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Elemental composition of wheat, common buckwheat, and tartary buckwheat grains under conventional production

Vsebnosti elementov v zrnju pšenice, navadne in tatarske ajde s polja s konvencionalno pridelavo

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Abstract: The elemental composition of cereal and pseudocereal grain is believed to significantly affect the portions of the minerals supplied for particular human populations. Therefore, care needs to be taken to improve the availability of the essential elements and to decrease unwanted metal accumulation in edible plant parts. In the present study, we have investigated the element accumulation in the grain of wheat (*Triticum aestivum* L.), common buckwheat *(Fagopyrum esculentum* Moench), and tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.), harvested from the same field under conventional grain production. Soil and grain element compositions were analysed using energy dispersive X-ray fluorescence spectrometry and total reflection X-ray fluorescence spectrometry. The wheat grain shows significantly higher ($p < 0.05$) higher element concentrations than both of the buckwheat species tested. The contents of elements in 100 g grain were higher than the concentrations listed in the literature for wheat and buckwheat flours, which indicates significant losses of elements during milling and polishing. Concerns are raised due to the high and unwanted metal accumulation in wheat and buckwheat. The data indicate that both of these buckwheat species accumulate less metal contaminants when compared to wheat.

Keywords: dietary reference intake; energy dispersive X-ray fluorescence spectrometry, *Fagopyrum esculentum*, *Fagopyrum tataricum*, metals, minerals, trace elements, *Triticum aestivum*; total reflection X-ray fluorescence spectrometry.

Izvleček: Žita in psevdožita so pomemben vir mineralnih elementov v prehrani določenih svetovnih populacij, zato je pomembno izboljšati elementno sestavo žit in zmanjšati vnos neželenih kovin v užitne dele rastlin. V raziskavi smo proučevali akumulacijo mineralnih elementov v zrnju pšenice (*Triticum aestivum* L.), navadne ajde (*Fagopyrum esculentum* Moench) in tatarske ajde (*Fagopyrum tataricum* (L.) Gaertn.) s polja s konvencionalno pridelavo. Elemente v tleh in zrnju smo analizirali z energijsko disperzijsko rentgensko fluorescenčno spektroskopijo, oziroma rentgensko fluorescenčno spektroskopijo s popolnim odbojem. Zrnje pšenice je imelo višje ($p < 0.05$) koncentracije elementov od zrnja navadne in tatarske ajde. Vsebnosti mineralnih elementov v 100 g zrnja pšenice in ajde so bile višje od vsebnosti navedenih v literaturi za moko pšenice in ajde, kar kaže na izgubo elementov med postopki za pripravo moke. Zaskrbljujoče so visoke vsebnosti nekaterih nezaželenih kovin v pšenici in ajdi. Iz rezultatov je razvidno, da navadna in tatarska ajda v zrnju akumulirata manj nezaželenih kovin kot pšenica.

Ključne besede: Energijska disperzijska rentgenska fluorescenčna spektroskopija, *Fagopyrum esculentum*, *Fagopyrum tataricum*, elementi v sledeh, kovine, minerali, prehranski referenčni vnosi za odrasle, *Triticum aestivum*, rentgenska fluorescenčna spektroskopija s popolnim odbojem.

Introduction

Wheat is one of most widely cultivated crops in developing countries, where up to 70% of the daily energy demands of the people are covered by its products (Cakmak et al. 2010). The biochemical characteristics of cereal grain tissues (e.g., starch , ferulic, coumaric and phytic acids, alkylresorcinols) are the major determinants of the quality of the products that are to be prepared from these ingredients (Hemery et al. 2009). Furthermore, grain represents an important source for the supply of the 22 mineral microelements in particular populations, and therefore their mineral content and element bioavailability are of paramount importance (White and Broadley 2005). Slovenian wheat and buckwheat flours do not differ significantly in their total starch composition (Kreft et al. 1998). Significant differences between wheat and buckwheat flours have, however, been reported for essential mineral nutrient concentrations (Ikeda et al. 2006).

Only the bioavailable soil fraction of the essential elements in soil can be accessed by plants. As well as their natural deposition and bedrock weathering, the concentrations of bioavailable elements in the soil are also influenced by soil pH, organic matter content, and cationic exchange capacity, which control the solubility, and consequentially the availability, of elements and their uptake into plants (Marschner 1995; Moreno et al. 1996). Mineral nutrient concentrations in grain are successively determined by physiological processes, including nutrient uptake, xylem loading, remobilisation from leaves, and deposition in the seed structures. The rates of mineral nutrient uptake and remobilisation primarily depend on the presence and activity of particular element transporters, which results from the expression patterns of their genes (Waters and Sankaran 2011). Consequently, the partitioning of mineral nutrients between plant organs (with the exception of P) is typically characterised by lower mineral nutrient concentrations in seeds, when compared to leaves (Tyler and Zohlen 1998). Significant variations have also been observed between and within plant species. Recently, a genetic improvement of yield that resulted in mineral micronutrient dilution was recognised as one of the factors driving the variability in nutrient concentrations of wheat grain (McKevith 2004; Zhao et al. 2009).

Large quantities of fertilisers are routinely applied to crops, to supply adequate N, P and K levels for optimal plant growth and yield. The commercially available products used for this purpose, however, frequently contain heavy-metal contaminants. Furthermore, the use of pesticides adds to the unintentionally supplied metals in agricultural crops (Adriano 2001). It is estimated that crop production of 60% of the cultivated soils worldwide is hampered by either nutrient deficiency or toxicity (Cakmak 2002). Consequently, the accumulation and bioavailability of heavy metals in crop plants is of increasing concern, due to food safety issues and potential health risks (Wang et al.2009). Legislative government acts and guidelines (Ur. list RS 68/1996; US EPA 2002; NSF/ANSI 2003) have been aimed at determining the acceptable levels of elements in soils and plant parts. Thus, as well as a growing demand for sustainable crop production with optimised element contents, systematic monitoring procedures are needed to correctly address the constant threat of unwanted metal accumulation in the food chain.

The main goals of the present study were therefore: (i) to assess the biomass and element composition of selected wheat, common and tartary buckwheat grain produced in Slovenia; (ii) to estimate the soil element availability for selected species (grown in the same field) using bioconcentration factors (BCFs); (iii) to evaluate the element concentrations in grain with regard to the Dietary Reference Intake (USDA DRI 2004) levels for the intake of mineral nutrients; and (iv) to screen for potentially hazardous element accumulation in wheat and buckwheat grain and to compare these with the maximal tolerable levels of elements in plants used for food, according to the literature.

Materials and Methods

Experimental design

Wheat (*Triticum aestivum* L.) cv. Remus, common buckwheat (*Fagopyrum esculentum* Moench) cv. Darja, and tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.) cv. domestic population of Luxembourg, were sown on two plots (6 m × 24 m) in an experimental field within a wheat and buckwheat producing agricultural area in Moravče, near Ljubljana, Slovenia (382.6 m above sea level, 46°8’34.75’’N, 14°41’54.71’’E). For each of the plots, the grain were sown in a 6 × 3 factorial experimental design (4 parallels/species). The individual seeding beds of 2 m × 2 m were separated by 1-m-wide belts. On average, 200 grains/m^2 were sown for wheat, and 400 grains/m^2 for buckwheat. The wheat grain were sown in April 2011 and harvested when they reached maturity, which was 94 days after sowing. The common and tartary buckwheat varieties were sown in May 2011, and harvested at maturity at 136 days and 128 days after sowing, respectively. Grain yield estimates calculated from the average biomass of grain per plots were: 112.5 kg/ha for wheat, 969.7 kg/ha for common buckwheat, and 751.1 kg/ha for tartary buckwheat.

Soil samples collected prior to the experiment were examined at the Agricultural Institute of Slovenia, and these demonstrated that the soil was moderately acidic (pH 6.4; ISO 10390), with an organic matter content of 4.9% (ISO 14235). The concentrations of the biologically available nutrients were as follows: 89 mg/100 g P_2O_5 (MET/Z/016); 70 mg/100 g K_2O (MET/Z/017); 21 mg/100g Mg (MET/Z/018); and 7.7 mg/kg NO_3-N (RQ – flex).

Rhizosphere soils

At harvest, the rhizosphere soil of each plant was collected, passed through a 1-mm sieve, and dried at 50 °C for 24 h. Energy dispersive X-ray fluorescence spectrometry (EDXRF) was used to determine the total element concentrations of the soil. The concentrations of the biologically available elements were determined using total reflection X-ray fluorescence spectrometry (TXRF), at the Jožef Stefan Institute.

For the determination of the total soil element concentrations, 250 mg soil per sample was powdered and compressed into pellets using a pellet die and a hydraulic press. These pellets were analysed using a EDXRF spectrometer. An annular radioisotope excitation source of Fe-55 and Cd-109 from Isotope Products Laboratories U.S.A. was used as the primary excitation source. The emitted fluorescence radiation was measured by an energy dispersive X-ray spectrometer composed of a Si(Li) detector (Canberra), a spectroscopy amplifier (Canberra M2024), an analog-to-digital converter (Canberra M8075), and a PC-based multichannel analyser card (S-100, Canberra). The energy resolution of the spectrometer was 175 eV at 5.9 keV. The estimated uncertainty of the analysis was from 5% to 10% (Nečemer et al. 2008).

Analysis of the bioavailable elements was performed according to Baker et al. (1994). In brief, 5 g dried soil was suspended in 25 ml 1 M ammonium acetate solution (pH 7) and shaken for 2 h at 23 °C. The extracts were filtered through 0.4 μm Millipore membrane filters. For TXRF analysis, the 10 ml soil extracts were spiked with 100 μl Ga standard solution (Sigma-Aldrich), as an internal standard. From these spiked solutions, 10 μl was applied twice to a quartz sample carrier plate and dried in a desiccator. The X-ray spectrometer was based on a Si(Li) detector (Princeton Gamma Tech.), with a resolution of approximately 145 eV at 5.9 keV, an integrated signal processor (M 1510, Canberra), and a PC-based multichannel analyser card (S-100, Canberra). A Seifert X-ray generator (Rich Seifert & Co) model ISO-DEBYFLEX 3003 (60 kV, 80 mA), and a Mo anode fine focus

X-ray tube (FK 60-04, Rich. Seifert & Co.) were used. The estimated uncertainty of the element analysis was between 5% and 10% (Nečemer et al. 2008). The sensitivity level, however, strongly depended on the atomic number of the element; although it extended down to a few ppb (1 ng/g dry weight) for the TXRF (Schwenke and Knoth 1993), compared to a few ppm (1 mg/g dry weight) for the heavier elements using EDXRF (Vogel-Mikuš et al. 2010).

Grain analysis

The mature dry harvested grain of the wheat and common and tartary buckwheat were weighed and ground in liquid nitrogen using a porcelain mortar and pestle. The element concentrations were then determined using TXRF. In brief, 100 mg grain powder was placed in Teflon vessels and spiked with 3 ml 65% HNO_3. A CEM MARS 5 microwave oven (Matthews, NC, USA) was used for chemical digestion of the grain samples. The vessels were gently shaken to wet the samples with the acid, and then covered using vessel caps and put onto the rotor plate. The digestion procedure was performed using the following temperature programme: ramp up to 180 °C over 20 min, hold at 180 °C for 20 min, and cool over 20 min. Upon cooling, the Teflon vessels were vented and the vessel caps removed (Nečemer et al. 2008). The element compositions in these grain samples were then determined by TXRF.

The BCFs of the elements were calculated as [(total grain concentration)/(bioavailable soil concentration)] (Baker 1981; Mensch et al. 2010).

To define the contributions of the elements to the daily recommended dietary allowances, the relative proportions of the elements in 100 g grain with respect to the Dietary Reference Intakes (DRIs) were calculated as follows: Element content in 100 g grain (mg/100g)/DRI (mg/d). These data are expressed as percentages, in terms of the Recommended Dietary Allowances (RDAs), the Adequate Intake Levels (AIs) and/or the Tolerable Upper Intake Levels (ULs) (USDA DRI 2004).

The total concentrations of phosphorous, were measured using a UV-VIS spectrophotometer (Shimadzu UV-1800) at the Biotechnical Faculty of the University of Ljubljana (Olsen et al. 1982). The grain were mineralised by microwave-assisted wet digestion, as described above. After digestion, 1 ml digest was spiked with 2 ml MoV reagent and 7 ml 0.2% HNO_3. Absorption of the samples was measured at 400 nm. A standard phosphorous solution (Sigma-Aldrich) was used to prepare the calibration curve.

Statistical analysis

Statistical analysis of the element concentrations was performed using Statistica Statsoft 8.0 software. One-way ANOVA and *post-hoc* Duncan's tests were used to calculate the differences in the grain biomass, the concentrations of the elements in the soil and grain, and the BCFs ($p < 0.05$).

Results

Nutrients in soil

The soil nutrient concentrations were determined at the Agricultural Institute of Slovenia prior to the experiments (see Materials and Methods). These were compared to the recommended values of the elements in soil and the norms for fertilising (Mihelič et al. 2010), which showed that the nutrient supply was in general good or in excess. The element composition of the rhizosphere soil of each of the plants was determined after the harvest, using EDXRF (Tab. 1), and these data confirmed the high total element concentrations. For the total soil concentrations, Zn (122 mg/kg) was within the range of acceptable levels (Ur. list RS 68/1996), Cu (80 mg/kg) and Pb (91 mg/kg) were close to the alert concentrations, Ni (84.4 mg/kg) was in the range of the alert levels, and Cr (366 mg/kg) was close to the critical values. With the soil ammonium acetate extractable fraction analysis, however, only Cr (1.94 mg/kg) exceeded the values defined in the guidelines for field, horticulture and homeowner soil tests for heavy metals (Grubinger and Ross 2011).

Plant growth and nutrient accumulation

The grain biomass of the wheat (0.023 g) and common buckwheat (0.024 g) did not differ significantly, whereas the biomass of the tartary buckwheat grain was significantly lower (0.017 g;

Table 1: Total and biologically available element concentrations in the rhizosphere soil determined by EDXRF, and recommended rates of supply[a,b] or soil pollution classification concentrations[c].

Tabela 1: Skupne in biološko razpoložljive koncentracije elementov v rizosfernih tleh določene z EDXRF, priporočene vsebnosti[a,b] in klasifikacija koncentracij za onesnažena tla[c].

Element	Soil concentrations (mg/kg)		Rates of supply of the soil[a,b] Levels in soils[c] (mg/kg)		
	Total	Available	Poor[a,b] Limit[c]	Adequate[a,b] Alert[c]	Extreme[a,b] Critical[c]
K	17325 ± 1126	nd	nd	nd	nd
Ca	7318 ± 301	1529 ± 31.1	<1000[b]	nd	>2000[b]
Cr	366 ± 62.8	1.94 ± 0.08	100[c]	150[c]	380[c]
Mn	2200 ± 68.9	9.76 ± 0.92	30[a]	45[a]	60[a]
Fe	44600 ± 204	5.93 ± 1.39	nd	nd	nd
Ni	84.4 ± 10.6	0.43 ± 0.06	50[c]	70[c]	210[c]
Cu	80 ± 7.4	0.46 ± 0.05	<3[a] 60[c]	5.5[a] 100[c]	8[a] 300[c]
Zn	122 ± 4.2	1.18 ± 0.56	<1.1[a] 200[c]	2.05[a] 300[c]	>3.0[a] 720[c]
Ti	10600 ± 227	3.25 ± 0.17	nd	nd	nd
Br	nd	0.27 ± 0.02	nd	nd	nd
Pb	91 ± 2.7	0.39 ±0.18	85[c]	100[c]	530[c]

[a](Mihelič et al. 2010); [b](Marx et al. 1999); [c](Ur. list RS št. 68/1996).
nd –not determined.
Data are means ± SE (n = 4)
Srednja vrednost ± SN (n = 4)

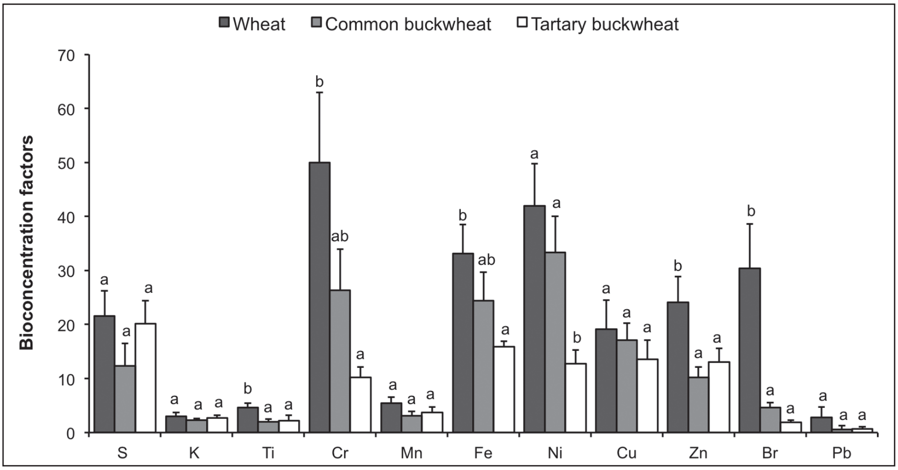

Figure 1: Bioconcentration factors for the elements in the wheat, common and tartary buckwheat grain (as indicated), as calculated from (total grain concentration)/(bioavailable soil concentration). Data are means ± SE, ($n_{\text{Wheat}} = 7$; $n_{\text{Common buckwheat}} = 7$; $n_{\text{Tartary buckwheat}} = 6$). Different letters indicate statistically significant differences in the one-way ANOVA and Duncan's *post-hoc* tests ($p < 0.05$).

Slika 1: Biokoncentracijski faktorji elementov pšenice, navadne in tatarske ajde [(celotne koncentracije v semenih)/(biološko razpoložljive koncentracije v tleh)] (srednja vrednost ± SN, $n_{\text{Pšenica}} = 7$, $n_{\text{Navadna ajda}} = 7$, $n_{\text{Tatarska ajda}} = 6$). Črke nad stolpci povprečnih vrednosti označujejo statistično značilne razlike testa enosmerne ANOVA in Duncanovega *post-hoc* testa ($p < 0.05$).

$p < 0.05$; one-way ANOVA and Duncan's *post-hoc* tests).

The concentrations of the measured macronutrients (P, S, K) were higher in the wheat than in the common and tartary buckwheat, whereas the highest concentration of Ca was in the tartary buckwheat (Tab. 2). The wheat also contained the highest concentrations of the microelements Cr, Fe, Ni, Cu and Zn, and the highest concentration of Br.

The grain BCFs (as [total grain concentration]/[bioavailable soil concentration]; Baker 1981; Mensch et al. 2010) for S, K, Mn and Pb did not differ significantly between these species, whereas the BCFs of Ti, Zn and Br were higher in the wheat than in the common and tartary buckwheat (Fig. 1). In addition, the BCFs for Cr, Fe and Ni were significantly lower in the tartary buckwheat, as compared to the wheat.

The nutritive values of the grain were compared on the basis of the grain element contents in a sample of 100 g grain. The results show that the contents of the macroelements in wheat are in general higher than in both of the buckwheat species. The amounts of the daily needs of adults that a portion of grain covers were calculated for each of the elements through a comparison of the grain contents (mg/100 g) with the DRI (mg/d) for adults (considering the RDAs and the AIs (USDA DRI 2004) (Tab. 2)). If all of the minerals in the consumable seed tissues were in a form available for absorption, a portion of the wheat grain (100 g) would almost cover the daily needs

Table 2: Element concentrations in the grain of the wheat, common and tartary buckwheat, and relevant Dietary Reference Intakes for adults, where available.

Tabela 2: Koncentracije elementov v zrnju pšenice, navadne in tatarske ajde in prehranski referenčni vnosi za odrasle (DRI).

Element		Concentration (µg/g)			DRI		
		Wheat	Common buckwheat	Tartary buckwheat	RDA (mg/d)	AI (mg/d)	UL (mg/d)
Macro	P	620 ± 6.0 a	315 ± 28.0 b	263 ± 14.0 c	700	nd	4000
	S	322 ± 23.0 a	170 ± 33.0 b	326 ± 32.0 a	nd	nd	nd
	K	1663 ± 96.0 a	1182 ± 102.0 b	1356 ± 94.0 b	nd	4700	nd
	Ca	314 ± 31.0 b	233 ± 16.0 b	440 ± 37.0 a	nd	1000	2500
Micro	Cr	40.5 ± 2.8 a	16.8 ± 1.6 b	10.8 ± 1.3 b	nd	0.030	0.2*
	Mn	12.5 ± 1.1 a	9.52 ± 0.57 a	10.9 ± 1.3 a	2.05	nd	11
	Fe	115 ± 6.0 a	56.6 ± 3.2 b	52.6 ± 5.2 b	nd	13	45
	Ni	12 ± 0.4 a	6.46 ± 0.32 b	3.9 ± 0.12 c	nd	0.0275	1.0
	Cu	5.08 ± 0.19 a	4.24 ± 0.37 b	2.69 ± 0.27 c	0.90	nd	10
	Zn	25.4 ± 1.5 a	15.7 ±1.0 b	17.6 ± 2.3 b	9.5	nd	40
Trace	Ti	6.07 ± 0.85 a	4.48 ± 0.35 ab	2.73 ± 0.66 b	nd	0.35**	nd
	Br	8.34 ± 1.13 a	1.16 ± 0.04 b	0.39 ± 0.05 b	nd	nd	nd
	Pb	1.33 ± 0.33 a	1.45 ± 0.12 a	0.83 ± 0.17 a	nd	0.27*	1.75*

DRI, Dietary Reference Intakes for adults (USDA DRI 2004); RDA, Recommended Dietary Allowance; AI, Adequate Intake Level; UL, Tolerable Upper Intake Level; *(NSF/ANSI 173 2003); **(WHO 1982).
nd, not determined.
Data are means ± SE ($n_{\text{Wheat}} = 15$; $n_{\text{Common buckwheat}} = 7$; $n_{\text{Tartary buckwheat}} = 9$).
Different letters indicate statistically significant differences across the columns of one-way ANOVA and Duncan's *post-hoc* tests ($p < 0.05$) between plant species.

DRI, prehranski referenčni vnosi za odrasle (USDA DRI 2004); RDA, priporočeni dnevni prehranski referenčni vnosi; AI, primerni dnevni prehranski referenčni vnosi; UL, zgornje dopustne vrednosti dnevnega vnosa; *(NSF/ANSI 173 2003); **(WHO 1982).
nd, ni določeno.
Srednja vrednost ± SN; ($n_{\text{Pšenica}} = 15$, $n_{\text{Navadna ajda}} = 7$, $n_{\text{Tatarska ajda}} = 9$)
Črke ob povprečnih vrednostih po stolpcih označujejo statistično značilne razlike testa enosmerne ANOVA in Duncanovega *post- hoc* testa ($p < 0,05$) med rastlinskimi vrstami.

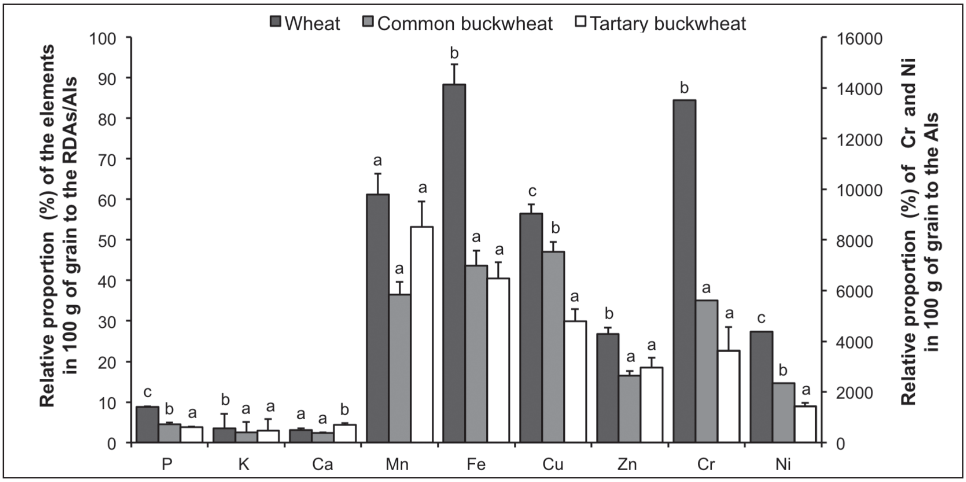

Figure 2: Elements in 100 g of the wheat, common and tartary buckwheat grain relative [%] to the RDAs or AIs (USDA DRI 2004) (see Materials and methods for details). Data are means ± SE ($n_{\text{Wheat}} = 15$; $n_{\text{Common buckwheat}} = 7$; $n_{\text{Tartary buckwheat}} = 9$). Different letters indicate statistically significant differences in the one-way ANOVA and Duncan's *post-hoc* tests ($p < 0.05$).

Slika 2: Elementi v 100 g zrnja pšenice, navadne in tatarske ajde v odstotnih deležih [%] priporočenih dnevnih vnosov (RDAs) oziroma vrednosti primernih dnevnih vnosov (AIs; USDA DRI 2004) (Glej Materiale in metode). (Srednja vrednost ± SN ($n_{\text{Pšenica}} = 15$, $n_{\text{Navadna ajda}} = 7$, $n_{\text{Tatarska ajda}} = 9$). Črke nad stolpci povprečnih vrednosti označujejo statistično značilne razlike testa enosmerne ANOVA in Duncanovega *post-hoc* testa ($p < 0.05$).

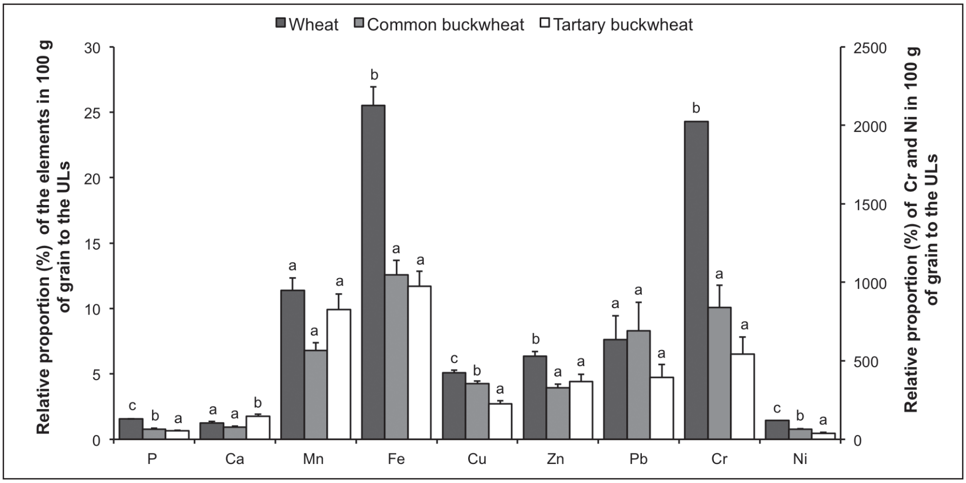

Figure 3: Elements in 100 g of the wheat, common and tartary buckwheat grain relative [%] to the ULs (USDA DRI 2004) (see Materials and methods for details). Data are means ± SE ($n_{\text{Wheat}} = 15$; $n_{\text{Common buckwheat}} = 7$; $n_{\text{Tartary buckwheat}} = 9$). Different letters indicate statistically significant differences in the one-way ANOVA and Duncan's *post-hoc* tests ($p < 0.05$).

Slika 3: Elementi v 100 g zrnja pšenice, navadne in tatarske ajde v odstotnih deležih [%] zgornjih dopustnih vrednosti (ULs (USDA DRI 2004) (Glej Materiale in metode). (Srednja vrednost ± SN, $n_{\text{Pšenica}} = 15$, $n_{\text{Navadna ajda}} = 7$, $n_{\text{Tatarska ajda}} = 9$). Črke nad stolpci povprečnih vrednosti označujejo statistično značilne razlike testa enosmerne ANOVA in Duncanovega *post-hoc* testa ($p < 0.05$).

of adults for Fe, with 60% for Mn, and 50% for Cu (Fig. 2). In comparison, a portion of common buckwheat (100 g) would cover 50% of the daily requirement for Fe and Cu, whereas for tartary buckwheat grain it would cover 50% of the daily needs for Mn and 40% for Fe.

It is also of importance that the concentrations of Cr and Ni in wheat critically exceeded the DRI AIs, and the recommended concentrations were also exceeded in the grain of both of the buckwheats (Fig. 2). Therefore, the contents in 100 g of grain are compared to the ULs (USDA DRI 2004) (Tab. 2). These data show that the contents of Cr in 100 g of wheat and common and tartary buckwheat exceed the upper limits by 20.3-fold, 8.5-fold and 5.5-fold, respectively, whereas the contents of Ni only slightly exceed the upper limits (1.2-fold) in wheat, but not in common and tartary buckwheat (Fig. 3).

Discussion

Large variations in the mineral element compositions of the edible portions have been reported between different crop species (White and Broadley 2005), and efforts to improve the element composition of wheat have resulted in the selection of crop cultivars with significantly improved use of Fe and Zn (Cakmak et al. 2010). In the present study, higher BCFs are seen in wheat for Cr, Fe, Ni, Cu, Zn and Br when compared to both of the buckwheat species, which has been identified as one of the most important factors that drives the higher efficiency of wheat element bioextraction from the same soluble soil mineral nutrient pool. As a consequence, wheat shows higher concentrations of these elements in the grain when compared to both of the buckwheat species. These differences can be attributed to differences in the physiology of nutrient uptake, xylem loading, element remobilisation from the leaves, and seed deposition processes in wheat, when compared to buckwheat.

The total grain element concentrations in the whole grain of these analysed species are significantly higher than the concentrations of macronutrients and micronutrients that have been commonly reported for wheat and buckwheat flours (Czerniejewski et al. 1964; Ikeda et al. 2000; 2006). Element localisation studies within the grain have demonstrated that the majority of the essential nutrients in the grain of wheat and buckwheat are stored in the embryo and aleurone tissues in specialised cellular and subcellular compartments, while their concentrations in the endosperm are generally very low (Mazzolini et al. 1985; Vogel-Mikuš et al. 2009; Lombi et al. 2011; Pongrac et al. 2011; Regvar et al. 2011). As a consequence of these structurally related localisation patterns, large amounts of mineral nutrients are readily lost by milling and polishing of the grain. It has therefore been suggested that different flour fractions that are prepared by successive milling can be successfully reintroduced as a dietary source of essential elements (Ikeda et al. 2000). Thus, as well as the need for optimisation of the grain element accumulation properties, refinements in flour production technology should prove useful in future attempts to resolve the problem of mineral malnutrition in humans.

Based on the comparison of the mineral compositions with the intake of minerals (the AIs), we show here that on average 50% of the needed daily intake of Mn can be covered by 100 g of wheat or tartary buckwheat grain. All three species are also good sources of Fe, and also of Cu. It should be noted, however, that although the total amounts of elements might be the same as in other food sources, Fe and Zn from vegetable sources are likely to be less available for absorption due to the differences in their chemical forms and/or to the presence of phytic acid and other constituents that can reduce the absorption (Hunt 2003), thus further diminishing the nutritive value of grain.

Intensive agricultural approaches can easily result in unintentional increases in the accumulation of various heavy metals in soils. The application of multi-element analytical techniques for analysis and screening of soils and edible plant parts is therefore particularly rewarding in contemporary monitoring programmes that are aimed at the detection of unintended contaminant metal accumulation. Application of EDXRF and TXRF analyses here shows that the field soils from conventional grain production and the grain produced on these soils can contain a wide range of unwanted metals that can easily remain overlooked in the majority of the classical soil analyses. A particularly disturbing aspect is the total soil concentrations of Cr, Ni, Cu and Pb, with Cr reaching critical levels (Ur. list RS 68/1996). In addition to these, the soil extractable Cr levels exceed those values defined in the guidelines for field, horticulture and homeowner soil tests for heavy metals (Grubinger and Ross 2011), which confirms that soil Cr concentrations in particular are of considerable concern. As a consequence, the grain of all three species here accumulated Cr in concentrations that exceeded the ULs (USDA DRI 2004). The same was also true for the accumulation of Ni in wheat. Wheat grains are known to be prone to Cu and Ni accumulation when grown in sludge-enriched soils (Wang et al. 2009). With the buckwheat grain, Ni is localised in the embryonic axis and the aleurone (Pongrac et al. 2011) as a result of the specific physiology of the grain-filling process. During milling and polishing of durum wheat, however, up to a 61% reduction in Ni and a 65% reduction in Cr have been shown in the milling product (semolina), compared to dry grain (Cubadda et al. 2005). It is therefore reasonable to expect that the metal concentrations in the milling products will be considerable lower than those found in the grain. In addition, it is of interest that this unwanted element accumulation is less severe in the buckwheat grain. Taken together, these data indicate the need for careful monitoring of such unintentional metal accumulation in grain, and the greater applicability of common and tartary buckwheat for growth in moderately polluted soils through their lower accumulation of these unwanted metals, when compared to wheat.

Conclusions

1. The higher bioconcentration capacity of wheat, when compared to the buckwheats, results from differences in the physiology of the element uptake and partitioning. This is identified as one of the most important factors that drive the greater potential for bioextraction in wheat from the same bioavailable pool of the mineral element in the soil in the field for conventional grain production. As a consequence, this results in higher concentrations of these elements at the whole grain level.
2. The low content of the nutrient elements reported for wheat and buckwheat flours compared to the grain imply that as well as optimisation of the plant accumulation properties, further changes in the flour production technology should prove useful to successfully address the problem of mineral malnutrition in humans.
3. The data indicate an accumulation of Ni and Cr in grain from soils under conventional grain production, which will primarily result from unintentional soil deposition of these elements due to agricultural activities. The application of multi-elemental analytical techniques in contemporary screening and monitoring programmes for the detection of unwanted metal accumulation is therefore suggested.
4. The lower accumulation of unwanted metals in the common and tartary buckwheat grains, when compared to wheat, indicates the greater applicability of both of these buckwheat species for grain production in metal-enriched soils that have resulted from conventional field management practices.

Povzetek

Žita in psevdožita so pomemben vir mineralov v prehrani nekaterih populacij, zato bi bilo pomembno izboljšati elementno sestavo žit in zmanjšati vnos neželenih kovin v užitne dele rastlin. Rastline lahko absorbirajo samo biološko razpoložljive elemente, ki so določene z naravno depozicijo v tleh, pH vrednostjo tal, vsebnostjo organske snovi in sposobnostjo kationske izmenjave (Marschner 1995; Moreno et al. 1996). Poleg teh dejavnikov je pomembna tudi sposobnost rastlin za privzem, transport in razporejanje esencialnih elementov v rastlinskih organih (Waters and Sankaran 2011). V tleh s konvencionalno pridelavo rastlin, pa tkiva lahko vsebujejo tudi presežne vrednosti nezaželenih elementov, ki se posledično nalagajo v rastlinah.

Izvedli smo raziskavo akumulacijske sposobnosti pšenice (*Triticum aestivum*), navadne ajde (*Fagopyrum esculentum*) in tatarske ajde (*Fagopyrum tataricum*) s polja s konvencionalno pridelavo semen. Elementno sestavo rizosfernih tal rastlin smo določili z EDXRF, in potrdili dobro preskrbljenost tal. Skupne koncentracije Zn v tleh (122 mg/kg) so bile pod mejnimi vrednostmi, koncentracije Cu in Pb (80 in 91 mg/kg) so bile blizu opozorilnih vrednosti, koncentracije Ni (84.4 mg/kg) so presegale opozorilne vrednosti, koncentracije Cr (366 mg/kg) pa so bile blizu kritičnih vrednosti (Ur. list RS, 68/1996; Tab. 1).

Biomasa zrnja pšenice (0.023 g) in navadne ajde (0.024 g) se ni značilno razlikovala, biomasa tatarske ajde (0.017 g) pa je bila statistično značilno nižja ($p < 0.05$; enosmerna ANOVA in Duncanov *post-hoc* test). Koncentracije izmerjenih makroelementov (P, S, K) in mikroelementov Cr, Fe, Ni, Cu, Zn in Br v zrnju izbranih rastlinskih vrst, določene s TXRF, so bile najvišje v zrnju pšenice, najvišje koncentracije Ca pa je imela tatarska ajda (Tab. 2). Vzorci pšenice so imeli višje biokoncentracijske indekse (BCF) za Cr, Fe, Ni, Zn in Br od tatarske ajde (Sl. 1). Biokoncentracijske faktorje smo izračunali iz razmerja med skupno koncentracijo elementov v zrnju in koncentracijo biološko razpoložljivih elementov v tleh in so pomemben pokazatelj ekstrakcijske sposobnosti izbranih rastlinskih vrst za posamezne mineralne nutriente.

Vsebnosti elementov v 100 g zrnja smo primerjali s prehranskimi referenčnimi vnosi za odrasle (USDA DRI 2004). Če bi bili vsi elementi v zrnju biološko dostopni, bi z uživanjem 100 g pšenice dnevno lahko pokrili priporočene dnevne vnose Fe 80%, dnevne vnose Mn 60%, in polovico priporočenih dnevnih vnosov Cu. Z uživanjem 100 g navadne ajde bi lahko pokrili polovico dnevnih potreb po Fe in Cu, medtem ko bi s 100 g tatarske ajde pokrili polovico dnevnih potreb po Mn in 40% priporočene vrednosti za Fe. Vendar je pri teh ocenah potrebno upoštevati, da imajo elementi v zrnju zmanjšano biološko dostopnost za absorpcijo zaradi vezanosti na fitnsko kislino in nekatere strukturne komponente semen (Hunt 2003). Nizke vsebnosti elementov v moki pšenice in ajde navedene v literaturnih virih (Czerniejewski et al. 1964; Ikeda et al. 2000; 2006) v primerjavi s koncentracijami v zrnju nakazujejo, da bi bilo poleg povečevanja privzema esencialnih elementov v zrnje koristno prilagoditi tudi tehnološke postopke priprave mlevskih izdelkov, če želimo v njih povečati količino mineralnih nutrientov.

Vsebnosti Cr in Ni so presegle primerne dnevne prehranske referenčne vnose (Adequate Intake Levels – AIs; USDA DRI 2004; Tab. 2). Primerni dnevni prehranski referenčni vnosi za Cr in Ni so bili najbolj preseženi v pšenici, vendar so bili le-ti preseženi tudi pri navadni in tatarski ajdi (Sl. 2). S primerjavo vsebnosti elementov v zrnju z zgornjimi dopustnimi vrednostmi dnevnega vnosa (Tolerable Upper Intake Levels -ULs; USDA DRI 2004; Sl. 3) smo ugotovili, da vsebnosti Cr v zrnju pšenice, navadne in tatarske ajde presegajo zgornje dopustne vrednosti za 20.3, 8.5 oziroma 5.5 krat, presežena pa je bila tudi meja dopustnega dnevnega vnosa za Ni pri pšenici. Rezultati kažejo na potrebo po sistematičnem spremljanju vnosa nezaželenih kovin v zrnje izbranih rastnskih vrst in večjo uporabnost navadne in tatarske ajde za vzgojo v tleh s konvencionalno pridelavo.

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