

ඝාග

Sinkovič, L., Meglič, V. and Pipan, B. (2024) 'Grain characteristics of eleven buckwheat varieties (*Fagopyrum* spp.) grown under Central European climatic conditions', *Journal of Elementology*, 29(2), 419-431, available: https://doi.org/10.5601/jelem.2023.28.4.3243

RECEIVED: 29 November 2023 ACCEPTED: 8 May 2024

ORIGINAL PAPER

Grain characteristics of eleven buckwheat varieties (*Fagopyrum* spp.) grown under Central European climatic conditions*

Lovro Sinkovič, Vladimir Meglič, Barbara Pipan

Crop Science Department Agricultural Institute of Slovenia, Ljubljana, Slovenia

Abstract

Common buckwheat and Tartary buckwheat are the most extensively cultivated and consumed Fagopyrum species worldwide. The evaluation of grain size characteristics and nutritional properties of different buckwheat varieties plays an important role in their effective utilisation and dissemination. Eleven buckwheat varieties (ten common, one Tartary) were cultivated in north-eastern Slovenia, i.e. under the Central European growing conditions, in two consecutive years. Whole grain characterization included various physical properties (TGW - thousand-grain weight, R-width, R-length, L/W ratio), determination of total phenolic compounds (TPC) and multi-element analysis. The TGW ranged from 12.3-29.4 g, the grain length from 4.1-6.8 mm and the grain width from 2.8-5.3 mm, while the mean L/W ratio reached 1.44. According to the TGW, buckwheat varieties were divided into four groups, two groups based on grain length and three groups based on grain width. Under the given growing conditions, the Billy variety developed the largest grains in both years, and La Harpe and Doris had the smallest grains. The TPC varied between 4.4 and 15.3 mg GAE g⁻¹, and was significantly higher in the Tartary buckwheat variety. The content of macro- (K, Mg, P, Ca, S) and microelements (Na, Cr, Mn, Fe, Co, Cu, Zn, Mo) varied considerably between these varieties. The highest coefficients of variation were found for Fe (51.4%), TPC (39.9%), Ca and Co (34.4%) and Cr (32.9%). A very strong significant positive Pearson correlation (≥0.80) was observed for eight pairs of variables. The present evaluation of buckwheat varieties revealed considerable diversity in the traits among this species grown under Central European conditions.

Keywords: buckwheat variety, ICP-MS, elemental profile, grain size, total phenolic compounds

Lovro Sinkovič, PhD, Research associate; Crop Science Department, Agricultural Institute of Slovenia, Hacquetova ulica 17, SI-1000 Ljubljana, Slovenia, EU; phone: +386 (0)1 280 52 78, e-mail: lovro.sinkovic@kis.si

^{*} This research has received funding from the Agrobiodiversity research programe (P4-0072; ARIS – Slovenian Research and Innovation Agency) and the ECOBREED project under the European Union's Horizon 2020 research and innovation programme, grant agreement No. 771367.

INTRODUCTION

Buckwheat has aroused great interest in the global scientific community due to its nutritional and pharmaceutical properties (Chettry, Chrungoo 2021, Podolska et al. 2021). Although the genus Fagopyrum (Polygonaceae) comprises almost 30 species, only two species, Fagopyrum esculentum Moench (common buckwheat) and Fagopyrum tataricum (L.) Gaertn. (Tartary buckwheat), are extensively cultivated and used as food (Ohsako, Li 2020). An agriculturally important feature of cultivated plants of both F. tataricum and F. esculentum is the absence of a constriction with a cleavage layer on the flower stalk, which prevents the grains from shedding (Sokoloff et al. 2023). Both crops are well adapted to marginal growing conditions, do not require high agricultural inputs, can be grown as intercrops or in rotation with other staple crops, and have been designated as "Future Smart Foods" by the Food and Agriculture Organization – FAO (Chettry, Chrungoo 2021, Li et al. 2023). Buckwheat is a nutrient-rich and well-suited pseudocereal for diversifying our future cropping systems and adapting to changing environmental conditions (Singh et al. 2020).

Grain size, including grain length, grain width and length-to-width ratio, plays a key role in determining grain yield as it influences the thousand--grain weight (Li et al. 2023). Grain weight and size also influence nutritional value, appearance and consumer preferences. Currently, data on the physical characteristics of grains of different buckwheat varieties grown under the same conditions are scarce. The accumulation of valuable nutrients such as phenolic compounds and essential elements in buckwheat grains depends on a number of factors, including species, varieties and environmental conditions (Huda et al. 2021, Podolska et al. 2021). Buckwheat can be considered the best source of phenolic compounds among pseudocereals (275-1290 mg GAE 100 g⁻¹), with the content in Tartary buckwheat being higher than in common buckwheat (Liu et al. 2019, Rocchetti et al. 2019, Sinkovič et al. 2021). In the context of nutrition, minerals are inorganic elements that are essential nutrients required by organisms, including humans, to fulfil vital functions (Godswill et al. 2020). According to current knowledge, seven macrominerals are essential, namely Na, K, Mg, Ca, Cl, P and S. In addition, some micro- or trace minerals are defined as essential, namely Mn, Fe, Cu, Zn, Se, Co, Mo and I, for plants or animals (Zoroddu et al. 2019). Compared to other cereals, buckwheat contains a significantly higher amount of such elements as K, Ca, Mg, Zn, Cu, Mn, Se as well as other elements, which are abundant in the outer membrane of the seeds and the seed coat (Huda et al. 2021, Luthar et al. 2021, Podolska et al. 2021).

In Slovenia, the long tradition of buckwheat cultivation is documented by several local populations or traditional varieties. These are mainly grown on small farms as part of low-input production systems. In 2022, buckwheat was grown in Slovenia as a main crop on 418 ha with a yield of 337 t, and as a second crop on 4.012 ha with a yield of 2.746 t (SI-STAT 2023). The breeding of buckwheat at the Agricultural Institute of Slovenia has a long tradition and is supported by a national breeding program. In addition to the autochthonous buckwheat variety Čebelica, the conservation varieties Eva and Doris have recently been registered or are in the process of registration (National List of Varieties 2023). The aim of the present study was to investigate the variation in grain size characteristics and some nutritional properties (total phenolic compounds, elements) of eleven buckwheat varieties grown in two consecutive years under Central European growing conditions.

MATERIALS AND METHODS

A range of eleven representative commercially available buckwheat varieties (*Fagopyrum* spp.) were used in this study. Ten varieties belong to common buckwheat (*Fagopyrum esculentum* Moench) originating from the Czech Republic (Zita and Zoe), the Russian Federation (Panda), France (La Harpe), Poland (Kora and Hruszowska), Austria (Bamby and Billy) and Slovenia (Eva and Čebelica), and one to Tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.) originating from Slovenia (Doris). The seeds were obtained from seed companies in various countries as part of the European Horizon 2020 project ECOBREED (Figure 1). All varieties were grown



Fig. 1. Seeds of the buckwheat varieties studied

at the experimental site Rakičan (46°37'23.7" N, 16°11'11.4" E; 183 m a.s.l.) in north-eastern Slovenia as a second crop in two consecutive growing seasons in 2019 (I) and 2020 (II). The previous crop in both years was winter wheat. The field trial was conducted using the randomised complete block method with four replicates. The sowing density was 400 seeds m⁻² and the size of the individual plots was 15 m². The sowing dates were 26 July 2019 and 28 July 2020, and the harvest dates were 25 October 2019 and 2 November 2020. Soil analysis prior to sowing revealed an average NO₂-N content of 6.60 mg kg⁻¹ and NH₄⁺ N content of 1.20 mg kg⁻¹, with no mineral fertilisers or pesticides used during cultivation. Sowing was performed with a plot seeder for small grains (Plotseed TC, Wintersteiger, Austria), and harvesting was carried out at full maturity with a plot harvester (Nursery Master, Wintersteiger, Austria). Representative 10 g cleaned and air-dried whole grains with a moisture content below 12% from each of the four individual plots were collected as bulk samples (40 g) for further analysis. The thousand-grain weight (TGW), grain length (R-length) and grain width (R-width) were determined using the Marvin system (MarviTech GmbH, Germany).

The buckwheat grains for the determination of the elements and total phenolic compounds were homogenised and pulverised in a laboratory ball mill (Retsch MM 400) at a frequency of 30 Hz for 2 min directly before analysis. Inductively coupled plasma mass spectrometry (ICP-MS) was used for the multi-element analysis. Each sample was digested and diluted in the microwave before determination with the Agilent 7900 ICP-MS. The calibration curve was prepared using the standard solution IV-STOCK-50, and individual standard solutions of P and S (Inorganic Ventures, USA) were added separately to the mixture. The accuracy of the results was verified with two certified reference materials: NIST SRM 1573a tomato leaves and NIST SRM 1547 peach leaves (Gaithersburg, MD, USA). All results are reported on a dry weight basis and expressed as g kg⁻¹ for macroelements or mg kg⁻¹ for microelements. Total phenolic compounds (TPC) were determined using the Folin-Ciocalteu (FC) assay first described by Singleton and Rossi (1965). The samples were first extracted with 70% ethanol in an ultrasonic bath and thoroughly vortex-mixed several times. After 1 h extraction at room temperature, the sample solutions were centrifuged $(15.000 \times g; 5 \text{ min})$ and filtered through 0.45 µm PTFE syringe filters. A reagent mixture was prepared by mixing diluted FC reagent and sample extract and then adding 20% Na_oCO_o. The TPC were determined in triplicate and expressed as mg gallic acid equivalent (GAE) g⁻¹. Differences between varieties and growing years were analysed using least-squares mean tests. The statistics included mean, minimum (Min), maximum (Max), standard error (SE) and coefficient of variation (CV). Analysis of variance (ANOVA; p>0.05) and principal component analysis (PCA) were performed to identify significant differences and the most influential variables in Statgraphics Centurion XVI (2009).

RESULTS AND DISCUSSION

This manuscript describes grain size properties (TGW, R-length, R-width, L/W ratio) and nutritional characteristics (TPC, macro- and microelements) of several buckwheat varieties grown for the first time under Central European cultivation conditions. A total of 18 parameters were determined in the grains of eleven buckwheat varieties from two years of cultivation, and the results showed high variability between samples. The results of grain size characteristics and TPC for the studied varieties are summarised in Table 1.

Table 1

Vear	Variety	TGW	R-length	R-width	L/W	TPC
Tear	variety	(g)	(mm)	(mm)	ratio	(mg GAE g ⁻¹)
I	Zita	$21.45 \ bc$	$5.74 \ bc$	4.06 b	1.41 g	5.43 c-e
	Zoe	22.16 b	$5.96 \ b$	$4.03 \ b$	$1.48 \ d$	$5.93 \ bc$
	Panda	22.21 b	$5.78 \ bc$	4.11 b	1.41 g	4.76 fg
	La Harpe	15.72 e	4.28 e	$3.27 \ d$	1.31 h	$6.28 \ b$
	Kora	22.23 b	$5.78 \ bc$	4.11 b	1.41 g	$5.58 \ cd$
	Hruszowska	20.71 <i>b-d</i>	$5.79 \ bc$	$3.99 \ b$	1.45 e	$5.31 \ de$
	Bamby	$19.50 \ d$	$5.47 \ c$	3.64 c	1.50 b	4.63 g
	Billy	28.01 a	$6.47 \ a$	$5.03 \ a$	1.29 i	4.96 e-g
	Eva	21.59 bc	$5.59 \ bc$	$3.92 \ bc$	1.43 f	5.25 <i>d</i> -f
	Čebelica	20.02 cd	$5.73 \ bc$	3.84 bc	1.49 c	4.91 e-g
	Doris	16.40 e	$4.90 \ d$	$3.08 \ d$	$1.59 \ a$	11.98 a
	Mean	20.91±3.27	5.59 ± 0.60	3.92 ± 0.52	1.43±0.08	5.91 ± 2.02
П	Zita	22.14 <i>b</i> - <i>d</i>	$5.75 \ b$	4.09 bc	1.41 f	$5.14 \ d$
	Zoe	22.91 b	$5.96 \ ab$	$4.07 \ bc$	$1.47 \ d$	4.80 d
	Panda	$22.53 \ bc$	$5.76 \ b$	4.20 b	$1.37 \ h$	$5.35 \ cd$
	La Harpe	17.07 g	4.33 e	3.27 e	1.33 i	7.42 b
	Kora	21.23 b-e	$5.74 \ b$	4.11 bc	1.39 g	$5.08 \ d$
	Hruszowska	20.90 с-е	$5.79 \ b$	$3.98 \ bc$	1.45 e	$5.30 \ cd$
	Bamby	18.53 fg	$5.21 \ cd$	$3.53 \ de$	1.48 c	5.84 c
	Billy	25.50 a	$6.41 \ a$	4.94 a	1.30 j	$5.07 \ d$
	Eva	$20.50 \ de$	$5.56 \ bc$	3.96 bc	1.41 f	$5.27 \ cd$
	Čebelica	20.09 ef	$5.79 \ b$	$3.83 \ cd$	1.51 b	$4.79 \ d$
	Doris	13.02 h	$4.86 \ d$	2.89 f	1.68 a	14.60 a
	Mean	20.40±3.32	5.56 ± 0.60	$3.90{\pm}0.54$	1.44±0.10	6.24±2.79
	Range	12.32-29.41	4.07-6.79	2.75 - 5.28	1.29-1.68	4.40-15.33
	CV (%)	15.90	10.64	13.44	6.32	39.89

Grain	size	characteristics	and	total	phenolic	content	of	buckwheat	varieties	grown
			iı	n two	consecut	ive year	\mathbf{s}			

The data are mean values (n=3). Mean values with different letters (a-i) in a column are significantly different ($p\leq0.05$, differences between varieties), TGW – thousand-grain weight, TPC – total phenolic compounds, GAE – gallic acid equivalents, CV – coefficient of variation

The TGW ranged considerably from 12.32 to 29.41 g, and the average dimensions of these grains were 5.58 mm in length and 3.91 mm in width. Based on the average two-year TGW, buckwheat varieties can be divided into four groups: very high grain weight (≥ 26.0 g; Billy) > high grain weight (22.1-25.9 g; Zoe, Panda) > medium grain weight (18.1-22.0 g; Zita, Kora,)Eva, Hruszowska, Čebelica, Bamby) > low grain weight (14.1-18.0 g; La Harpe, Doris). In general, the TGW of Tartary buckwheat is lower than that of common buckwheat (Mazahir et al. 2023), which was also shown in our study. Buckwheat varieties can also be divided into two groups based on grain length: high grain length (5.6-6.5 mm; Billy, Zoe, Panda, Zita, Kora, Eva, Hruszowska, Cebelica) > medium grain length (4.6-5.5 mm; Bamby, La Harpe, Doris); and in three groups according to grain width: high grain width (4.2-4.9 mm; Billy, Zoe, Panda) > medium grain width (3.4-4.1 mm;Zita, Kora, Eva, Hruszowska, Cebelica, Bamby) > low grain width (2.6-3.3 g; La Harpe, Doris). The results showed that the Billy variety developed significantly larger grains under the given growing conditions in both years. In comparison, the varieties La Harpe and Doris developed significantly smaller grains than the other varieties tested (Table 1). The L/W ratio of the Tartary buckwheat variety Doris was significantly higher than that of the other common buckwheat varieties.

The TPC in the buckwheat grains varied considerably from 4.63 to 14.60 mg GAE g⁻¹. The mean TPC was slightly higher in 2020 than in 2019 (6.24 and 5.91 mg GAE g⁻¹, respectively), but these differences were not significant. The Tartary buckwheat variety Doris had a significantly higher TPC in both years and contained over twice as much TPC as the common buckwheat varieties. Among the common buckwheat varieties, La Harpe had a significantly higher TPC compared to the other varieties. Liu et al. (2019) reported a similar range for the TPC of common buckwheat from China, while it was lower in Tartary buckwheat compared to our data. ANOVA showed significant differences in physical properties of grain size and TPC among varieties, but not between the growing years (Table 1). The highest coefficient of variation was calculated for the parameter TPC (39.89%) and the lowest for the L/W ratio (6.32%).

A total of 13 elements were determined in the 22 buckwheat samples, which can be subdivided into macroelements (>0.5 g kg⁻¹) Mg, P, S, K and Ca (Table 2), and microelements (>0.01 mg kg⁻¹) Cr, Mn, Fe, Co, Cu, Zn and Mo (Table 3). The highest coefficient of variation among the macroelements was calculated for Ca (33.43%) and the lowest for Mg (6.23%), and among the microelements for Fe (51.40%) and Mn (7.49%), respectively. Significantly higher levels of K and Zn were found in both growing seasons in the Tartary buckwheat variety Doris and in Ca, Mn and Mo in the common buckwheat variety La Harpe. ANOVA showed significant differences in the multi-element composition of grains between varieties, except for P in the first year (I), and between growing years for the macroelements P, S, K and Ca (Table 2) and the microelements Co, Cu, Zn and Mo (Table 3). Domingos and Bilsborrow (2021) studied Bamby and Čebelica varieties grown in three com-

Table 2

37		Macroelement (g kg ⁻¹)								
Year	Variety	Mg	Р	S	K	Ca				
	Zita	$2.47 \ a$	4.22	2.06 ab	5.87 bc	0.68 e				
	Zoe	2.39 a	4.16	1.98 ab	$5.85 \ bc$	0.70 de				
	Panda	2.45 a	4.19	1.99 ab	5.76 c	0.60 f				
Ι	La Harpe	2.53 a	4.24	2.06 ab	6.27 b	1.08 a				
	Kora	2.49 a	4.29	2.07 ab	5.79 bc	$0.75 \ cd$				
	Hruszowska	2.41 a	4.19	2.10 a	5.77 bc	0.59 f				
	Bamby	2.40 a	4.17	1.92 b	5.61 c	0.81 bc				
	Billy	2.43 a	4.23	1.97 ab	5.97 bc	0.82 b				
	Eva	2.37 a	4.20	1.99 ab	5.69 c	0.70 de				
	Čebelica	2.47 a	4.41	2.05 ab	$5.93 \ bc$	0.76 <i>b-d</i>				
	Doris	2.01 b	4.16	1.65 c	6.83 a	1.09 a				
	Mean	$2.40{\pm}0.17$	4.22±0.19 A	$1.99{\pm}0.15~A$	$5.94{\pm}0.41~A$	$0.78{\pm}0.17~B$				
Ш	Zita	2.33 a-c	3.76 bc	1.94 ab	4.40 cd	0.73 f				
	Zoe	2.33 a-c	3.86 <i>a-c</i>	1.87 ab	4.62 bc	0.86 de				
	Panda	2.28 bc	3.89 <i>a-c</i>	1.92 ab	$4.25 \ cd$	0.73 f				
	La Harpe	$2.52 \ a$	3.74 bc	1.94 ab	$4.40 \ cd$	1.80 a				
	Kora	2.40 a-c	3.87 <i>a-c</i>	1.88 ab	$4.56 \ c-d$	$0.93 \ d$				
	Hruszowska	$2.35 \ a$ -c	3.67 c	1.84 b	$4.40 \ cd$	0.76 f				
	Bamby	2.35 <i>a-c</i>	3.79 bc	1.84 b	$4.20 \ d$	1.14 c				
	Billy	2.48 ab	3.92 <i>a</i> -c	2.03 a	4.87 b	1.07 c				
	Eva	2.36 <i>a-c</i>	4.01 ab	1.94 ab	$4.51 \ c-d$	0.81 ef				
	Čebelica	2.43 ab	4.01 ab	1.97 ab	$4.57 \ c-d$	0.85 de				
	Doris	2.22 c	$4.15 \ a$	1.83 b	5.97 a	1.62 b				
	Mean	2.37±0.13	$3.88{\pm}0.21~B$	$1.91{\pm}0.10~B$	$4.61 \pm 0.51 B$	$1.03{\pm}0.36~A$				
	Range	1.91-2.66	3.48-4.63	1.57 - 2.21	3.99–7.17	0.56 - 1.89				
	CV (%)	6.23	6.51	6.68	15.37	33.43				

Macroelement composition of the grains of buckwheat varieties grown in two consecutive years

The data are mean values (n=3). Mean values with different letters (a-f) in a column are significantly different ($p\leq0.05$, differences between varieties), mean values with different capital letters (A,B) are significantly different ($p\leq0.05$, differences between years), CV – coefficient of variation

secutive years at two sowing dates in the UK. They reported similar Zn contents and higher Fe contents; however, no significant interactions were found for any of the study treatments. Podolska et al. (2021) reported lower Mg, Mn and Zn contents and higher Zn contents in the Kora and Panda varieties grown in Poland, suggesting a significant influence of the environment on the elemental composition of the grains.

		Microelement	composition of	f the grains of t	uckwheat varie	ties grown in t	wo consecutive	years	
Voon	Womiotor				Microeleme	nt (mg kg ⁻¹)			
I ear	variety	Na	\mathbf{Cr}	Mn	Fe	C_0	Cu	Zn	Mo
	Zita	12.13~g	$0.20 \ ef$	$16.78 \ bc$	47.94 <i>e</i>	$0.04 \ c-e$	8.11 a	$26.33 \ b$	1.04 d-f
	Zoe	14.20 f	$0.37 \ b$	16.66 c	$49.94 \ e$	$0.06 \ b$	$8.00 \ a$	$27.60 \ b$	$1.12 \ cd$
	Panda	$12.89 \ fg$	$0.32\ c$	$16.69 \ c$	$57.64 \ d$	$0.04 \ d-f$	$8.12 \ a$	$27.47 \ b$	$0.88 \ g$
	La Harpe	$21.72 \ b$	0.20 ef	19.47 a	$94.17 \ b$	$0.05 \ cd$	8.50 a	$27.93 \ b$	1.56 a
	Kora	$12.83 \ fg$	$0.26 \ d$	$16.87 \ bc$	$47.18 \ e$	$0.03 \ fg$	8.16 a	$26.58 \ b$	$1.00 \ ef$
F	Hruszowska	$18.78 \ c$	$0.51 \ a$	$17.18 \ bc$	$50.82 \ e$	$0.04 \ d-f$	$7.97 \ a$	$26.86 \ b$	$0.99 \ ef$
-	Bamby	$17.49 \ cd$	0.19 f	$17.94 \ bc$	$74.97 \ c$	$0.05 \ bc$	$8.39 \ a$	$28.11 \ b$	$0.95 \ fg$
	Billy	$17.70 \ c$	0.19f	$17.90 \ bc$	$48.13 \ e$	0.04 <i>e-g</i>	8.47 a	$27.85 \ b$	0.86~g
	Eva	$16.07 \ de$	$0.22 \ e$	$16.88 \ bc$	$45.70 \ e$	0.03~g	$7.92 \ a$	$26.32 \ b$	$1.17 \ bc$
	Čebelica	$15.79 \ e$	0.18f	$17.29 \ bc$	$50.88 \ e$	0.03~g	$8.12 \ a$	$27.76 \ b$	$1.08 \ c-e$
	Doris	$23.24 \ a$	$0.33 \ c$	$18.21 \ ab$	$142.95 \ a$	$0.08 \ a$	$6.83 \ b$	40.16 a	$1.25 \ b$
	Mean	16.62 ± 3.58	0.27 ± 0.10	17.44 ± 1.11	64.58 ± 29.15	$0.04{\pm}0.01A$	$8.05{\pm}0.55~A$	$28.45\pm3.99 A$	$1.08 \pm 0.20 B$

426

Table 3

cont. Table 3

Voor	V. oniotor				Microeleme	nt (mg kg ⁻¹)			
Iear	variety	Na	\mathbf{Cr}	Mn	Fe	Co	Cu	Zn	Mo
	Zita	14.62 <i>e-g</i>	$0.26 \ ef$	$16.02 \ de$	36.70 f-h	$0.03 \ c$	$7.50 \ b-d$	$22.20 \ cd$	$1.22 \ cd$
	Zoe	$25.91 \ a$	0.24 f	$16.70 \ cd$	38.87 <i>e-g</i>	$0.03 \ c$	$7.65 \ b-d$	$23.76 \ b-d$	$1.27 \ c$
	Panda	$13.91 \ g$	0.21~g	$15.15 \ e$	32.09 h	0.02 d	7.08 d	$23.40 \ cd$	$1.05 \ e$
	La Harpe	$16.52 \ cd$	0.31~c	$19.93 \ a$	$44.10 \ de$	$0.03 \ c$	$8.09 \ ab$	$25.76 \ b$	$2.22 \ a$
	Kora	$16.92 \ c$	$0.30 \ cd$	$16.28 \ de$	39.20 <i>e-g</i>	0.03~c	$7.54 \ b-d$	$21.80 \ d$	$1.18 \ cd$
Ц	Hruszowska	$16.07 \ cd$	$0.30 \ cd$	$17.80 \ bc$	143.34 a	$0.03 \ c$	$7.27 \ cd$	$22.89 \ cd$	$1.26 \ c$
Ħ	Bamby	$15.91 \ c-e$	$0.28 \ de$	$18.84 \ ab$	$41.25 \ d-f$	$0.03 \ c$	$7.68 \ b-d$	$23.95 \ bc$	$1.25 \ cd$
	Billy	$14.07 \ fg$	0.20~g	$18.10 \ bc$	$44.95 \ d$	$0.03 \ c$	8.48 a	$22.72 \ cd$	$1.14 \ de$
	Eva	13.64~g	0.24~f	$17.02 \ cd$	$34.71 \ gh$	$0.02 \ d$	$7.61 \ b-d$	$23.35 \ cd$	$1.51 \ b$
	Čebelica	$19.96 \ b$	$0.38 \ b$	$17.23 \ cd$	$74.31 \ b$	$0.05 \ a$	$7.78 \ bc$	$24.22 \ bc$	$1.40 \ b$
	Doris	$15.40 \ d-f$	$0.50 \ a$	$17.28 \ cd$	68.90 c	$0.04 \ b$	$6.20 \ e$	$33.90 \ a$	$1.23 \ cd$
	Mean	16.63 ± 3.52	0.29 ± 0.08	17.31 ± 1.48	54.40 ± 31.56	$0.03{\pm}0.01 B$	$7.54{\pm}0.64~B$	$24.36 \pm 3.39 B$	$1.34{\pm}0.31~A$
	Range	11.52 - 27.20	0.17 - 0.54	14.39-20.93	30.48 - 150.50	0.02 - 0.08	5.89 - 8.92	20.71 - 42.17	0.82 - 2.33
	CV (%)	21.19	32.89	7.49	51.40	34.44	8.32	15.96	23.84
The da	ta are mean va	lues $(n=3)$. Mes	an values with	different letter	rs $(a-h)$ in a col	umn are signifi	icantly differen	t (<i>p</i> ≤0.05, differ	ences between

varieties), mean values with different capital letters (A.B) are significantly different ($p\leq 0.05$, differences between years), CV – coefficient of variation

The Pearson correlation coefficients with a significance of p>0.05between the 18 variables examined are listed in Table 4. A very strong significant correlation (≥ 0.89) was found between TGW, R-length and R-width. A moderate correlation between grain length and grain width was reported for common buckwheat (Unal et al. 2017). Among the macroelements, S showed a very strong significant correlation with Mg (0.90) and a strong significant correlation with P (0.66). P showed a very strong significant correlation with K (0.81), while Ca showed a strong significant correlation with TPC (0.66). Among the microelements, Cu showed a very strong significant correlation with Mg and S (>0.80). Zn showed a very strong significant correlation with K (0.81), strong significant correlations with TPC and Co (>0.76) and a moderately strong significant correlation with Fe (0.54). Huang et al. (2014) also reported a positive relationship between Fe and Zn in their study of 123 Tartary buckwheat accessions native to China. In addition, correlation coefficients between Zn, Cu and Mn were reported in different common buckwheat grains (Ikeda, Yamashita 1994).

Principal component analysis was performed for a data structure study on a reduced dimension to extract maximum information from the data. The PCA plot (2D) of the component weights for 18 variables is shown in Figure 2. The first five principal components accounted for 86.23%



Fig. 2. PCA plot of the component weights

of the total variation for these grain traits. The relative contribution of component 1 to this total variance was 35.71%, with the main contributing variables (in descending order) being grain width, TGW, TPC, grain length and L/W ratio. The relative contribution of component 2 to the total variance was 21.64%, which was mainly due to the content of the elements P, K, Cu, Mn and Zn. Table 4

Pearson correlation matrix between the variables under investigation

18	-0.43	-0.55	-0.41	-0.12	0.23	0.20	-0.24	-0.02	-0.29	0.71	0.25	0.10	0.56	0.08	-0.09	0.01	-0.03	su	
17	-0.41	-0.27	-0.43	0.55	0.77	-0.24	0.57	-0.14	0.82	0.30	0.33	0.33	0.35	0.54	0.76	-0.14		su	
16	0.54	0.39	0.55	-0.59	-0.56	0.86	0.52	0.80	0.24	-0.20	0.02	-0.37	0.49	-0.20	0.01		su	su	
15	-0.29	-0.19	-0.33	0.43	0.44	-0.21	0.38	-0.15	0.69	0.05	0.39	0.30	0.26	0.60		ns	***	su	
14	-0.37	-0.27	-0.37	0.36	0.41	-0.26	0.06	-0.32	0.36	0.11	0.40	0.18	0.36		***	ns	***	su	-
13	-0.19	-0.24	-0.14	-0.11	0.24	0.50	0.31	0.28	0.27	0.59	0.36	0.05		**	*	***	**	***	:
12	-0.38	-0.13	-0.34	0.55	0.52	-0.15	0.04	-0.06	0.13	0.25	0.12		ns	ns	*	**	**	su	-
11	-0.17	-0.16	-0.22	0.20	0.18	-0.11	0.08	-0.16	0.19	0.19			**	***	***	ns	**	*	-
10	-0.55	-0.58	-0.50	0.15	0.66	0.00	-0.15	-0.22	-0.05		su	*	***	ns	ns	ns	*	***	
6	-0.11	-0.03	-0.11	0.24	0.40	0.08	0.81	0.26		su	su	ns	*	**	***	ns	***	*	
8	0.43	0.44	0.51	-0.40	-0.38	0.90	0.66		*	su	su	ns	*	**	ns	***	ns	su	· -
7	0.14	0.27	0.17	0.12	0.14	0.49		***	***	su	su	ns	**	ns	**	***	***	*	_
9	0.39	0.34	0.47	-0.49	-0.41		***	***	ns	su	su	ns	***	*	ns	***	su	su	1110
5	-0.65	-0.47	-0.61	0.63		***	ns	**	***	***	su	***	*	***	***	***	***	su	E
4	-0.56	-0.20	-0.59		***	***	ns	***	ns	su	su	***	ns	**	***	***	***	su	•
3	0.98	0.90		***	***	***	ns	***	ns	***	su	**	ns	**	**	***	***	***	-
2	0.89		***	ns	***	**	*	***	ns	***	su	ns	*	*	ns	***	*	***	100
1		***	***	***	***	***	ns	***	ns	***	su	**	ns	**	*	***	***	***	
Variable	TGW	R-length	R-width	L/W ratio	TPC	Mg	Р	\mathbf{s}	К	Ca	Na	Cr	Mn	Fe	Co	Cu	Zn	Mo	+
No.	1	2	3	4	5	9	7	8	6	10	11	12	13	14	15	16	17	18	1 0 1

* p≤0,05, ** p≤0,01, *** p≤0,001, ns - not significant, TGW - thousand-grain weight, TPC - total phenolic compounds

CONCLUSIONS

In this study, the grain size characteristics and nutritional properties of eleven buckwheat varieties grown in Central Europe were analysed. Physical properties, phenolic compounds and multi-element composition of whole grains differed significantly between varieties and crop years. Strong correlations were found between certain variables (TGW and grain length and width, grain length and width, S and Mg, P and K, Cu and Mg, Cu and S, K and Zn). The Billy variety developed the largest grains, while La Harpe and Doris had the smallest grains. The buckwheat varieties were divided into four groups according to the TGW. Tartary buckwheat had more than twice as many phenolic compounds as common buckwheat varieties, with La Harpe having the highest total phenolic content. Tartary buckwheat had higher levels of K and Zn, while Ca, Mn and Mo were more abundant in the common buckwheat variety La Harpe. However, further studies are needed to fully understand these complex relationships.

Author contributions

L.S. – conceptualization, B.P. and V.M. – funding acquisition, L.S. – investigation, L.S. and B.P. – methodology, L.S. – visualization, L.S. and B.P. – writing – original draft preparation, V.M. – writing – review & editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

ACKNOWLEDGMENTS

The authors would like to thank Mag Vida Žnidaršič Pongrac for performing the ICP-MS analysis and Dr Aleš Kolmanič for managing the seed production. This research has received funding from the Agrobiodiversity Research Programme (P4-0072, ARIS – Slovenian Research and Innovation Agency) and the ECOBREED project under the European Union's Horizon 2020 research and innovation programme, grant agreement No. 771367.

REFERENCES

- Chettry, U. and Chrungoo, N.K. (2021) 'Beyond the cereal box: breeding buckwheat as a strategic crop for human nutrition' *Plant Foods for Human Nutrition*, 76, 399-409, available: https://doi.org/10.1007/s11130-021-00930-7
- Godswill, A.G., Somtochukwu, I.V., Ikechukwu, A.O., Kate. E.C. (2020) 'Health benefits of micronutrients (vitamins and minerals) and their associated deficiency diseases: A systematic review', *International Journal of Food Sciences*, 3(1), 1-32, available: https://doi. org/10.47604/ijf.1024

- Huda, M.N., Lu, S., Jahan, T., Ding, M., Jha, R., Zhang, K., Zhang, W., Georgiev, M.I., Park, S.U., Zhou, M. (2021) 'Treasure from garden: Bioactive compounds of buckwheat', *Food Chemistry*, 335, 127653, available: https://doi.org/10.1016/j.foodchem.2020.127653
- Ikeda, S. and Yamashita, Y. (1994) 'Buckwheat as a dietary source of zinc, copper and manganese' Fagopyrum, 14(29), 29-34.
- Li, R., Chen, Z., Zheng, R., Chen, Q., Deng, J., Li, H., Huang, J., Liang, C., Shi, T. (2023) 'QTL mapping and candidate gene analysis for yield and grain weight/size in Tartary buckwheat', *BMC Plant Biology*, 23(1), 58, available: https://doi.org/10.1186/s12870-022-04004-x
- Liu, Y., Cai, C., Yao, Y., Xu, B. (2019) 'Alteration of phenolic profiles and antioxidant capacities of common buckwheat and tartary buckwheat produced in China upon thermal processing', *Journal of the Science of Food and Agriculture*, 99(12), 5565-5576, available: https://doi. org/10.1002/jsfa.9825
- Luthar, Z., Golob, A., Germ, M., Vombergar, B., Kreft, I. (2021) 'Tartary buckwheat in human nutrition' *Plants*, 10(4), 700, available: https://doi.org/10.3390/plants10040700
- Mazahir, M., Ahmed, A., Khan, M.A., Mariam, A., Riaz, S. (2023) 'Comparative study of physicochemical and functional properties of different buckwheat varieties and their milling fractions', *International Food Research Journal*, 30(5), 1261-1273, available: https://doi. org/10.47836/ifrj.30.5.14
- National List of Varieties (2023) 'Republic of Slovenia. Ministry of Agriculture. Forestry and Food; Administration for Food Safety. Veterinary Sector and Plant Protection', available: https://www.gov.si/drzavni-organi/organi-v-sestavi/uprava-za-varno-hrano-veterinarstvo-invarstvo-rastlin/o-upravi/sektor-za-zdravje-rastlin/sortna-lista-republike-slovenije/ (Accessed: 14.11.2023)
- Ohsako, T. and Li, C. (2020) 'Classification and systematics of the Fagopyrum species', Breeding Science, 70(1), 93-100, available: https://doi.org/10.1270/jsbbs.19028
- Podolska, G., Gujska, E., Klepacka, J., Aleksandrowicz, E. (2021) 'Bioactive compounds in different buckwheat species', *Plants*, 10(5), p.961, available: https://doi.org/10.3390/plants10050961
- Rocchetti, G., Lucini, L., Rodriguez, J.M.L., Barba, F.J., Giuberti, G. (2019) 'Gluten-free flours from cereals. pseudocereals and legumes: Phenolic fingerprints and in vitro antioxidant properties', *Food Chemistry*, 271, 157-164, available: https://doi.org/10.1016/j.foodchem. 2018.07.176
- Singh, M., Malhotra, N., Sharma, K. (2020) 'Buckwheat (Fagopyrum sp.) genetic resources: What can they contribute towards nutritional security of changing world?', Genetic Resources and Crop Evolution, 67(7), 1639-1658, available: https://doi.org/10.1007/s10722-020-00961-0
- Singleton, V.L. and Rossi, J.A. (1965) 'Colorimetry of total phenolics with phosphomolybdicphosphotungstic acid reagents', American Journal of Enology and Viticulture, 16(3), 144-158.
- Sinkovič, L., Sinkovič, D.K., Meglič, V. (2021) 'Milling fractions composition of common (Fagopyrum esculentum Moench) and Tartary (Fagopyrum tataricum (L.) Gaertn.) buckwheat', Food Chemistry, 365, 130459, available: https://doi.org/10.1016/j.foodchem.2021.130459
- SI-STAT (2023) 'Republic of Slovenia. Statistical office Production of crops. Slovenia. annually', available: http://stat.si (Accessed: 14.11.2023)
- Sokoloff, D.D., Malyshkina, R.A., Remizowa, M.V., Rudall, P.J., Fomichev, C.I., Fesenko, A.N., Fesenko, I.N., Logacheva, M.D. (2023) 'Reproductive development of common buckwheat (*Fagopyrum esculentum* Moench) and its wild relatives provides insights into their evolutionary biology', *Frontiers in Plant Science*, 13, 1081981, available: https://www.frontiersin. org/journals/plant-science/articles/10.3389/fpls.2022.1081981/full
- Unal, H., Izli, G., Izli, N., Asik, B.B. (2017) 'Comparison of some physical and chemical characteristics of buckwheat (*Fagopyrum esculentum* Moench) grains', *CyTA-Journal of Food*, 15(2), 257-265, available: https://doi.org/10.1080/19476337.2016.1245678
- Zoroddu, M.A., Aaseth, J., Crisponi, G., Medici, S., Peana, M., Nurchi, V.M. (2019) 'The essential metals for humans: a brief overview', *Journal of Inorganic Biochemistry*, 195, 120-129, available: https://doi.org/10.1016/j.jinorgbio.2019.03.013