc}	48.4 ^c	11.9 ^{ab}	7.12 ^{abc}	0.82 ^{ab}	0.11 ^{ab}	0.52 ^{ab}	0.94 ^b	0.031 ^{ab}	0.0067^{ab}
sd	5.69	0.29	0.60	0.35	0.09	0.01	0.03	0.06	0.004	0.0005
ML								1.00*	0.10*	

Legend: BL - Blaufränkisch, DE - Devín, CF - Cabernet Franc, DU - Dunaj, M - Merlot, CS - Cabernet Sauvignon, sd- standard deviation (n=4), ML- maximum level *Maximum level of Pb in other foodstuffs set by Ordinance No. 18558/2006-SL Coll., Maximum level of Cd in grape seed set by COMMISSION REGULATION (EU) 2023/915

Content of microelements and risk elements in grape pomace

The most abundant microelement in all analyzed samples was Fe. The total content of Fe ranged from 79.5 (Cabernet Franc) to 245 mg.kg⁻¹ (Blaufränkisch). The total content of Cu ranged from 6.18 (Devín) to 48.4 mg.kg-1 (Merlot). The total content of Mn ranged from 10.3 (Devín) to 22.6 mg.kg⁻¹ (Blaufränkisch). The total content of Zn ranged from 4.19 (Cabernet Franc) to 17.0 (Cabernet Sauvignon). The total content of Ni ranged from 0.66 (Devín) to 1.36 mg.kg⁻¹ (Cabernet Sauvignon). The total content of Cr ranged from 0.05 (Cabernet Franc, Devín, Dunaj) to 2.33 (Cabernet Sauvignon). The total content of Co ranged from 0.42 (Devín) to 0.63 mg.kg-1(Cabernet Franc). Pb and Cd were detected in the grape pomace of Merlot (0.94 mg.kg⁻¹, 0.03 mg.kg⁻¹ respectively) and Cabernet Sauvignon (0.36 mg.kg⁻¹, 0.08 mg.kg⁻¹ respectively). The total content of Hg ranged from 0.0055 (Dunaj) to 0.0080 mg.kg⁻¹ (Devín). Statistical analysis of results showed that there are differences in the content of micronutrients among cultivars. Cultivars Blaufränkisch and Cabernet Sauvignon had the highest Fe, Mn, Zn, Ni, and Cr content, while cultivar Merlot had the highest content of Cu. On the other hand, grape pomace of cultivars Devín and Cabernet Frand had the highest content of Hg. Šimko et al. (2019) reported similar content of Fe (66.2 – 99.1 mg.kg⁻¹), Cu $(11.7 - 15.4 \text{ mg.kg}^{-1})$, Mn $(11.0 - 14.0 \text{ mg.kg}^{-1})$, and Zn $(14.3 - 32.0 \text{ mg.kg}^{-1})$ in grape pomace of Pinot Blanc from different localities in Slovakia. Chikwanha et al. (2018) reported similar levels of Fe (78.9 – 147 mg.kg⁻¹), Cu (6.75 – 13.4 mg.kg⁻¹) ¹), Mn (14.2 – 18.5 mg.kg⁻¹), and Zn (6.9 – 19.2 mg.kg⁻¹) in grape pomace of three cultivars from South Africa. Kolláthová et al. (2019) reported similar levels of Fe $(42.4 - 153 \text{ mg.kg}^{-1})$, Mn $(7.11 - 17.8 \text{ mg.kg}^{-1})$, Cu $(16.7 - 60.5 \text{ mg.kg}^{-1})$, and higher levels of Zn (18.9 - 41.3 mg.kg⁻¹) in grape pomace of three cultivars from Austria and Slovakia. Corbin et al. (2015) reported similar levels of Zn (15.0 mg.kg⁻¹), but lower levels of Fe (85.0 mg.kg⁻¹) in grape pomace from Cabernet Sauvignon. Ziarati et al. (2017) reported similar levels of Cu (48.7 mg .kg⁻¹), Mn (31.0 mg.kg⁻¹), Co (0.91 mg.kg⁻¹), and Cr (0,44 mg.kg⁻¹), but higher levels of Fe (460.2 mg.kg⁻¹), Zn (427.3 mg.kg⁻¹) in grape pomace of 5 different cultivars. Tangolar et al. (2018) reported lower content of Fe (13.9 - 19.6 mg.kg⁻¹), and similar content of Cu (5.2 - 18.4 mg.kg⁻¹), Mn (3.6 - 18.4 mg.kg⁻¹), and Zn (2.6 -

4.7 mg.kg⁻¹) in grape pomace of 6 different cultivars. In grape pomace of Cabernet Sauvignon, they reported lower content of Fe (18.9 mg.kg⁻¹), Cu (18.4 mg.kg⁻¹), Mn (10.9 mg.kg⁻¹), and Zn (4.7 mg.kg⁻¹). Pereira et al. (2020) reported similar content of Fe ($86.6 - 215 \text{ mg.kg}^{-1}$), and a wider range of content of Zn (1.60 - 28.3mg.kg⁻¹), similar and higher content of Cu (6.17 - 87.7 mg.kg⁻¹), Mn (19.1 - 84.1 mg.kg⁻¹), and higher content of Ni (3.75 mg.kg⁻¹), Cr (2.50 mg.kg⁻¹), Pb (5.00 mg.kg⁻¹) in grape pomace from eight cultivars. In Merlot, they reported similar content of Fe (119 mg.kg⁻¹), and higher content of Mn, Zn, Ni, Cr, and Pb (84.1, 13.8, 3.75, 2.50, and 5.00 mg.kg⁻¹ respectively), but lower content of Cu and Hg (30.1 and 0.004 mg.kg-1 respectively). In Cabernet Sauvignon, they reported similar content of Mn and Cr (19.1 and 2.50 mg.kg-1 respectively) and higher content of Ni and Pb (3.75 and 5.00 mg.kg-1 respectively), but lower content of Fe, Cu, Zn, and Hg (161, 16.0, 11.6, and 0.004 mg.kg⁻¹ respectively). Sagdic et al. (2014) reported similar average content of Fe (220 mg.kg-1), but higher content of Pb (9.25 – 32.0 mg.kg⁻¹) in grape pomace of 5 Turkish grape cultivars. The content of Zn, Cu, Cr, Co, and Cd were less than 5 mg.kg⁻¹.

In addition to genetic factors, variations in soil composition, climate, vineyard management practices, and other environmental factors can all contribute to differences in the content of minerals in grapes. Different soil types contain varying levels of minerals, which are absorbed by the grapevine roots and subsequently incorporated into the grapes (Likar *et al.*, 2015). Environmental factors, such as air and water pollution, can introduce contaminants that may impact soil health and subsequently affect the composition of grapes (Jimenéz-Ballesta *et al.*, 2022). Processing techniques, such as winemaking methods and storage conditions, can also affect the mineral content of grapes (Shimizu *et al.*, 2020).

While there are no set limits regarding contaminants in grape pomace, European legislation sets the maximum levels of Cd in grape seeds at 0.10 mg.kg⁻¹, and Slovak legislation sets the maximum level of Pb in other foodstuffs at 1.00 mg.kg⁻¹. These levels were not exceeded. Considering that grape pomace would be used as an ingredient in relatively low concentrations, it would not pose a risk for consumers. However, it is important to monitor risk elements in materials and try to minimize the intake of these elements.

Table 3 Relationships between monitored parameters

Variables	Κ	Ca	Р	Mg	Na	Fe	Cu	Mn	Zn	Ni	Cr	Co	Pb	Cd	Hg
K	1														
Ca	0.650	1													
Р	0.293	0.586	1												
Mg	0.243	0.363	0.412	1											
Na	-0.109	-0.722	-0.370	0.198	1										
Fe	-0.378	-0.385	-0.448	-0.980	-0.254	1									
Cu	0.458	0.414	0.356	-0.567	-0.545	0.457	1								
Mn	-0.393	-0.074	-0.332	-0.831	-0.595	0.900	0.428	1							
Zn	-0.342	-0.130	-0.243	-0.914	-0.532	0.951	0.564	0.971	1						
Ni	-0.241	0.027	-0.197	-0.726	-0.623	0.811	0.435	0.900	0.889	1					
Cr	-0.424	-0.225	-0.351	-0.898	-0.463	0.960	0.428	0.973	0.983	0.922	1				
Co	0.087	0.618	0.552	0.636	-0.480	-0.525	-0.223	-0.203	-0.308	0.049	-0.277	1			
Pb	0.750	0.463	0.529	-0.172	-0.251	0.037	0.816	-0.075	0.093	0.124	-0.015	-0.017	1		
Cd	0.041	-0.034	0.077	-0.575	-0.314	0.596	0.514	0.497	0.603	0.782	0.631	0.054	0.529	1	
Hg	0.333	-0.315	-0.569	0.133	0.650	-0.168	-0.378	-0.392	-0.403	-0.230	-0.296	-0.230	-0.015	0.021	1

Legend: Values in bold are significant (p< 0.05)

Pearson correlation showed that the content of Ni positively correlated with the content of Mn and Zn, and the content of Cu positively correlated with the content of Pb. The contents of Fe, Mn, Zn, and Cr positively correlated with each other, on the other hand, the content of these elements correlated negatively with the content of Mg. **Pereira** *et al.* (2020) reported a positive correlation between the content of Cu and Fe, and between the content of Cu and Zn in grape pomace.

CONCLUSION

REFERENCES

Our results suggest that the content of biogenic and risk elements in pomace grapes is variable depending on genetic factors. Grape pomace of cultivars Blaufränkisch and Cabernet Sauvignon could be characterized by the higher Fe, Mn, Zn, Ni, and Cr content, while grape pomace of cultivar Merlot by higher Mg content. With the increasing interest in the use of by-products of grape processing in food production, it is necessary to carry out further studies that can indicate the influence of cultivar, but also of locality and processing method, on the content of essential biogenic elements and, in particular, of hazardous risk elements. Grape pomace can serve as a good source of minerals, mainly K, in the human diet, with a relatively low content of risk elements. Including grape pomace in industrial food production could be a step toward the future of human nutrition and health.

Acknowledgments: This research was supported by the Slovak Research and Development Agency under grant No. APVV-22-0255

Bennemann, G. D., de Assis, C. F., Moreira, G. C. R. C., de Lima, L. H., Carvalho, K. K., Torres, Y. R., & Botelho, R. V. (2016). Mineral analysis, anthocyanins and phenolic compounds in wine residues flour. In *BIO Web of Conferences* (Vol. 7, p. 04007). EDP Sciences. <u>https://doi.org/10.1051/bio.org/20160704007</u>

Čeryová, N., Bajčan, D., Lidiková, J., Musilová, J., Šnirc, M., Jančo, I., ... & Bláhová, M. (2021). Phenolic content and antioxidant activity of slovak varietal wines of muscat type. *Journal of microbiology, biotechnology and food sciences*, *10*(5), e4292-e4292. https://doi.org/10.15414/jmbfs.4292

Čeryová, N., Lidiková, J., Šnirc, M., Harangozo, Ľ., Pintér, E., Bobko, M., ... & Vollmannová, A. (2023). Heavy metals in onion (Allium cepa L.) and environmental and health risks. *Food Additives & Contaminants: Part B*, 1-11. https://doi.org/10.1080/19393210.2023.2291369

Dumitriu, G. D., Teodosiu, C., Morosanu, I., Plavan, O., Gabur, I., & Cotea, V. V. (2021). Heavy metals assessment in the major stages of winemaking: Chemometric analysis and impacts on human health and environment. *Journal of Food*

Composition and Analysis, 100, 103935. https://doi.org/10.1016/j.jfca.2021.103935

European Commission (EC). (2023). Commission regulation (EU) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing regulation (EC) No 1881/2006. Official Journal of the European Union. L119: 103-157

Ferrer-Gallego, R., & Silva, P. (2022). The Wine Industry By-Products: Applications for Food Industry and Health Benefits. *Antioxidants*, *11*(10), 2025. https://doi.org/10.3390/antiox11102025

Fiket, Ž., Mikac, N., & Kniewald, G. (2011). Arsenic and other trace elements in wines of eastern Croatia. *Food Chemistry*, *126*(3), 941-947. https://doi.org/10.1016/j.foodchem.2010.11.091

García-Lomillo, J., & González-SanJosé, M. L. (2017). Applications of wine pomace in the food industry: Approaches and functions. *Comprehensive reviews in food science and food safety*, *16*(1), 3-22. <u>https://doi.org/10.1111/1541-4337.12238</u>

Hanušovský, O., Gálik, B., Bíro, D., Šimko, M., Juráček, M., Rolinec, M., ... & Gierus, M. (2019). The differences in macromineral profiles in wine by-products from Slovakia and Austria. In *X International Agriculture Symposium, Agrosym 2019, Jahorina, Bosnia and Herzegovina, 3-6 October 2019. Proceedings* (pp. 1453-1459). University of East Sarajevo, Faculty of Agriculture.

Herrero-Hernández, E., Andrades, M. S., Rodriguez-Cruz, M. S., Arienzo, M., & Sánchez-Martin, M. J. (2012). Long-term variability of metals from fungicides applied in amended young vineyard fields of La Rioja (Spain). *Environmental monitoring and assessment*, *184*, 3359-3371. <u>https://doi.org/10.1007/s10661-011-2194-4</u>

Chikwanha, O. C., Raffrenato, E., Muchenje, V., Musarurwa, H. T., & Mapiye, C. (2018). Varietal differences in nutrient, amino acid and mineral composition and in vitro rumen digestibility of grape (Vitis vinifera) pomace from the Cape Winelands vineyards in South Africa and impact of preservation techniques. *Industrial Crops and Products*, *118*, 30-37. https://doi.org/10.1016/j.indcrop.2018.03.026

Chowdhary, P., Gupta, A., Gnansounou, E., Pandey, A., & Chaturvedi, P. (2021). Current trends and possibilities for exploitation of Grape pomace as a potential source for value addition. *Environmental Pollution*, 278, 116796. https://doi.org/10.1016/j.envpol.2021.116796

Jara-Palacios, M. J. (2019). Wine lees as a source of antioxidant compounds. *Antioxidants*, 8(2), 45. <u>https://doi.org/10.3390/antiox8020045</u>

Jiménez-Ballesta, R., Bravo, S., Amorós, J. A., Pérez-De-Los-Reyes, C., García-Pradas, J., Sanchez, M., & García-Navarro, F. J. (2022). Soil and leaf mineral element contents in Mediterranean vineyards: Bioaccumulation and potential soil pollution. *Water, Air, & Soil Pollution, 233*(1), 20. <u>https://doi.org/10.1007/s11270-021-05485-6</u>

Kalli, E., Lappa, I., Bouchagier, P., Tarantilis, P. A., & Skotti, E. (2018). Novel application and industrial exploitation of winery by-products. *Bioresources and Bioprocessing*, *5*(1), 1-21. <u>https://doi.org/10.1186/s40643-018-0232-6</u>

Kolláthová, R., Hanušovský, O., Gálik, B., Šimko, M., Juráček, M., Rolinec, M., ... & Bíro, D. (2019). Microelement profile analysis of grape by-products from Slovakia and Austria. In X International Agriculture Symposium, Agrosym 2019, Jahorina, Bosnia and Herzegovina, 3-6 October 2019. Proceedings (pp. 1434-1439). University of East Sarajevo, Faculty of Agriculture.

Lidiková, J., Čeryová, N., Šnirc, M., Musilová, J., Harangozo, Ľ., Vollmannová, A., ... & Grygorieva, O. (2021). Heavy metals presence in the soil and their content in selected varieties of chili peppers in Slovakia. *Foods*, *10*(8), 1738. https://doi.org/10.3390/foods10081738

Likar, M., Vogel-Mikuš, K., Potisek, M., Hančević, K., Radić, T., Nečemer, M., & Regvar, M. (2015). Importance of soil and vineyard management in the determination of grapevine mineral composition. *Science of the Total Environment*, 505, 724-731. https://doi.org/10.1016/j.scitotenv.2014.10.057

Lumivero (2024). XLSTAT statistical and data analysis solution. https://www.xlstat.com/en.

Ministry of Agriculture and Rural Development of the Slovak Republic. (2023). Vinič hroznorodý, hroznové víno. Komoditná, situačná a výhľadová správa k 31.7.2023. ISSN 1339-0937. https://www.mpsr.sk/download.php?ftD=24500

Musilová, J., Fedorková, S., Podhorecká, K., Harangozo, L., Mesárošová, A., Vollmannová, A., ... & Orsák, M. (2024). Carbohydrates and mineral substances in sweet chestnuts (Castanea sativa Mill.) from important growing areas in Slovakia. *European Food Research and Technology*, 250(2), 565-572. https://doi.org/10.1007/s00217-023-04408-5

Ordinance of the Ministry of Agriculture of the Slovak Republic and the Ministry of Health of the Slovak Republic No 18558/2006-SL of 11 September 2006, issuing the Title of the Codex Alimentarius of the Slovak Republic regulating contaminants in foodstuffs

Pereira, P., Palma, C., Ferreira-Pêgo, C., Amaral, O., Amaral, A., Rijo, P., ... & Nicolai, M. (2020). Grape pomace: A potential ingredient for the human diet. *Foods*, 9(12), 1772. <u>https://doi.org/10.3390/foods9121772</u>

Sagdic, O., Ozturk, I., Yetim, H., Kayacier, A., & Dogan, M. (2014). Mineral contents and nutritive values of the pomaces of commercial Turkish grape (Vitis vinifera L.) varieties. *Quality Assurance and Safety of Crops & Foods*, 6(1), 89-93. <u>https://doi.org/10.3920/QAS2012.0191</u>

Shimizu, H., Akamatsu, F., Kamada, A., Koyama, K., Iwashita, K., & Goto-Yamamoto, N. (2020). Variation in the mineral composition of wine produced using different winemaking techniques. *Journal of bioscience and bioengineering*, *130*(2), 166-172. https://doi.org/10.1016/j.jbiosc.2020.03.012

Statistical Office of the Slovak Republic. (2022). Food consumption in the SR in 2022. ISBN 978-80-8121-912-2 (online)

Šimko, M., Bíro, D., Gálik, B., Juráček, M., Rolinec, M., & Hanušovský, O. (2019). The effect of locality on the grape pomace mineral content from the different locations of Slovakia. *Journal of International Scientific Publications:* Agriculture & Food, 7, 185-190.

Tangolar, S., Torun, A. A., Tangolar, S., & Torun, M. B. (2018). Evaluation of the mineral element profile of wastes of some wine grape (Vitis vinifera L.) varieties. *International Journal of Agriculture Environment and Food Sciences*, 2(1), 1-6. <u>https://doi.org/10.31015/jaefs.18001</u>

Ziarati, P., Moshiri, I. M., Sadeghi, P., & Mohammadi, S. (2017). Grape pomace flour (Vitis spp.) from Shiraz in South of Iran by high trace mineral elements as food supplements. *SciFed Drug Delivery Research Journal*, *1*(1), 1-9.