Evaluation of Essential and Toxic Elements Concentrations in Different Parts of Buckwheat

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Abstract

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The elements concentrations in different parts of buckwheat and the commercial products of it were analysed by experimental and chemometric approaches. The results indicated that the essential and toxic elements concentrations were significantly different in various parts of the buckwheat, with the seeds revealing the lowest concentrations. The elemental patterns were not significantly different between *Fagopyrum tataricum* (L.) Gaertn and *F. esculentum* Moench. Abundant essential elements were found in the commercial buckwheat tea. The detection of heavy metals manifested the potential toxicity of buckwheat.

Keywords: *Fagopyrum tataricum* (L.) Gaertn; *F. esculentum* Moench; ICP-OES; essential element; toxic element; chemometrics

Belonging to *Fagopyrum* (Polygonaceae), buckwheat has been planted worldwide as food and for drinks (Wijngaard & Arendt 2006). *Fagopyrum tataricum* (L.) Gaertn and *F. esculentum* Moench are two most planted ones. Researchers have revealed the great values of buckwheat from the nutritional and pharmacological views (Christa & Soral-Smietana 2008). Buckwheat is abundant in proteins, vitamins, and essential elements, and is generally richer in them than rice, wheat, and corn. The amino acids in buckwheat are more balanced, making it suitable for human beings (Pomeranz & Robbinas 1972). The pharmacological activities of buckwheat were reported, benefiting the blood glucose (Yao *et al.* 2008), blood cholesterol (Lin *et al.* 2008), and oxidative stress (Inglett *et al.* 2011). Therefore, more and more commercial buckwheat products have been produced and consumed since recently.

The intake of enough essential elements is important for the health. The lack and excess of essential elements result in toxicity. Because of the pollution, toxic elements may accumulate in buckwheat. Unfortunately, the information on the elements concentrations in buckwheat is still scarce. The elements concentrations in buckwheat have been reported by several studies. Bonafaccia *et al.* (2003) found that more trace elements were accumulated in the bran. Mestek *et al.* (2007) detected Co, Cu, Fe, Mn, Mo, Ni, P,

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and Zn in the extract of buckwheat flour. Other studies tested the metals concentrations in the buckwheat grain (Pongrac *et al.* 2011). Previous studies only analysed a limited number of metals. The elemental pattern of buckwheat has not been determined.

Herein, we studied the essential and toxic elements concentrations in buckwheat and the commercial products. Different parts of buckwheat were analysed after microwave-assisted digestion on inductively coupled plasma optical emission spectrometer (ICP-OES). The data were subjected to the correlation analysis (CA), Principal Component Analysis (PCA), and hierarchical cluster analysis (HCA) for chemometrics analyses. The elements concentrations were significantly regulated by the buckwheat parts. The elemental patterns were not distinct between *F. tataricum* (L.) Gaertn and *F. esculentum* Moench. Very high Pb concentrations were found in commercial buckwheat tea, while abundant essential elements were detected.

MATERIAL AND METHODS

Material. Buckwheat samples were obtained from Chengdu University, China (Table 1). Buckwheat teas were obtained from local supermarkets (Table 2). Calibration solutions were purchased from National Analysis Center for Iron & Steel, Beijing, China. Certified reference material (CRM, GBW10011) was obtained from the Institute of Geophysical and Geochemical Exploration, Langfang, China.

Elemental concentration analysis. The samples were dried, ground and put into the microwave digestion can. After incubating with HNO_3 (5 ml, 15 min), each sample was digested with a Microwave Digestion System (WX-8000; Preekem Co., Shanghai, China). Two drops of H_2O_2 were added and the final volume was adjusted to 10 ml. After filtration, the elements concentrations were determined by ICP-OES (6300 Radial; Thermo Fisher Scientific Co., Franklin County, USA). The ICP-OES was calibrated before the measurements (Table 1). A CRM (GBW 10011) was prepared in the same way (Table 2).

Table 1. Sources of the buckwheat samples (Locality Chengdu University)

No.	Brand	Taxon
K1	Wild buckwhea 6	*F. tataricum* (L.) Gaertn.
K2	Xiqiao 1	*F. tataricum* (L.) Gaertn.
K3	Xiqiao 2	*F. tataricum* (L.) Gaertn.
K4	Inner mongolia Wensha	*F. esculentum* Moench
K5	Erdos	*F. esculentum* Moench
K6	Meng 103-3	*F. esculentum* Moench

Table 2. Sources of the commercial buckwheat tea samples (Producing area Sichuan)

No.	Brand	Trade name
S1	Yixiangren	bitter buckwheat tea
S2	Yixiangren	black tarary buckwheat whole plant tea
S3	Yixiangren	black tarary buckwheat whole bran tea
S4	Yixiangren	black tarary buckwheat whole embryo tea
S5	Sanjiang	buckwheat black tea
S6	Sanjiang	black tarary buckwheat whole plant tea
S7	Sanjiang	bitter buckwheat tea
S8	Sanjiang	black tarary buckwheat whole embryo tea

Data analysis. The chemometrics analyses (CA, PCA, and HCA) were performed with SPSS Version 17.0 (Kara 2009; Wang & Liu 2010). In HCA, the data were standardised to the mean of 1. In our calculation, the Ward's method of clustering was applied with the Chi-squared measurement.

RESULTS AND DISCUSSION

Elements concentrations in different parts of buckwheat

The dominating accumulation parts of certain elements were different (Tables 3–6). Al, Co, Cr, Cu, Fe, Ti, and V were mainly contained in the root and while their contents in the seed were minimised. Ca, Na, K, Ni, Sr, and Zn accumulated more in the stem, their concentrations there being slightly higher than those in the root and leaf. Again, the accumulation in the seed was the lowest. Interestingly, the Ni concentration in the root of *F. tataricum* (L.) Gaertn. was much higher than that in the stem, while *F. esculentum* Moench showed similar Ni concentrations in both these parts. B, Mg, Mo, Si, Cd, and Pb accumulated in the leaf and P was mostly detected in the seed. Other elements, including Mn, Se, Sn, As, and Hg, were distributed among all the four parts. Since the elements concentrations varied in different parts, the ingestion of different parts would affect the intake of essential and toxic elements.

Moreover, the elemental concentrations in the root, stem, and leaf were much higher than those in the seed. Therefore, when taking the whole plant, the acceptable daily intake (ADI) should be seriously evaluated. Our results showed a good agreement with the results given in literature. Bonafaccia *et al.* (2003) compared the elements concentrations in the grain, bran, and leaf of buckwheat, where the leaf showed higher elements concentrations than the grain. For example, Fe concentration was 1607 μg/g in leaf flour and the value dropped to 462 μg/g in the grain. In our study, Fe concentration was 100–1246 μg/g in the leaf and 13.86–251.4 μg/g in the seed. When comparing item by item, most elements shared the same order of magnitude and the exact values differed between the samples. Mestek *et al.* (2007) detected Co, Cu, Fe, Mn, Mo, Ni, P, and Zn in buckwheat flour. In particular, P concentration was very high (3180 μg/g). This was similar to our observations, where P concentration was very high in the seed (588–2243 μg/g). Pongrac *et al.* (2011) mapped the elemental composition (Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, and Zn) of buckwheat grain. Those elements were also detected in our study.

Correlation analysis

The correlation matrix analysis is presented in Table 3. The positive/negative correlations between the elements are indicated by the correlation coefficients (r). When the absolute value of r is close to 1 (marked in boldface type), the correlation is strong. For example, As was highly correlated with Al, Fe, Co, Cr, Cu, V, and Cd. Both Al and Fe were correlated with several toxic metals, including Co, Cr, and As.

Principal component analysis

The first four principal components (PCs) explained 82% of the total variance in the data (Table 4). The loading expressed how well the PCs correlated with the old variables. The first PC explained 38.37% of variance. It was positively correlated with Al, Fe, Zn, Co, Cr, Cu, Ni, Ti, V, As, and Hg. The second PC explained 26.39% of variance and correlated closely with Mg, Si, Mo, Se, Cd, and Pb. The second PC negatively correlated with P. PCs will be effective enough, when the total variance is higher than 70%. Here, four

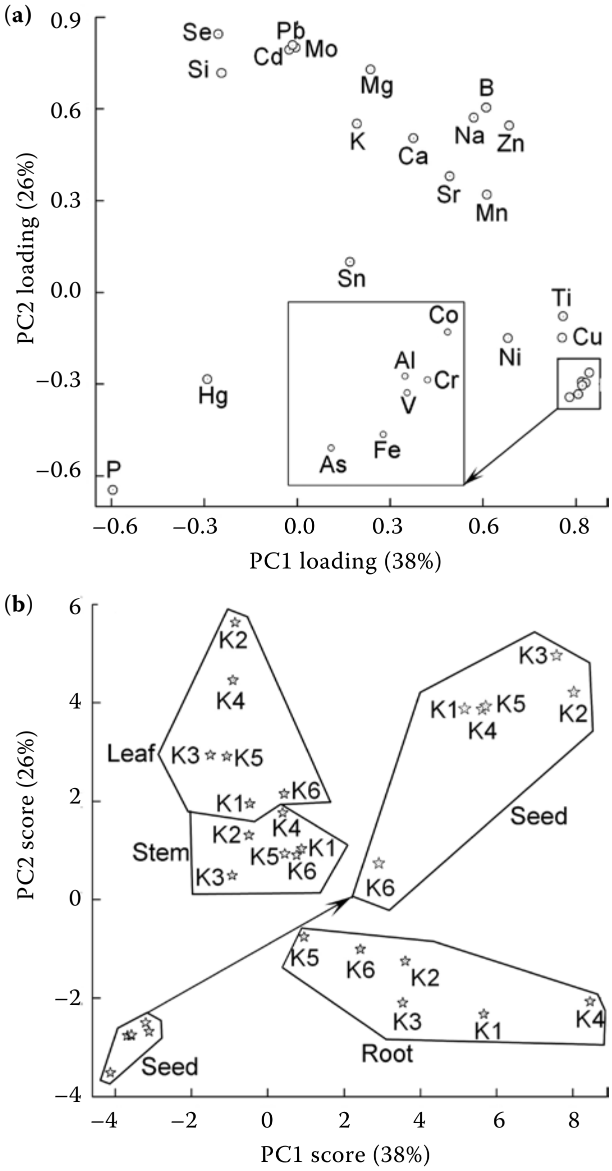

Figure 1. Varimax rotated principal component loadings (**a**) and scores (**b**). The insets indicated by the arrows are the magnifications of the crowded area

PCs were satisfied. Obviously, Al, Fe, Zn, Co, Cr, Cu, Ni, Ti, V, As, Hg, Mg, Si, Mo, Se, Cd, and Pb were the characteristic elements.

The first two varimax rotated PC loadings and scores are presented in Figure 1. The elements with high loadings influenced the data structure to a greater extent. The similarities and correlations could be defined between two elements by their loadings. Two close associations were observed. As, Fe, V, Al, Cr, and Co shared similar PC loadings. Another association was between Cd, Pb, and Mo. The rest were distributed more randomly. The scores in Figure 1b indicated the similarities and correlations between two parts of buckwheat.

Table 3. Correlation matrix for the element concentrations in buckwheat samples

	Ca	Na	K	Al	Mg	P	Fe	Si	Zn	B	Co	Cr	Cu	Mn	Mo	Ni	Se	Sn	Sr	Ti	V	As	Hg	Cd	Pb
Ca	1.00																								
Na	**0.80**	1.00																							
K	0.58	0.70	1.00																						
Al	0.14	0.27	-0.10	1.00																					
Mg	0.41	0.42	0.18	0.06	1.00																				
P	−0.63	**−0.80**	−0.58	−0.30	−0.51	1.00																			
Fe	0.06	0.24	−0.13	0.95	0.01	−0.29	1.00																		
Si	−0.02	0.06	0.21	−0.36	0.43	−0.27	−0.38	1.00																	
Zn	0.61	0.81	0.73	0.40	0.43	−0.75	0.40	0.18	1.00																
B	0.26	0.55	0.30	0.39	0.56	−0.68	0.41	0.47	0.72	1.00															
Co	0.14	0.29	−0.07	**0.99**	0.07	−0.34	**0.97**	−0.35	0.45	0.45	1.00														
Cr	0.10	0.30	−0.07	**0.97**	0.03	−0.32	**0.97**	−0.38	0.44	0.44	**0.99**	1.00													
Cu	0.12	0.30	0.10	**0.86**	0.10	−0.33	**0.80**	−0.24	0.53	0.52	**0.87**	**0.88**	1.00												
Mn	0.23	0.33	0.04	0.54	0.55	−0.49	0.46	0.08	0.49	0.65	0.56	0.48	0.51	1.00											
Mo	0.09	0.22	0.09	−0.15	0.75	−0.38	−0.15	0.74	0.30	0.59	−0.13	−0.17	−0.14	0.38	1.00										
Ni	0.29	0.49	0.36	0.60	−0.03	−0.40	0.62	−0.28	0.46	0.23	0.60	0.61	0.55	0.08	−0.23	1.00									
Se	0.25	0.33	0.45	−0.50	0.57	−0.42	−0.53	0.68	0.26	0.41	−0.46	−0.46	−0.27	0.19	0.61	−0.34	1.00								
Sn	0.26	0.49	0.45	0.04	−0.07	−0.22	0.01	−0.17	0.25	0.10	0.07	0.17	0.22	−0.15	−0.21	0.15	0.17	1.00							
Sr	**0.90**	**0.80**	0.47	0.26	0.33	−0.63	0.23	−0.14	0.59	0.31	0.29	0.29	0.29	0.18	0.03	0.35	0.20	0.35	1.00						
Ti	0.22	0.42	0.06	0.79	0.13	−0.45	**0.88**	−0.23	0.56	0.51	**0.82**	**0.80**	0.60	0.54	0.02	0.57	−0.38	−0.04	0.25	1.00					
V	0.07	0.26	−0.15	**0.97**	0.05	−0.32	**0.99**	−0.38	0.40	0.43	**0.98**	**0.98**	**0.82**	0.52	−0.12	0.59	−0.49	0.01	0.24	**0.86**	1.00				
As	0.01	0.15	−0.18	**0.98**	0.03	−0.24	**0.95**	−0.35	0.33	0.39	**0.98**	**0.97**	**0.87**	0.53	−0.15	0.54	−0.48	0.01	0.18	0.74	**0.97**	1.00			
Hg	−0.26	−0.32	−0.21	−0.15	−0.20	0.63	−0.14	−0.07	−0.24	−0.25	−0.15	−0.15	−0.13	−0.22	−0.10	−0.19	−0.16	−0.09	−0.26	−0.19	−0.15	−0.12	1.00		
Cd	0.19	0.21	0.13	−0.16	0.63	−0.34	−0.20	0.67	0.30	0.54	−0.15	−0.20	−0.11	0.33	**0.90**	−0.28	0.53	−0.17	0.08	0.00	−0.17	−0.18	−0.13	1.00	
Pb	0.15	0.24	0.19	−0.16	0.60	−0.37	−0.20	0.69	0.33	0.57	−0.15	−0.19	−0.07	0.32	**0.89**	−0.26	0.57	−0.10	0.06	0.00	−0.17	−0.18	−0.14	**0.98**	1.00

The number in bold means the correlation of two elements is strong

Table 4. Varimax rotated factor loadings of the first four principal components

Variable	Principal component			
	1	2	3	4
Ca	0.376	0.503	–0.573	–0.362
Na	0.570	0.571	–0.517	–0.004
K	0.193	0.551	–0.628	0.294
Al	**0.920**	–0.294	0.173	–0.016
Mg	0.238	**0.729**	0.255	–0.224
P	–0.595	**–0.647**	0.224	0.154
Fe	**0.908**	–0.334	0.183	–0.007
Si	–0.244	**0.717**	0.353	0.256
Zn	**0.684**	0.545	–0.232	0.185
B	0.611	0.604	0.282	0.252
Co	**0.942**	–0.263	0.162	0.023
Cr	**0.932**	–0.296	0.112	0.093
Cu	**0.856**	–0.149	0.084	0.271
Mn	0.612	0.320	0.399	–0.157
Mo	–0.004	**0.801**	0.522	–0.005
Ni	**0.681**	–0.150	–0.331	0.072
Se	–0.254	**0.844**	–0.048	0.144
Sn	0.171	0.099	–0.600	0.491
Sr	0.493	0.380	–0.569	–0.291
Ti	**0.859**	–0.079	0.143	–0.080
V	**0.921**	–0.305	0.207	–0.021
As	**0.880**	–0.343	0.253	0.042
Hg	–0.289	–0.284	0.142	0.405
Cd	–0.025	**0.793**	0.460	–0.027
Pb	–0.015	**0.808**	0.435	0.073
Explained variance	9.59	6.60	3.25	1.09
Proportion of total variance (%)	38.37	64.76	77.74	82.11

The number in bold means the correlation between element and principal component is strong in positive or negative

The spots could be artificially divided into four groups. The characteristics of the seed were more distinguished, the spots gathering closely in the negative area. The spots of the leaf and stem were very close to one another, indicating that the two parts were similar. The spots of the root were scattered separately.

Hierarchical cluster analysis

HCA is the most used unsupervised pattern recognition technique. The four parts of buckwheat

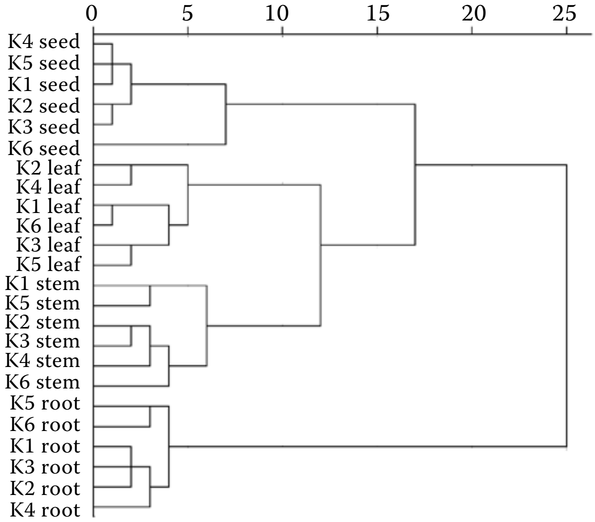

Figure 2. Dendrogram of hierarchical cluster analysis for the different parts of buckwheat

were unambiguously distinguished (Figure 2). There was no significant difference between *F. tataricum* (L.) Gaertn and *F. esculentum* Moench. This indicated that the elements concentrations of buckwheat were regulated by the parts, rather than the genetic relationship. Obviously, the HCA and PCA results were consistent, where the leaf and stem were closer to each other.

Elemental concentrations in commercial buckwheat tea

There are mainly 5 categories of commercial buckwheat teas, including bitter buckwheat tea, black tarary buckwheat, black tarary buckwheat whole plant tea, black tarary buckwheat whole bran tea, and black tarary buckwheat whole embryo tea. Here, we analysed the commercial products from Yixiangren and Sanjiang (Table 2). As listed in Table 2 sample S7, the elements concentrations in buckwheat teas were different. The whole embryo tea (samples S4 and S8) had the lowest elements concentrations. There were significant differences between the two brands in Na and Al concentrations. The products from Yixiangren had much higher Na and Al concentrations. Pb concentrations in the whole bran tea (sample S3, 6.31 μg/g) and the whole plant tea (S6, 10.28 μg/g) were very high. This was expectable, because the leaf showed high Pb concentrations (73.37–393.6 μg/g). Sample S2 (the whole plant tea) was an exception, whose Pb concentration being only 0.81 μg/g, one order of

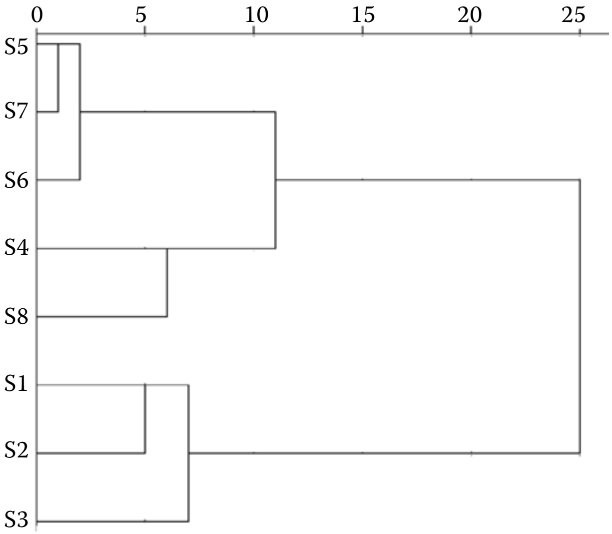

Figure 3. Dendrogram of hierarchical cluster analysis for the commercial buckwheat tea

magnitudes lower than those in samples S3 and S6. Other toxic elements, such as Hg and As, were not detected among the 8 products.

The difference was clearly indicated by HCA. The whole embryo teas from both brands (samples S4 and S8) were in the same group (Figure 3), suggesting that the character of the whole embryo tea was distinct. On the other hand, the bitter buckwheat tea, the whole plant tea and the whole bran tea from Yixiangren (S1–S3) were in the same group, while the black tarary buckwheat, the whole plant tea, and the bitter buckwheat tea from Sanjiang (S5–S7) were in another one. This suggested that the source and producing protocol had a great impact on the elemental concentrations of these products.

Buckwheat tea it a good source of essential elements. The macroelements are important to maintain the normal metabolism. The ADI of Ca is 210–1300 mg/day, which varies with age (Bowman & Russell 2006). The ADI for other essential elements are also available, e.g. 4000 mg per day for P and 80–350 mg/day for Mg. There were 183.4-810 µg/g of Ca, 1124–3646 µg/g of P, and 353–1366 µg/g of Mg in buckwheat tea, enabling it to act as a macroelements supply. Many essential trace elements were found, too. Therefore, buckwheat tea could be used as the supply of trace elements.

However, special attention should be paid to heavy metals. In particular, Pb concentrations in the whole plant tea and whole bran tea were very high, implying that the planting soil might be polluted. The ADI value of Pb is 5–50 µg/day (Llobet *et al.* 2003; Bowman & Russell 2006). The drinking of such buckwheat tea should be restricted to avoid the Pb toxicity. The Cd concentrations were generally low, comparing to the ADI (70 µg/day) (Llobet *et al.* 2003; Bowman & Russell 2006). Thus, the drinking of buckwheat tea is safe from this point of view.

CONCLUSION

In summary, we studied the elements concentrations in buckwheat and the commercial products of it where the elements concentrations were significantly different in various parts of the buckwheat. The chemometrics analyses suggested that the elemental patterns were not distinct between *F. tataricum* (L.) Gaertn and *F. esculentum* Moench. The whole embryo tea had the lowest elements concentrations among the commercial products. The high Pb concentrations in the whole plant tea and the whole bran tea should be of serious concern in future. Our results will stimulate more interest in the applications and toxicological evaluation of buckwheat.

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