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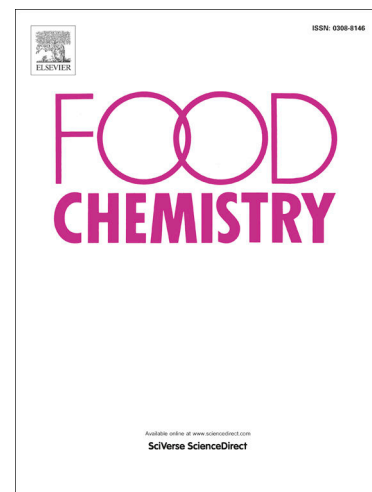
Milling Fractions Composition of Common (*Fagopyrum esculentum* Moench) and Tartary (*Fagopyrum tataricum* (L.) Gaertn.) Buckwheat

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1 **Milling Fractions Composition of Common (*Fagopyrum esculentum* Moench)**
2 **and Tartary (*Fagopyrum tataricum* (L.) Gaertn.) Buckwheat**

3

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13 Abstract

14 Buckwheat is a pseudocereal with important nutritional qualities and great potential for broad
15 consumption. The study aimed to determine the biochemical composition, antioxidant properties
16 and multi-mineral composition of the whole grains, hulls, bran, and the light flour of common
17 (*Fagopyrum esculentum* Moench) and Tartary (*Fagopyrum tataricum* (L.) Gaertn.) buckwheat
18 harvested in two consecutive years. Significant differences between fractions of both species
19 were observed. On the other hand, the differences between the production years were not so
20 significant. Biochemical and multi-mineral compositions of common and Tartary buckwheat
21 were comparable, while significant differences between species were observed in antioxidant
22 properties. The antioxidant potential (AOP), total phenolic content (TPC), and total flavonoid
23 content (TFC) were higher in all fractions of Tartary buckwheat compared to individual fractions
24 of common buckwheat. Fourteen minerals were quantified in fractions. Contents of all major
25 minerals and most of the trace minerals were the highest in bran fraction.

26

27 **Keywords:** whole grain; hulls; bran; light flour; bioactive compounds; phenolics

28

29 1 Introduction

30 Two species of buckwheat are among the most extensively produced and consumed
31 around the world: common buckwheat (*Fagopyrum esculentum* Moench) and Tartary buckwheat
32 (*Fagopyrum tataricum* (L.) Gaertn.). Common buckwheat and Tartary buckwheat have been in
33 cultivation for 5000-6000 and 4000 years, respectively. Both species originated in China;
34 however, it is suggested that cultivated buckwheat species may have multiple origins since
35 independent domestication events occurred (Mizuno and Yasui, 2019; Zhang et al., 2021). The
36 major producers of buckwheat are China, Russia, France, Ukraine, and Poland (FAOSTAT,
37 2018). Both worldwide available traditional foodstuffs are not only a good source of energy and
38 nutrition for maintenance of the body but are also a source of bioactive compounds that are
39 health beneficial (Christa and Soral-Śmietana, 2008). The nutritional value of Tartary buckwheat
40 is much higher than of a common buckwheat. Tartary buckwheat is richer in nutrients, including
41 vitamin B and some antioxidants, such as rutin, and has good medicinal properties (Ruan et al.,
42 2020; Zhao et al., 2018). Both species have a high polyphenol and mineral contents in seeds
43 (Tsai et al., 2012). Previous studies have also shown high levels of antioxidants in buckwheat
44 (Ruan et al., 2020). Since the favorable nutritional composition of protein, lipid, dietary fiber,
45 and minerals, and combination with other health beneficial components, buckwheat can be
46 characterized as a so-called functional food (Giménez-Bastida and Zielinski, 2015; Krkošková
47 and Mrázová, 2005).

48 The main form of buckwheat for consumption is a grain. The nutrient composition of
49 buckwheat products depends on the milling fraction, which reflects the relative abundance of the
50 seed tissues (Steadman et al., 2001a). Buckwheat seed milling fractions are obtained through the
51 milling process involving the separation of the hulls from buckwheat seeds. The results of further

52 milling are usually light flour, grits/semolina, and bran fractions. The traditional milling process
53 is carried out by using stone mills, which usually have a smaller milling capacity and are
54 appropriate for smaller producers. Milling fractions contain different proportions of central
55 endosperm, embryo, and maternal tissues, each of which can vary in composition. Light flour
56 mainly contains central endosperm, grits are hard chunks of endosperm, while bran contains seed
57 coat and embryo tissues (Steadman et al., 2001a, 2001b). Common buckwheat and Tartary
58 buckwheat yields after milling process with traditional stone mill are similar; approximately 56%
59 of flour, 24% of bran, 17% of husks, and 3% of losses (Bonafaccia et al., 2003).

60 The main constituents in buckwheat are carbohydrates. Among different fractions,
61 buckwheat flour contains the highest portion of carbohydrates (70-90%) (Huda et al., 2021).
62 Buckwheat bran is the milling fraction with the highest portions of proteins and lipids (Skrabanja
63 et al., 2004; Steadman et al., 2001a). Liu et al. (2018) showed a high impact of milling processes
64 on physicochemical properties of Tartary buckwheat flours due to the proportion of the bran, and
65 degree of damage and size of the particles.

66 Buckwheat has already been proven to be a good source of antioxidants (Kiproviski et al.,
67 2015; Li et al., 2013). Overall, almost 180 bioactive compounds were identified in buckwheat
68 (Huda et al., 2021). The antioxidant capacity of extracts from different buckwheat seed fractions
69 had different efficiencies (Li et al., 2013; Quettier-Deleu et al., 2000). Total phenolic content
70 was found higher in Tartary buckwheat, compared to common buckwheat (Liu et al., 2019).
71 Buckwheat is also a good source of minerals. Tartary buckwheat is a richer source of minerals
72 than common buckwheat, as well as other cereals and pseudocereals. It contains high levels of
73 trace minerals, especially manganese, copper, and magnesium (Bonafaccia et al., 2003), but also
74 iron and zinc (Krupa-Kozak et al., 2011). A gluten-free diet is often categorized by low contents

75 of some nutritional components, such as proteins and minerals. Therefore, buckwheat flour is a
76 promising gluten-free product enriched in proteins, major and trace minerals (Krupa-Kozak et
77 al., 2011).

78 The objective of the present study was to analyze the basic chemical composition, multi-
79 mineral contents, and bioactive compounds contents of the whole grains, hulls, bran, and light
80 flour of common and Tartary buckwheat fractions obtained by traditional stone-milling harvested
81 in two consecutive years. Although buckwheat is recognized as nutritionally valuable, a detailed
82 composition of milling fractions is incomplete. Therefore, the aim of the study was to evaluate
83 and compare the properties of individual fractions of the two buckwheat species.

84

85 **2 Materials and methods**

86

87 *2.1. Materials*

88 Common buckwheat (*Fagopyrum esculentum* Moench; population from Dolenjska
89 region) and Tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.; traditional Slovene
90 population) were cultivated as a catch crop in Slovenia in the Posavje region (46°02' N 15°13' E,
91 194 m above sea level) in a moderate soil and harvested in two consecutive years. Both
92 buckwheat species were grown from the second week of July (sowing time) until the last week of
93 October (harvest time) each year. The average monthly temperature was 17.2 °C in the first year
94 and 17.4 °C in the second year of production. There were little differences in total accumulated
95 rainfall in each growing season, with the peak of rainfall in September. Each species was
96 cultivated on a 400 m² plot area each year. After harvest, the grains were dried in a wooden
97 drying chamber with ventilation at ambient temperature. To obtain different milling fractions

98 traditional stone mill (capacity 15 kg h⁻¹) was used for the milling 50 kg of each buckwheat
99 species each year. Clean undamaged whole grains were subjected to successive milling and
100 sieving. Fractions were divided into bran, hulls, and light flour, and were subsequently manually
101 checked to remove residues. The samples were stored at room temperature and low relative
102 humidity in the paper bags until analysis.

103

104 2.2. *Sample preparation*

105 The whole grains and fractions of buckwheat were homogenized in a laboratory ball mill
106 (Retsch MM400) directly before analysis. The samples used for the determination of antioxidant
107 potential, total phenolic content, and total flavonoid content were extracted with 70% ethanol.
108 Approximately 50 mg of the homogenized sample was weighed in a centrifuge tube and 1300 μ L
109 of extraction solvent was added. Samples were thoroughly mixed on vortex, extracted in an
110 ultrasonic bath for 10 min, incubated for 1h in the dark, and mixed again. After extraction, the
111 samples were centrifuged at 13,200 \times g for 5 min and filtered through 0.20 μ m PTFE syringe
112 filters (Macherey-Nagel) before analyses.

113

114 2.3. *Basic chemical composition*

115 In all of the samples the chemical composition was determined, i.e. the determination of
116 dry matter content, crude fats, protein content, ash, and crude fiber, and calculation of moisture
117 and total carbohydrates content. Dry matter content was determined by drying samples at 103 °C
118 for 48 h. Crude fats were analyzed with petroleum ether extraction. Five grams of the
119 homogenized sample was transferred to an extraction thimble, placed in an extractor, and
120 extracted for six hours with light petroleum. The petroleum extract was collected in a dry,
121 weighed flask. The solvent was distilled off and the residue was dried in the drying oven till

122 constant weight. For the determination of crude protein content, Kjeldahl method was used
123 (ISO 5983-2, 2009). Ash was determined by weight difference before and after incineration at
124 550 °C for 4 h. Results of chemical composition are presented as g kg⁻¹. The crude fiber was
125 determined according to ISO 6865:2000. After 1 g of the sample was weighed, 350 mL of
126 0.13 mol L⁻¹ H₂SO₄ was added and heated under the boiling state for 30 min. Then the sample
127 was rinsed with water three times. After adding 350 mL of 0.23 mol L⁻¹ KOH, the sample
128 solution was heated under the boiling state for another 30 min. Then the sample was rinsed with
129 boiling water three times, rinsed with acetone, dried for 2 h at 130 °C, weighed and ashed for 2 h
130 at 580 °C. The total carbohydrates content was calculated by the equation: total
131 carbohydrates = 100 – (% protein + % crude fat + % ash + % moisture) (Dziadek et al., 2016).

132

133 2.4. DPPH radical-scavenging activity

134 The antioxidant potential (AOP) of the samples was determined spectrophotometrically,
135 as the 2,2-diphenyl-1-picrylhydrazyl (DPPH; Sigma-Aldrich) free-radical-scavenging capacity,
136 based on the modified method of Brand-Williams et al. (1995). The absorbance was measured
137 after 50 min incubation at room temperature, using a spectrophotometer at 517 nm, against
138 methanol as the blank. Calibration was done through seven-point standard curve of Trolox
139 (Sigma-Aldrich). AOP of the samples was determined in triplicate, and expressed in g kg⁻¹ of
140 Trolox equivalents (TE).

141

142 2.5. Total phenolic content

143 Total phenolic content (TPC) was determined according to the Folin-Ciocalteu method
144 described by Singleton and Rossi (1965), with minor modifications. The absorbance was
145 measured after 50 min incubation at room temperature, using a spectrophotometer at 765 nm,

146 against deionised water as the blank. Calibration was done through a seven-point standard curve
147 of gallic acid (Fluka, Buchs, Switzerland). TPC of the samples was determined in triplicate and
148 expressed in g kg^{-1} of gallic acid equivalents (GAE).

149

150 2.6. Total flavonoid content

151 Total flavonoid content (TFC) was determined according to the slightly modified method
152 described by Lin and Tang (2007). The absorbance was measured after 40 min incubation at
153 room temperature, using a spectrophotometer at 415 nm, against deionized water as the blank.
154 Calibration was done through a seven-point standard curve of quercetin (Sigma-Aldrich). TFC of
155 the samples was determined in triplicate and expressed in g kg^{-1} of quercetin equivalents (QE).

156

157 2.7. Multi-mineral analyses using ICP-MS

158 Milestone ETHOS 1600 microwave digestion system was used for sample digestion. The
159 dried, milled, and homogenized samples, 0.250 g, were weighed into polytetrafluoroethylene
160 (PTFE) vessels. Two mL of hydrogen peroxide (30%, v/v; Suprapur, Merck) and 6.0 mL of
161 nitric acid (65%, v/v; Suprapur, Merck) were added into the vessels. Digested samples were
162 cooled to room temperature and diluted to 50 mL with doubly de-ionized water (resistivity of
163 $18.2 \text{ M}\Omega$; Millipore). Prior to the analysis the digested samples were diluted by a factor of 20 and
164 consisted of 1% (v/v) nitric acid.

165 Contents of minerals were determined using an Agilent ICP-MS 7900 (Tokyo, Japan)
166 with a 4th generation collision/reaction cell, the Octopole Reaction System (ORS⁴). The sample
167 introduction system consisted of a quartz double-pass spray chamber and a MicroMist nebulizer
168 connected to the peristaltic pump of the spectrometer with Tygon[®] tubes. Nickel sampler and
169 skimmer cones were used. Helium was used as reaction gas at the flow rate of 5.0 mL min^{-1} in

170 He mode, and 10.0 mL min⁻¹ in HEHe mode. Five major minerals (> 1 g kg⁻¹ DW) Mg, P, S, K
171 and Ca, and nine trace minerals (> 1 mg kg⁻¹ DW) Na, V, Cr, Mn, Fe, Co, Cu, Zn and Mo were
172 determined. The isotopes monitored were ²³Na, ²⁴Mg, ³¹P, ³⁴S, ³⁹K, ⁴³Ca, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe,
173 ⁵⁹Co, ⁶³Cu, ⁶⁶Zn, and ⁹⁵Mo. The majority of minerals were measured in He mode, while P, S, and
174 Se were measured in HEHe mode.

175 The quantitative determinations of minerals were performed using the external calibration
176 method. The calibration curve was prepared using IV-STOCK-50 standard solution (Inorganic
177 Ventures); P and S single standard solutions (Inorganic Ventures) were added separately to the
178 mixture. Internal standards ⁴⁵Sc, ¹⁰³Rh, ¹¹⁵In, and ¹⁷⁵Lu were added in a concentration of
179 200 µg L⁻¹ (1% (v/v) nitric acid).

180 For quality control analytical blanks, independent quality control (QC) standards, and
181 standard reference material were used. QC standards were prepared from ICP multi-mineral
182 standard solution VIII (Merck, 109492) and ICP multi-mineral standard solution XVI (Merck,
183 109487). A certified reference material (NIST SRM 1573a tomato leaves, Gaithersburg, MD,
184 USA) was used. All sample results are quoted on a dry weight basis.

185

186 2.8. Data analysis

187 Statistical analyses were performed using the R commander software (version 3.3.3). To
188 ensure the appropriateness of ANOVA, the variances between fractions were determined using
189 Levene's tests ($\alpha > 0.05$). Further ANOVA was performed with *post-hoc* Tukey's tests; *,
190 $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$. Significant differences between common and Tartary
191 buckwheat among individual fractions were obtained using a t-test. Pearson product-moment
192 correlation test was performed to evaluate the correlation.

193

194 3 Results

195 The basic chemical composition of whole grain, hulls, bran, and light flour of common
196 and Tartary buckwheat harvested in two consecutive years is presented in Table 1. Significant
197 differences between fractions were observed for all studied parameters, i.e. ash, carbohydrates,
198 fats, fiber, moisture, and protein content. Moreover, differences for all parameters were observed
199 between common and Tartary buckwheat. There were minor differences between production
200 years, however, results were comparable and had no significant effect on further data
201 interpretation. The most pronounced differences between fractions were found for carbohydrate,
202 protein, and fat content. The ash content in common and Tartary buckwheat was the highest in
203 the bran (4.6–5.8%) and the lowest in light flour (1.0–1.3%). Carbohydrate content was the
204 highest in the hulls (81.2–88.1%), followed by light flour (75.6–77.5%), whole grain (72.5–
205 73.6%), and bran (48.4–53.0%). Contrary, fat content was the highest in the bran (4.1–5.2%) and
206 the lowest in hulls (0.4–0.7%). As expected, fiber content was the highest in hulls and
207 represented approximately 50% and the lowest in light flour with less than 1%. Overall the
208 highest difference between fractions was observed in protein content. Protein content for both
209 buckwheat species was highest in bran with over 25%, followed by whole grain with over 10%.
210 The difference between common and Tartary buckwheat was most noticeable for carbohydrate,
211 fiber, and fat content, e.g. carbohydrate and fiber contents were higher in hulls of Tartary
212 buckwheat, while fat content was higher in bran.

213 The antioxidant potential (AOP), total phenolic content (TPC), and total flavonoid
214 content (TFC) were higher in all fractions of Tartary buckwheat compared to individual fractions
215 of common buckwheat (Table 2). There was a very strong positive correlation between
216 antioxidant potential with total phenolic content (R^2 over 0.9) and total flavonoid content (R^2

217 over 0.9). In both buckwheat species the highest AOP was in bran and ranged between 9.51 and
218 12.53 $\mu\text{mol g}^{-1}$ for common buckwheat, and between 72.80 and 102.34 $\mu\text{mol g}^{-1}$ for Tartary
219 buckwheat. AOP in whole grain was approx. 6 $\mu\text{mol g}^{-1}$ for common buckwheat and approx.
220 35 $\mu\text{mol g}^{-1}$ for Tartary buckwheat.

221 Fourteen minerals were quantified in whole grains and milling fractions of common and
222 Tartary buckwheat. Minerals can be divided into two groups: the major minerals ($> 1 \text{ g kg}^{-1}$ DW)
223 Mg, P, S, K and Ca, and trace minerals ($> 1 \text{ mg kg}^{-1}$ DW) Na, V, Cr, Mn, Fe, Co, Cu, Zn and Mo
224 (Table 3). The order of the minerals from the most to the least abundant (based on mean values)
225 is: K (6.23 g kg^{-1}), P (4.64 g kg^{-1}), Mg (2.71 g kg^{-1}), S (1.74 g kg^{-1}), Ca (1.08 g kg^{-1}), Fe
226 (65.88 mg kg^{-1}), Zn (37.74 mg kg^{-1}), Na (31.03 mg kg^{-1}), Mn (27.50 mg kg^{-1}), Cu (8.75 mg kg^{-1}),
227 Mo (1.35 mg kg^{-1}), Cr (0.30 mg kg^{-1}), V (0.07 mg kg^{-1}) and Co (0.05 mg kg^{-1}). The highest
228 relative difference was observed for P, where bran fraction contained 12-fold, 5-fold, or 3-fold
229 higher concentrations of P than hulls, light flour, or whole grains, respectively. The highest
230 relative difference among trace minerals was observed for Zn. Bran fraction on average
231 contained almost 5-fold, over 3-fold, or 2-fold more Zn than hulls, light flour, or whole grains,
232 respectively.

233

234 4 Discussion

235 Considerable efforts are being made to improve human nutrition and increase the amount
236 of consumed bioactive compounds with a beneficial effect on human health. Pseudocereals, with
237 buckwheat as one of the important species, are interesting for wide human consumption, while
238 they are gluten-free and possess high nutritional value.

239 Basic chemical composition, multi- mineral contents, and bioactive compounds contents
240 of whole grains and milling fractions of common and Tartary buckwheat were studied. There
241 were significant differences between fractions for all studied parameters. Differences between
242 buckwheat species were also observed, however the year of production had a lower impact on
243 the contents of bioactive compounds. Some differences were observed between the two
244 production years, but results were comparable.

245 The average protein content of the whole grains was slightly higher than 11%, regardless
246 of the buckwheat species. In literature, the protein content of buckwheat grains ranges between
247 12.0 and 18.9% (Krkošková and Mrázová, 2005; Steadman et al., 2001a). The protein
248 concentrations were the highest in bran fractions of both buckwheat species and similar to results
249 presented by Steadman et al. (2001a), where protein content of six different bran fractions ranged
250 from 18.6 to 39.3%. Bran fractions that contained hulls had lower protein content, as among
251 fractions hulls contain the least proteins, i.e. about 4% (Pomeranz and Robbins, 1972; Steadman
252 et al., 2001a). Protein contents in common buckwheat fractions were comparable to contents in
253 Tartary buckwheat. Although some differences were observed between both species, they were
254 not pronounced and usually not significant in both years of production. This shows a high effect
255 of the production year and milling process on the chemical composition of fractions. While,
256 Bonafaccia et al. (2003) presented comparable results of protein content in grain and flour of
257 common and Tartary buckwheat, a difference in protein contents in bran fractions was observed.
258 Protein content was higher in Tartary buckwheat bran fraction. However, in our case protein
259 content in bran fractions was higher in both species of buckwheat. Fat contents of buckwheat
260 ranged from 0.4 to 5.2%, regardless of buckwheat species and fractions. Fats in whole grains
261 represent about 2%, which is in agreement with Steadman et al. (2001a), who reported from 1.5

262 to 4% of total lipids in buckwheat grains. In our study, hulls of both buckwheat species contained
263 less than 1% of fats.

264 Antioxidant activity of buckwheat grains is up to 10-fold higher than the activity of oat,
265 barley, wheat, or rye (Zieliński and Kozłowska, 2000). Dave Oomah et al. (1996) determined
266 phenolic acid contents in five buckwheat cultivars grown at three locations in Canada for four
267 years and showed that variation in contents was mainly due to cultivar and seasonal effects while
268 growing location had no significant effect. In our research, differences in AOP, TCP, and TFC
269 between both buckwheat species were significant. All three tests showed higher activities in
270 Tartary buckwheat fractions, compared to common buckwheat. Jiang et al. (2007) showed that
271 rutin plays an important role in the antioxidant activity of buckwheat seed, since in all samples
272 rutin content in buckwheat seeds significantly correlated to the antioxidant activity. On the other
273 hand, Morishita et al. (2007) suggested that the contribution of polyphenols to antioxidant
274 activity is different between common and Tartary buckwheat. Not only rutin but also other
275 phenols significantly influence antioxidant activities, since quercetin was not even detected in
276 common buckwheat and epicatechin was not detected in Tartary buckwheat (Morishita et al.,
277 2007). Among three studied buckwheat species (*Fagopyrum esculentum*, *F. tataricum*, and *F.*
278 *homotropicum*) and in total 11 cultivars/accessions Tartary buckwheat had the highest
279 antioxidant activity and exhibited the most effective inhibition of LDL peroxidation (Jiang et al.,
280 2007). Similar results were presented by Morishita et al. (2007) who found out that Tartary
281 buckwheat grains possess 3-4 times higher antioxidant activity than common buckwheat grains.
282 In a detailed comparison of 83 studies on buckwheat species and cultivars, differences were
283 reported in the case of phenolics, especially flavonoids, tocopherols, β -glucans, and phytosterols
284 (Raguindin et al., 2021). In our study, the lowest AOP was measured in the light flour fraction of

285 both buckwheat species. Although light flour of Tartary buckwheat had the lowest AOP among
286 fractions, it was still comparable or even higher than the AOP of all common buckwheat
287 fractions. Several radical scavenging tests also showed differences between 12 common
288 buckwheat cultivars from 8 countries (Kiproviski et al., 2015) and groats and whole grains of two
289 common buckwheat cultivars (Yildiz et al., 2019). Differences among different buckwheat
290 species and cultivars in total and individual phenolic contents were also reported by Podolska et
291 al. (2021). Interestingly, variation in phenolic content among cultivars of the same buckwheat
292 species can be higher than between different buckwheat species (Li et al., 2013). Overall, bran,
293 especially that of Tartary buckwheat, had the highest TPC, which was also shown in previous
294 studies including both species and different cultivars (Guo et al., 2012; Li et al., 2013). Results
295 indicate that most bioactive compounds with antioxidant properties are located in outer layers of
296 the grain, i.e. bran. Hung and Morita (2008) determined TPC of 16 whole buckwheat grains
297 fractions and found that the outer layers of buckwheat grains had a higher amount of phenolic
298 compounds. Higher TPC along with higher amounts of protein, lipid, ash and dietary fiber are
299 considered to be good materials for cereal-based food processing. The flour milled from the
300 outer layers of buckwheat grains or bran fraction, which consist of outer layers, contains large
301 amounts of phenolic compounds, high antioxidant capacity, and is considered to have significant
302 health benefits (Hung and Morita, 2008).

303 There were significant differences in major and trace mineral contents between different
304 milling fractions. The highest levels for the four most abundant minerals K, P, Mg, and S were
305 found in the bran of both species of buckwheat, while Ca content was the highest in hulls.
306 Steadman et al. (2001b) reported on eleven milling fractions during the milling process. Contents
307 of all major minerals in three obtained bran fractions were comparable, however higher

308 compared to other fractions (Steadman et al., 2001b). Contents of trace minerals Fe, Zn, Cu, Mo,
309 and Co were also the highest in bran, for both buckwheat species and years of production. On the
310 other hand, contents of trace minerals Na, Mn, Cr, and V were the highest in hulls. Interestingly,
311 there were no pronounced differences in minerals contents between common and Tartary
312 buckwheat. The year of production had a similarly significant impact on the differences between
313 the contents as buckwheat species. Domingos and Bilsborrow (2021) studied two common
314 buckwheat varieties produced at two sowing dates in three consecutive years. They reported
315 similar contents of trace minerals Fe and Zn; however, there were no significant interactions
316 found for any of the study treatments (Domingos and Bilsborrow, 2021).

317 Although milling fraction, e.g. bran, are somewhat by-product of light flour production,
318 there is a potential for its implementation in a variety of products, such as rutin enriched material
319 made of bran (Cho et al., 2014). Especially, Tartary buckwheat has a high potential for further
320 product development, whilst it shows high nutritional value since it contains beneficial active
321 substances attributed to beneficial properties and medicinal value (Ruan et al., 2020).

322

323 **5 Conclusions**

324 The present study describes the general nutritional value of two common types of
325 buckwheat. Since buckwheat has immense potential in the food industry as a rich source of
326 nutrients and bioactive compounds, especially in a gluten-free diet, its composition should be
327 thoroughly studied to reveal its maximum potential. In our study, significant differences in basic
328 chemical composition, antioxidant properties, and multi-mineral composition between whole
329 grains of two buckwheat species, and their milling fractions were found. Significant differences
330 in antioxidant properties were observed between buckwheat species. Tartary buckwheat had

331 higher levels of total phenolics and flavonoids, compared to common buckwheat. On the other
332 hand, there were small differences between the species in the case of multi-mineral composition.
333 All analyses showed significant differences between milling fractions, regardless of buckwheat
334 species. Buckwheat is a novel and healthy food; therefore its consumption should be enhanced.
335 Buckwheat flour products are known and already popular worldwide, however other fractions of
336 the buckwheat milling processes are still considered as by-products or even waste. The purpose
337 of this study was to present the high nutritional value of buckwheat grains and their fractions.
338 Among fractions, bran showed the highest potential, since it contained the highest levels of
339 minerals and proteins and had the highest antioxidant potential. Bran is already used in several
340 products, such as tea, breakfast cereals or bread, but we believe it is not yet used to its full
341 potential.

342

343 **Conflicts of interests**

344 The authors have declared no conflict of interest.

345

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351

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465 Table 1: Basic chemical composition (%) of whole grain, hulls, bran and light flour of common and Tartary buckwheat harvested in two
 466 consecutive years (I, II).

Year	Buckwheat species	Fraction	Ash	Carbohydrates	Fats	Fiber	Moisture	Protein	Dry matter
I	Common	Whole grains	2.1 ±0.0 c	73.6 ±0.0 b	2.1 ±0.0 c	12.1 ±0.0 c	10.9 ±0.0 b	11.3 ±0.0 c	89.1 ±0.0 c
		Hulls	2.0 ±0.0 b	81.2 ±0.0 d	0.7 ±0.0 a	48.0 ±0.1 d	10.7 ±0.0 a	5.4 ±0.0 a	89.3 ±0.0 d
		Bran	4.6 ±0.0 d	53.0 ±0.2 a	4.1 ±0.0 d	2.7 ±0.1 b	13.1 ±0.0 c	25.3 ±0.2 d	87.0 ±0.0 b
		Light flour	1.0 ±0.0 a	76.4 ±0.0 c	0.8 ±0.0 b	0.6 ±0.0 a	14.8 ±0.0 d	7.0 ±0.1 b	85.2 ±0.0 a
	Tartary	Whole grains	2.5 ±0.0 c	75.2 ±0.1 b	2.5 ±0.0 c	19.8 ±0.2 c	9.8 ±0.0 b	10.0 ±0.0 c	90.2 ±0.0 c
		Hulls	2.0 ±0.0 b	88.1 ±0.1 d	0.4 ±0.0 a	56.1 ±0.2 d	6.2 ±0.0 a	3.4 ±0.1 a	93.8 ±0.0 d
		Bran	5.8 ±0.0 d	49.2 ±0.0 a	5.2 ±0.0 d	3.8 ±0.1 b	12.2 ±0.0 c	27.7 ±0.1 d	87.8 ±0.0 b
		Light flour	1.3 ±0.0 a	76.3 ±0.0 c	0.6 ±0.0 b	1.1 ±0.1 a	13.4 ±0.0 d	8.3 ±0.0 b	86.6 ±0.0 a
II	Common	Whole grains	2.4 ±0.0 c	72.9 ±0.0 b	2.3 ±0.0 c	14.0 ±0.2 c	10.8 ±0.0 b	11.7 ±0.1 c	89.2 ±0.0 c
		Hulls	2.2 ±0.1 b	83.4 ±0.3 d	0.5 ±0.0 a	51.8 ±0.3 d	9.6 ±0.0 a	4.3 ±0.2 a	90.4 ±0.0 d
		Bran	5.3 ±0.0 d	48.4 ±0.1 a	4.7 ±0.0 d	2.8 ±0.0 b	13.7 ±0.0 c	27.9 ±0.1 d	86.3 ±0.0 b
		Light flour	1.3 ±0.0 a	75.6 ±0.1 c	0.8 ±0.0 b	0.7 ±0.0 a	14.5 ±0.0 d	7.8 ±0.0 b	85.5 ±0.0 a
	Tartary	Whole grains	2.2 ±0.0 c	72.5 ±0.1 b	2.3 ±0.0 c	15.5 ±0.0 c	11.4 ±0.0 b	11.6 ±0.1 c	88.6 ±0.0 c
		Hulls	1.9 ±0.0 b	85.4 ±0.0 d	0.6 ±0.0 a	54.8 ±0.1 d	7.8 ±0.0 a	4.4 ±0.1 a	92.2 ±0.0 d
		Bran	4.7 ±0.0 d	52.0 ±0.1 a	4.9 ±0.0 d	2.0 ±0.1 b	13.2 ±0.0 d	25.2 ±0.1 d	86.8 ±0.0 a
		Light flour	1.0 ±0.0 a	77.5 ±0.0 c	0.9 ±0.0 b	0.8 ±0.0 a	12.6 ±0.0 c	8.0 ±0.0 b	87.4 ±0.0 b
Range			1.0–5.8	48.4–88.1	0.4–5.2	0.6–56.1	6.2–14.8	3.4–27.9	85.2–93.8

467 Data are means ± SD (n=3). Means with different letters within each buckwheat species are significantly different ($P < 0.05$).

468 Table 2: Antioxidant potential (AOP; $\mu\text{mol g}^{-1}$ TE), total phenolic content (TPC; mg g^{-1} GAE) and total flavonoid content (TFC; mg g^{-1} QE) of
 469 whole grain, hulls, bran and light flour of common and Tartary buckwheat harvested in two consecutive years (I, II).

Year	Buckwheat species	Fraction	AOP	TPC	TFC
I	Common	Whole grains	6.04 \pm 0.04 b,***	3.75 \pm 0.02 c,***	0.61 \pm 0.01 c,***
		Hulls	5.91 \pm 0.08 b,***	2.93 \pm 0.02 b,***	0.40 \pm 0.00 b,***
		Bran	9.51 \pm 0.08 c,***	7.29 \pm 0.09 d,***	1.20 \pm 0.00 d,***
		Light flour	2.27 \pm 0.08 a,***	1.71 \pm 0.01 a,***	0.20 \pm 0.00 a,***
	Tartary	Whole grains	37.95 \pm 0.36 c,***	12.90 \pm 0.02 c,***	9.12 \pm 0.05 c,***
		Hulls	20.74 \pm 0.24 b,***	7.07 \pm 0.09 a,***	2.50 \pm 0.01 a,***
		Bran	102.34 \pm 0.36 d,***	30.73 \pm 0.09 d,***	27.15 \pm 0.06 d,***
		Light flour	10.55 \pm 0.04 a,***	7.86 \pm 0.04 b,***	5.04 \pm 0.01 b,***
II	Common	Whole grains	6.58 \pm 0.12 b,***	3.81 \pm 0.01 c,***	0.47 \pm 0.00 c,***
		Hulls	9.79 \pm 0.04 c,***	3.61 \pm 0.08 b,***	0.38 \pm 0.00 b,***
		Bran	12.53 \pm 0.08 d,***	9.14 \pm 0.05 d,***	1.86 \pm 0.03 d,***
		Light flour	3.41 \pm 0.08 a,***	2.38 \pm 0.01 a,***	0.28 \pm 0.01 a,***
	Tartary	Whole grains	32.81 \pm 0.20 c,***	11.65 \pm 0.03 c,***	8.77 \pm 0.05 c,***
		Hulls	12.89 \pm 0.04 b,***	5.83 \pm 0.01 b,***	2.76 \pm 0.01 a,***
		Bran	72.80 \pm 0.48 d,***	25.61 \pm 0.05 d,***	20.73 \pm 0.03 d,***
		Light flour	10.81 \pm 0.04 a,***	4.95 \pm 0.05 a,***	3.74 \pm 0.07 b,***
Range			2.27–102.34	1.71–30.73	0.20–27.15

470 Data are means \pm SD (n=3). Means with different letters within each buckwheat species are significantly different ($P < 0.05$); means with * are significantly different
 471 (difference between buckwheat species), with significance indicated as follows: ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$.

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473 Table 3: Major mineral (g kg⁻¹) and trace mineral (mg kg⁻¹) content of whole grain, hulls, bran and light flour of common and Tartary buckwheat
 474 harvested in two consecutive years (I, II).

Year	Buckwheat species	Fraction	Major mineral content					Trace mineral content								
			Mg	P	S	K	Ca	Na	V	Cr	Mn	Fe	Co	Cu	Zn	Mo
I	Common	Whole grains	2.42	3.80	1.76	4.87	0.75	29.1	0.06	0.39	18.7	44.5	0.04	6.72	24.5	1.39
		Hulls	2.27	1.32	1.00	4.79	1.84	39.9	0.09	0.41	35.8	51.3	0.04	8.43	17.2	0.82
		Bran	5.42	10.28	3.43	9.80	0.75	37.8	0.06	0.22	28.0	77.9	0.06	10.95	57.6	2.32
		Light flour	1.12	1.90	1.20	2.54	0.48	35.4	0.05	0.28	8.1	33.2	0.05	5.22	21.5	1.20
	Tartary	Whole grains	2.22	3.82	1.52	5.73	1.88	27.7	0.06	0.23	39.4	53.5	0.05	8.73	46.5	3.31
		Hulls	1.37	0.65	0.64	5.28	2.82	34.8	0.05	0.36	55.1	42.0	0.04	7.47	18.7	0.79
		Bran	6.30	13.40	3.53	12.97	1.50	29.8	0.05	0.27	48.1	127.2	0.10	14.66	120.9	2.82
		Light flour	1.26	2.43	1.35	3.10	0.73	25.9	0.05	0.22	14.2	46.6	0.05	13.93	30.4	0.87
II	Common	Whole grains	2.39	3.97	1.62	5.84	0.67	36.5	0.09	0.40	21.5	86.9	0.05	8.30	27.6	0.96
		Hulls	1.40	0.85	0.70	7.05	1.06	31.7	0.10	0.25	34.4	52.1	0.04	6.47	9.1	0.58
		Bran	6.50	12.12	3.73	11.79	0.82	33.5	0.06	0.36	34.9	88.2	0.07	11.61	62.6	1.82
		Light flour	1.36	2.35	1.31	2.90	0.46	29.6	0.08	0.29	10.2	51.9	0.04	5.50	15.0	0.71
	Tartary	Whole grains	2.14	4.06	1.50	5.48	0.84	23.3	0.05	0.20	21.6	69.7	0.04	7.80	33.0	0.86
		Hulls	1.16	0.94	0.74	5.61	1.59	29.9	0.06	0.33	32.2	49.7	0.03	6.15	22.9	0.48
		Bran	5.06	10.42	2.68	9.57	0.55	22.1	0.07	0.20	27.9	102.8	0.06	10.53	70.5	1.84
		Light flour	1.03	1.90	1.15	2.41	0.50	29.5	0.07	0.32	9.9	76.6	0.05	7.47	25.8	0.88
Range			1.03– 6.50	0.65– 13.40	0.64– 3.73	2.41– 12.97	0.46– 2.82	22.10– 39.90	0.05– 0.10	0.20– 0.41	8.10– 55.10	33.20– 127.20	0.03– 0.10	5.22– 14.66	9.10– 120.90	0.48– 3.31

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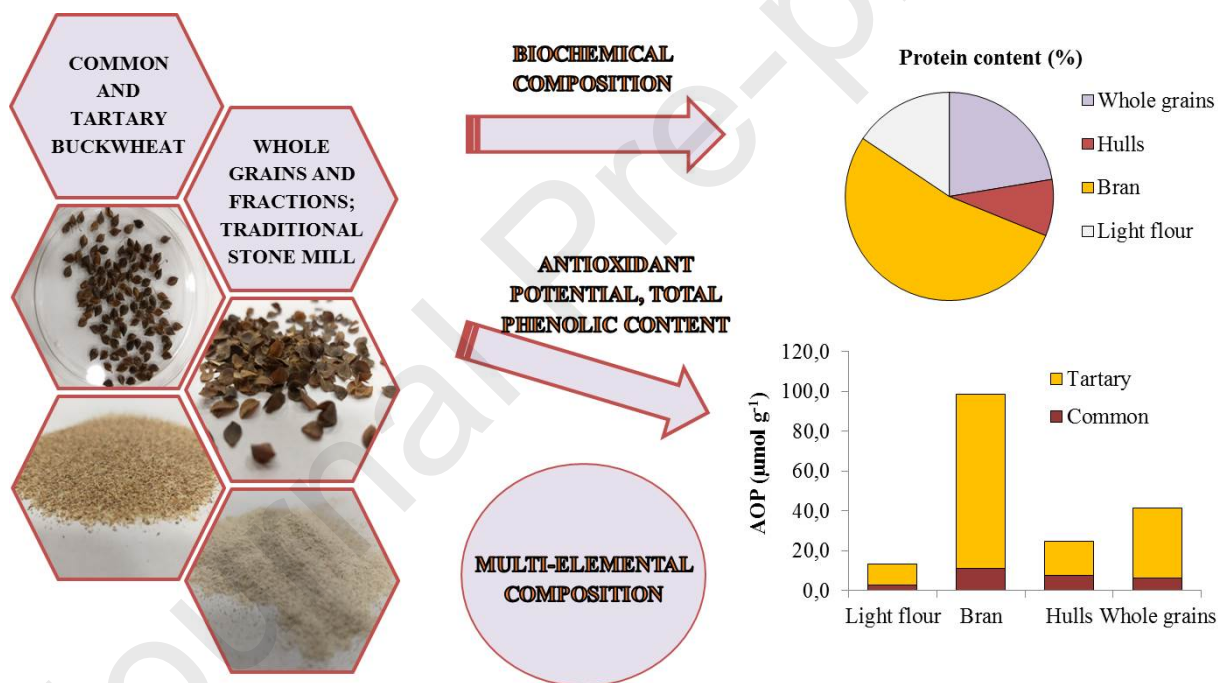
477 **CRedit authorship contribution statement**

478 **Lovro Sinkovič:** Investigation, Conceptualisation, Resources, Writing – Review & Editing. **Doris Kokalj Sinkovič:** Formal analyses,
479 Visualization, Writing - Original Draft. **Vladimir Meglič:** Supervision, Project administration, Funding acquisition, Writing – Review &
480 Editing.

481

482 Graphical abstract

483 Differences between common and tartary buckwheat, and their milling fractions obtained by traditional stone milling.



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487 **Highlights:**

- 488 • Biochemical composition of milling fractions of common and tartary buckwheat was evaluated.
- 489 • Significant differences between fractions were observed.
- 490 • Antioxidant properties of tartary buckwheat were higher compared to common buckwheat.
- 491 • Contents of all macroelements and most of the microelements were the highest in bran fraction.

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