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MACRO AND TRACE ELEMENTS IN BARLEY (HORDEUM VULGARE L.) BREEDS IN LATVIA DEPENDING ON VARIETY, ENVIRONMENT, AND AGRICULTURAL PRACTICE

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The aim of the study was to determine concentrations of 13 macro and trace elements in different barley genotypes depending on the year of growth (2011, 2012, and 2013) and agricultural practice (conventional/organic). Cd, Pb, Cr, Ni, and Al concentrations were determined by electrothermal atomic absorption spectrometry and K, Na, Zn, Cu, Ca, Mg, Mn, and Fe concentrations by flame atomic absorption spectrometry. Statistically different concentrations of Cr, Cu, and Zn occurred among genotypes; for Ca, Mn, and Fe concentrations between barley grains, grown conventionally and organically; for Cr and Ni concentrations between hulled and hull-less grain and for Cd, Cr, Ni, Cu, Zn, Al, K, and Na concentrations among the study years. Concentrations of potentially hazardous elements were low (Cd < 0.005–0.027, Pb 0.013–0.066, Cr 0.111–0.327, Ni 0.161–1.264, Cu 2.8–4.7 and Al 1.62–6.09 mg·kg⁻¹). Barley products can provide necessary macro and trace elements, especially of Mn, Mg, Fe, and Zn (7.8–16.1; 1024–1249; 29.2–52.9, and 20.5–33.7 mg·kg⁻¹, respectively).

Key words: conventional farming, organic agriculture, statistical indicators, risk assessment, nutritional aspects.

INTRODUCTION

Cereals are the most important food source for human consumption. From the approximately 2.3 billion tonnes of cereals currently produced, roughly 1 billion tonnes are used as a source of human food and world cereal supplies remain high (Anonymous, 2013). Cereal products provide significant amounts of most nutrients including relevant quantities of minerals and are an important part of a balanced diet in many countries. In Europe the average annual consumption of cereal grains is 131 kg per capita (Poutanen, 2012).

Barley (*Hordeum vulgare* L.) is one of the most important cereals grown worldwide and in 2016 barley production in the EU was 59 990 thousand tonnes, including 289 thousand tonnes produced in Latvia (Anonymous, 2016), where most of the yield is used for feed. Barley historically has been an important food source in many parts of the world, including in the Middle East, North Africa, Asia and northern and eastern Europe and there is increased interest in barley food because of its nutritional value (Baik and Ulrich,

2008), but human consumption of barley is still relatively low. According to the EU Cereals Balance Sheet for the marketing year 2016/2017, the human use of wheat is 47.8 million tonnes (from total use 117.0 million t) and human use of barley is only 0.4 million t (from the total use of cereals 51.0 million t) (Anonymous, 2017).

From the nutritional point of view, attention is mainly focused on essential macro elements (K, Ca, and Mg) and trace elements (Fe, Cu, Mn, and Zn) in grain products. Minerals in cereal grain, also in barley, are mostly found in the aleurone layer (Lui *et al.*, 2007; Poultanen, 2012). Mineral and vitamin deficiencies affect a greater proportion of the world's population than does protein energy malnutrition. Even though micronutrients are needed in a minute quantities (i.e. micrograms to milligrams per day), they have a tremendous impact on human health and wellbeing. Insufficient dietary intakes of these nutrients impair the functions of brain, immune and reproductive systems and energy metabolism (Graham *et al.*, 2001).

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Transfer of various elements to the food chain of humans is significantly affected by the geological origin of the soils and the groundwater basin as well as the growing area of the cereals. Some trace elements like Fe, Mg, Zn, and Co, are essential micronutrients with a variety of biochemical functions in all living organisms. However, the benefits of these micronutrients may be completely reversed at too high concentrations. Some heavy metals, particularly Cd and Pb, have been considered as serious soil and environment pollutants due to their toxicity at low concentrations (Korkmaz *et al.*, 2010).

Concentration of toxic heavy metals (Pb, Cd, Cr) and their effect on human health and the amounts of essential heavy metals (Ni, Cu, Zn) in agricultural products have been reported previously (Pirsaheb *et al.*, 2015). Pb and Cd are very toxic even at low concentrations, Cr is carcinogen, but it is essential at low concentrations, Ni can be toxic, but normally occurs at very low concentrations, and Zn and Cu are needed for humans at certain levels.

Hull-less barley as a whole grain cereal with increased content of soluble fibre has been recognised as more valuable and economic in the food industry than covered barley, because of interest of consumers and publicity on healthy food products (Baik and Ullrich, 2008). Research on hull-less barley and its cultivation is now receiving more emphasis and indicates potential for various end uses, also in Latvia (Bleidere *et al.*, 2013a; 2013b). Unlike hulled barley, it is possible to use hull-less barley in food products directly without de-hulling. The outer parts of grain, which contain more dietary quality related compounds, including macro and trace elements, can be included in food.

The quality of human life depends on the chemical composition of food and on the environment (Kabata-Pendias, 2011). Soil is the main source of trace elements for plants, both of micronutrients and pollutants (Kabata-Pendias and Mukherjee, 2007). The macro and trace element contents of plants are affected by the cultivar of plant, soil conditions, weather conditions during the period of growth, use of fertilisers and the state of the plant maturity at harvest (Kabata-Pendias, 2011). As agriculture is the primary source of all micronutrients for human consumption, agricultural systems must contribute to dysfunctional food systems failing to meet the nutritional needs of everyone (Welch and Graham, 2005).

Demand for organic agriculture and environmentally-friendly agricultural products is increasing worldwide. In this respect, it is not known whether and how different agriculture techniques and/or cultivation systems may affect the composition of nutrients in the final product. Comparison of organic and conventional foods in terms of nutritional value, sensorial quality and food safety has often highlighted controversial results. As a consequence, a clear link between cultivation system and nutritional profile of agricultural products is still missing (Bourn and Prescott, 2002).

The aim of the study was to determine macro and trace element concentrations in different barley genotypes depending on environment and agricultural practice, and evaluate risks regarding Cd, Pb, Cr, Ni, Cu, and Zn concentrations in barley and nutritional aspects regarding K, Na, Ca, Mn, Mg, Fe, Cu, Zn, and Cr concentrations in barley.

MATERIALS AND METHODS

Soil, climate and agronomical practice. Grain cultivation was carried out from 2011 to 2013 at the Stende Research Centre (SRC) (57°11'35" N, 22°33'19" E, ~80 m above mean see level). Barley was cultivated both organically and conventionally as described further.

Organic field. The soil type was sod-podzolic, sandy loam and loamy sand (Eutric Abeluvisols sandy loam). Organic substance concentration was 20.2–21.6 $\rm mg\cdot kg^{-1}$, $\rm pH_{KCl}$ was 5.27–5.89, and concentration of plant-available phosphorus ($\rm P_2O_5$) was 138–164 $\rm mg\cdot kg^{-1}$, and of potassium ($\rm K_2O)$ — 130–175 $\rm mg\cdot kg^{-1}$. Common agronomic practices for organic management were used during the vegetation period.

Conventional field. The soil type in the conventional field was sod-podzolic, sandy loam and loamy sand (Eutric Abeluvisols sandy loam), concentration of organic substances was 21–24 mg·kg⁻¹, pH_{KCl} was 5.4–5.8, available phosphorus (P_2O_5) concentration was 137.0–158.8 mg·kg⁻¹, and of potassium (K_2O) — 175.7–211.0 mg·kg⁻¹. The experimental treatment consisted of three N rates - N80, N120, and N160 in conventional growing conditions. Complex mineral fertiliser was used as a basic fertiliser at the rate 725 kg·ha⁻¹ $(N - 80, P - 28.6, K - 112.4 \text{ kg} \cdot \text{ha}^{-1})$. The application of N was split, part was applied at the time of sowing and the remaining half at the end of the tillering stage (growing stage/GS 29) of the crop. Ammonium nitrate (N 34%) was used as top-fertiliser in the following amounts: 40 kg N per ha (N120) and 80 kg N per ha (N160). The treatments were laid out in a randomised complete block design; the plot size was 10 m² and four replicates were used.

Weather conditions. The average air temperature from April to August differed annually in the period 2011–2013 (Table 1). The most significant differences in temperature were noticed in June: 13 °C in 2012) and 17 °C in 2011 and 2013). Temperature was similar in August in all study years (15.5 to 16.6 °C). Precipitation differences between the study years (Table 1) were most significant in July — 36 (2013) to 165 mm (2011). The weather conditions were warmer than long-term average observations with heavy rainfall occasionally during the growing period of 2011.

Description of the studied barley. In cooperation with the Stende Research Centre the following barley cultivars/genotypes were used in the study: three hull-less genotypes '1185', 'Kornelija', '1165', and hulled variety 'Ansis'. Hull-less breeding line '1185' is characterised by high grain yield, starch, α -tocopherol concentration and radical scavenging activity, line '1165' has high total phenol concentra-

Table 1

AVERAGE TEMPERATURE AND PRECIPITATION SUM AT STENDE, 2011–2013

Month	Ave	rage tem	perature	e, °C	Precipitation sum, mm						
	2011	2012	2013	2013 Norm		2012	2013	Norm			
April	6.9	5.6	4.0	4.3	26.8	42.7	34.9	37			
May	10.6	11.0	13.7	10.2	54.7	58.9	86.1	45			
June	16.8	13.2	16.9	14.2	59.6	78.7	74.5	57			
July	19.2	17.5	16.9	16.3	165.3	91.7	36.2	87			
August	16.3	15.5	16.6	15.5	155.0	115.1	45.2	87			
Average	14.0	12.6	13.6	12.1	92.3	77.4	55.3	62.6			

tion, and variety 'Kornelija' has high crude protein and β -glucan concentration in grain (Bleidere *et al.*, 2013a; Bleidere *et al.*, 2013b). Hulled barley 'Ansis' is a widely grown variety in Latvia. In the article coding is used for designation of the growing system (Table 2).

Barley genotypes were sown with a compact trial drill "Hege 80" in a well prepared seedbed at a rate of 500 germinating seeds per m². The plot size was 10 m² and four replicates were used. The yield was harvested using a combine "Hege 140". Sampling was done according to the ISO 950 Cereals-Sampling (as Grain) standard.

Analysis of macro and trace elements. Concentrations of thirteen macro and trace elements (Cd, Pb, Ni, Cr, Al, Cu, K, Na, Mn, Fe, Zn, Mg, Ca) were determined in cereal grain samples (n = 48) provided by the Stende Research Centre (collected in 2011–2013). Average moisture content in the grain was 10–13%.

Sample mineralisation. Grain was ground and 0.5–1.0 g was weighed in a crucible, which was placed in a muffle furnace with a programmable heating regime. Grain samples were dried for 1 h at 110 °C; then the temperature was increased (50 °C h⁻¹) until 450 °C and held for eight hours. Then the crucible was removed from the muffle furnace and cooled to room temperature, and 1–3 ml of water was added to the dry residue. This procedure was repeated until light grey or white ash was obtained. Then 2 ml 6 M HCl were added and evaporated. The residue was dissolved in 25 ml 0.1 M HNO₃ (Anonymous, 1999). The obtained solutions were used for chemical analysis.

Concentrations of five elements (Cd, Cr, Al, Pb, and Ni) were determined by electrothermal atomic absorption spectrometry with Zeeman background correction (ETAAS; Perkin Elmer AAnalyst 600, Shelton, USA) after dry digestion, and concentrations of eight elements (K, Na, Zn, Cu, Ca, Mg, Mn, and Fe) were determined by flame atomic absorption spectrometry (FAAS; Perkin Elmer AAnalyst 800, Shelton, USA).

Quality assurance. Analytical performance of the applied procedure was checked by the intra-laboratory validation procedure in accordance to the Commission Regulation (EC) No. 333.2007. Relative standard deviation % and accuracy within the interval 70–115% was obtained for all elements. Quantification limits of the applied analytical procedure varied between 0.005 mg·kg⁻¹ (cadmium) and 1 mg·kg⁻¹ (potassium and sodium). In addition, the analytical procedure was successfully checked (z-score below 2) by participation in the proficiency testing rounds organised by the European Union Reference Laboratory.

Data processing. For statistical analysis, the data were processed using the IBM Corp. Released 2013. IBM SPSS Statistics for Windows, Version 22.0. Armonk, NY: IBM Corp.

For data analysis descriptive statistics and non-parametric statistics methods (Kruskal-Wallis test and Mann-Whitney test) were used.

Human exposure and nutritional value assessment. Calculation of use of grain and grain products in Latvia was done using the data of the Central Statistical Bureau of Latvia on consumption of flour, dough, flakes, bread, pasta, pizza, pastry etc. per capita in 2015 (Anonymous, 2015a). The calculated human consumption was ~130 g per day per capita.

The values of Estimated Weekly Intake (EWI) or Estimated Daily Intake (EDI) were calculated using a formula published previously (Anonymous, 2005) and modified by Reinholds *et al.* (2017):

$$D = C \times 0.13 \times \frac{T}{60}$$

where: D (= EWI or EDI) — exposure dose in $\mu g \cdot kg^{-1}$ per week (or per day) per kg of body weight, C — element concentration $\mu g \cdot kg^{-1}$ grain, 0.13 — human intake of grain

Table 2

DESCRIPTION AND CODING SYSTEM OF THE BARLEY SAMPLES

Coding system		Lines	Description	Additional information	
Genotype +	growing systems				
1185	(1) Grown organically:	Simba/Wanubet	hull-less barley breeding line	SRC breeding material	
Kornelija	+BIO	IC360	hull-less barley breeding line	breed at SRC, 2014	
1165	(2-4) Grown conventionally:	Gainer/Freedom	hull-less barley breeding line	SRC breeding material	
Ansis	+80 N supply 80 kg/ha etc.	-	hulled, widely grown malting barley variety	breed at SRC, 1999	

Example of coding: '1185'+BIO – genotype 1185 grown organically; '1185'+80 – genotype 1185 grown conventionally with N supply 80 kg-ha⁻¹; SRC, Stende Research Centre

products in kg per capita per day, and T=7 days per week (or T=1 for daily intake), 60 — theoretical weight of human body 60 kg. The results were compared with published data and recommendations.

RESULTS

Concentrations of macro elements in four barley genotypes depending on growing conditions (conventional growing with three different nitrogen supplies and organic growing) are shown in Table 3.

Potassium (K) concentration was from 3914 mg· kg⁻¹ in 'Kornelija'+160 to 4801 mg·kg⁻¹ in "1185"+80, sodium (Na) concentration from 49 mg·kg⁻¹ in 'Ansis'+BIO to 142 mg·kg⁻¹ in 'Kornelija'+80, calcium (Ca) concentration was from 276 mg·kg⁻¹ in '1165'+BIO to 447 mg·kg⁻¹ in 'Ansis'+80 (see Table 3). K, Na, and Ca concentrations did not significantly differ between barley genotypes (Kruskal–Wallis test, p > 0.05).

Magnesium (Mg) concentration was from 1024 mg·kg⁻¹ in '1185'+160 to 1249 mg·kg⁻¹ in 'Kornelija'+120 (see Table 3). Mg concentration between barley genotypes significantly differed (Kruskal–Wallis test $\chi 2 = 12.626$, p = 0.006). Mg concentration significantly differed between barley varieties 'Kornelija' and '1185' (pairwise comparisons with Bonferroni correction, adjusted p = 0.012).

Iron (Fe) concentration was from 29.2 mg·kg⁻¹ in '1185'+ BIO to 52.9 mg·kg⁻¹ in 'Kornelija'+120 (see Table 3). Fe concentration between barley genotypes significantly differed (Kruskal–Wallis test, $\chi 2 = 15.002$, p = 0.002). Fe concentration significantly differed between barley varieties '1185' and 'Kornelija' and also '1185' and 'Ansis' (pairwise comparisons with Bonferroni correction, adjusted p-values 0.001, and 0.047, respectively).

Concentrations of trace elements in four barley genotypes depending on growing conditions (conventional growing with three different nitrogen supplies and organic growing) are shown in Table 4.

<u>Cadmium (Cd)</u> concentration was under the detection limit in 3 samples ('1185+120, '1185' BIO and '1165' BIO) and the highest value was $0.027 \text{ mg} \cdot \text{kg}^{-1}$, in 'Kornelija'+80 (see Table 4). The concentration of Cd did not significantly differ between barley genotypes (Kruskal–Wallis test, p > 0.05).

<u>Lead (Pb)</u> concentration was from 0.013 mg·kg⁻¹ in '1165'+80 to 0.066 mg·kg⁻¹ in 'Kornelija'+120 (see Table 4). Pb concentration did not significantly differ between barley genotypes (Kruskal–Wallis test, p > 0.05).

Chromium (Cr) concentration was from 0.111 mg·kg⁻¹ in '1185'+80 to 0.327 mg·kg⁻¹ in 'Ansis'+120 (see Table 4). The concentration of Cr between barley genotypes significantly differed (Kruskal–Wallis test $\chi 2 = 8.506$, p = 0.037).

Table 3 CONCENTRATIONS OF MACRO ELEMENTS IN BARLEY GENOTYPES DEPENDING ON GROWING CONDITIONS, mg·kg⁻¹

Element	Sample of	Convention	nal, N = 80*	Conventiona	al, N = 120**	Conventiona	l, N = 160***	Org	anic
	barley	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range
K	1185	4801 ± 535	4213-5260	4702 ± 742	3846-5150	4175 ± 448	3676-4540	4648 ± 207	4415-4810
	Kornelija	4097 ± 428	3630-4470	4558 ± 236	4295-4750	3914 ± 295	3611-4200	4128 ± 202	3990-4360
	1165	4161 ± 761	3494-4990	4608 ± 731	3765-5060	4463 ± 631	3910-5150	4327 ± 437	4050-4830
	Ansis	4342 ± 287	4067-4640	4526±366	4158-4890	4623 ± 460	4160-5080	4684 ± 94	4610-4790
Na	1185	127 ± 186	20-342	96 ± 116	22-230	86 ± 112	18-215	84 ± 89	24-186
	Kornelija	142 ± 202	20-375	131 ± 155	21-308	116 ± 159	20-299	95 ± 117	19-229
	1165	59 ± 37	18-90	90 ± 87	18-187	95 ± 92	18-197	98 ± 98	16-206
	Ansis	70 ± 43	21-101	88 ± 63	21-150	55 ± 44	20-105	49 ± 26	19–64
Ca	1185	326 ± 32	296-360	351 ± 16	337–368	350 ± 14	335–363	307 ± 9	298-315
	IC-360	361 ± 77	289-442	380 ± 77	302-456	382 ± 41	339-420	318 ± 28	291-347
	1165	323 ± 26	298-349	338 ± 38	315-381	335 ± 46	304-388	276 ± 20	260-298
	Ansis	447 ± 172	326-643	421 ± 157	322-602	443 ± 187	321-658	389 ± 115	309-520
Mg	1185	1024 ± 133	907-1169	1150 ± 70	1108-1231	1024 ± 62	968-1091	1171 ± 49	1117-1212
	Kornelija	1147 ± 88	1047-1211	1249 ± 77	1186-1335	1214 ± 41	1173-1254	1228 ± 50	1172-1268
	1165	1125 ± 70	1069-1203	1203 ± 44	1176-1254	1194 ± 77	1119-1272	1239 ± 133	1127-1385
	Ansis	1101 ± 40	1075-1155	1121 ± 41	1075-1155	1160 ± 81	1070-1225	1146 ± 12	1138-1160
Fe	1185	31.9 ± 0.2	31.6-32.0	33.8 ± 1.4	32.3-35.0	30.8 ± 4.5	26.0-35.0	29.2 ± 6.4	25.0-37.0
	Kornelija	36.8 ± 9.4	26.0-42.0	52.9 ± 10.6	46.0-65.0	49.4 ± 2.0	47.0-51.0	34.9 ± 2.8	32.0-38.0
	1165	40.4 ± 8.5	34.0-50.0	38.7 ± 4.2	34.0-42.0	36.7 ± 4.5	32.0-41.0	30.6 ± 6.3	26.0-38.0
	Ansis	39.3 ± 5.5	33.0-43.0	42.6 ± 4.5	38.0-47.0	38.3 ± 3.8	34.0-41.0	33.4 ± 2.7	31.0-36.0

^{*} N = 80 - N supply 80 kg·ha⁻¹, **N = 120 - N supply 120 kg·ha⁻¹, ***N = 160 - N supply 160 kg·ha⁻¹

Average value ± SD and range presents results from the year 2011, 2012, and 2013; highest and lowest concentrations for each element in bold

Element	Sample of	Convention	al, N = 80*	Conventiona	1, N = 120**	Conventional	, N = 160***	Org	anic	
	barley	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range	$\overline{\mathbf{x}} \pm \mathbf{SD}$	Range	$\overline{\mathbf{x}} \pm \mathbf{S}\mathbf{D}$	Range	$\overline{\mathbf{x}} \pm \mathbf{S}\mathbf{D}$	Range	
Cd	1185	0.006 ± 0.002	<0.005-0.008	< 0.005	< 0.005	0.007 ± 0.004	<0.005-0.012	< 0.005	< 0.005	
	Kornelija	0.027 ± 0.035	< 0.005-0.067	0.014 ± 0.011	< 0.005-0.026	0.016 ± 0.012	0.007-0.024	0.006 ± 0.002	<0.005-0.008	
	1165	0.006 ± 0.003	< 0.005-0.009	0.009 ± 0.005	0.005-0.014	0.007 ± 0.005	<0.005-0.013	< 0.005	< 0.005	
	Ansis	0.007 ± 0.002	< 0.005-0.009	0.014 ± 0.009	0.007-0.024	0.012 ± 0.012	<0.005-0.026	0.007 ± 0.005	.005-0.013	
Pb	1185	0.023 ± 0.013	<0.010-0.035	0.028 ± 0.018	<0.010-0.046	0.030 ± 0.027	<0.010-0.060	0.017 ± 0.006	0.013-0.024	
	Kornelija	0.028 ± 0.016	<0.010-0.039	0.066 ± 0.067	<0.010-0.140	0.024 ± 0.011	0.013-0.035	0.019 ± 0.008	0.012-0.028	
	1165	0.013 ± 0.006	< 0.010-0.020	0.015 ± 0.006	<0.010-0.021	0.020 ± 0.008	0.013-0.028	0.020 ± 0.003	0.018-0.023	
	Ansis	0.018±0.012	<0.010-0.032	0.025 ± 0.015	<0.010-0.040	0.035 ± 0.016	<0.010-0.021	0.014 ± 0.004	<0.010-0.018	
Cr	1185	0.111 ± 0.041	0.076-0.157	0.120 ± 0.009	0.115-0.131	0.155 ± 0.076	0.072 – 0.221	0.145 ± 0.091	0.068-0.245	
	Kornelija	0.245 ± 0.170	0.075-0.415	0.219 ± 0.163	0.086-0.400	0.259 ± 0.206	0.094-0.490	0.182 ± 0.118	0.110-0.318	
	1165	0.200 ± 0.172	0.085-0.398	0.131 ± 0.048	0.095-0.185	0.197 ± 0.110	0.087 - 0.306	0.125 ± 0.094	0.058-0.233	
	Ansis	0.309 ± 0.179	0.103-0.428	0.327 ± 0.195	0.156-0.539	0.291 ± 0.176	0.178-0.494	0.262 ± 0.206	0.112-0.497	
Ni	1185	0.240 ± 0.310	0.055-0.598	0.161 ± 0.148	0.055-0.330	0.187 ± 0.223	<0.05-0.444	0.277 ± 0.391	<0.05-0.729	
	Kornelija	0.242 ± 0.300	0.064-0.588	0.326 ± 0.460	< 0.05 – 0.857	0.187 ± 0.220	<0.05-0.440	0.222 ± 0.278	< 0.05 - 0.542	
	1165	0.314 ± 0.442	0.056-0.824	0.178 ± 0.204	<0.05-0.413	1.264 ± 2.073	< 0.05 – 3.657	0.223 ± 0.293	<0.05-0.561	
	Ansis	1.102 ± 1.625	0.104-2.977	0.440 ± 0.471	0.080-0.973	0.305 ± 0.236	0.063-0.535	0.387 ± 0.286	0.058-0.574	
Cu	1185	2.8 ± 1.3	1.7-4.2	3.4 ± 1.1	2.3-4.5	3.2 ± 1.2	1.9-4.2	4.1 ± 1.0	3.2-5.2	
	Kornelija	4.1 ± 1.6	2.7-5.9	4.7 ± 1.1	3.5-5.7	4.0 ± 0.3	3.8-4.4	4.1 ± 0.3	3.8-4.4	
	1165	3.5 ± 0.5	2.9-3.9	3.1 ± 0.7	2.4-3.7	3.5 ± 0.2	3.3-3.7	3.8 ± 0.3	3.4-4.0	
	Ansis	3.5 ± 0.5	3.1-4.0	3.6 ± 0.5	3.2-4.1	3.0 ± 0.2	2.8-3.2	3.3 ± 0.6	2.7-3.8	
Zn	1185	22.2 ± 7.6	18.0-31.0	22.9 ± 8.8	17.0-33.0	20.5 ± 7.4	16.0-29.0	22.0 ± 2.7	19.0-24.0	
	Kornelija	30.5 ± 13.5	22.0-46.0	33.7 ± 16.0	22.0-52.0	32.3 ± 11.00	26.0-45.0	26.7 ± 3.5	23.0-30.0	
	1165	23.2 ± 7.7	18.0-32.0	24.1 ± 6.9	19.0-32.0	23.6 ± 8.4	17.0-33.0	22.0 ± 2.7	19.0-24.0	
	Ansis	20.8 ± 3.7	18.0-25.0	24.3 ± 8.4	19.0-34.0	23.0 ± 8.7	18.0-33.0	26.3 ± 6.8	21.0-34.0	
Al	1185	2.65 ± 1.04	1.57-3.65	2.58 ± 1.29	1.11-3.51	2.90 ± 1.46	1.30-4.16	2.70 ± 1.03	1.56-3.56	
	Kornelija	4.06 ± 2.41	1.48-6.25	4.98 ± 4.56	1.65-10.18	3.36 ± 1.83	1.25-4.47	6.09 ± 5.92	1.36-12.72	
	1165	2.37 ± 0.90	1.33-2.95	3.01 ± 1.24	1.67-4.13	1.62 ± 0.50	1.14-2.14	2.31 ± 0.53	1.73-2.78	
	Ansis	3.10 ± 1.74	1.20-4.61	2.83 ± 1.67	1.14-4.48	2.81 ± 2.06	0.89-4.98	2.95 ± 1.17	1.61-3.78	
Mn	1185	10.4 ± 1.5	9.1-12.0	12.6 ± 1.5	11.0-14.0	11.5 ± 1.3	10.0-12.5	8.7 ± 1.0	7.7–9.8	
	Kornelija	13.8 ± 1.6	12.0-15.0	16.1 ± 1.1	15.0-17.2	15.9 ± 1.8	14.0-17.6	11.7 ± 4.7	8.8-17.1	
	1165	11.9 ± 0.12	11.8-12.0	12.5 ± 0.9	12.0-13.6	13.2±1.4	12.0-14.7	7.8 ± 1.6	6.7–9.7	
	Ansis	11.3 ± 1.2	10.0-12.0	13.9 ± 1.0	13.0-15.0	14.1 ± 1.0	13.0-15.0	9.3 ± 1.0	8.2-10.0	

^{*} N = 80 - N supply $80 \text{ kg} \cdot \text{ha}^{-1}$, **N = 120 - N supply $120 \text{ kg} \cdot \text{ha}^{-1}$, ***N = 160 - N supply $160 \text{ kg} \cdot \text{ha}^{-1}$

Average value ± SD and range represents results from the years 2011, 2012, and 2013; highest and lowest concentrations for particular element in bold

Cr concentration significantly differed between barley varieties 'Ansis' and '1185', and also 'Ansis' and '1165' (Mann–Whitney test, z = -2.656, p = 0.008; z = -2.136, p = 0.033, respectively).

Nickel (Ni) concentration was from 0.161 mg·kg⁻¹ in '1185'+120 to 1.264 mg·kg⁻¹ in '1165'+160 (see Table 4). Concentration of Ni did not significantly differ between barley genotypes (Kruskal—Wallis test, p > 0.05).

Copper (Cu) concentration was from 2.8 mg·kg⁻¹ in '1185'+80 to 4.74 mg·kg⁻¹ in 'Kornelija'+120 (see Table 4).

The differences of Cu concentration between barley genotypes were statistically significant (Kruskal–Wallis test $\chi 2 = 9.000$, p = 0.029). Cu concentration significantly dif-

fered between barley varieties 'Kornelija' and 'Ansis', and also 'Kornelija' and '1165' (Mann–Whitney test, z = -2.744, p = 0.006; z = -2.430, p = 0.015, respectively).

Zinc (Zn) concentration was from 20.5 mg·kg⁻¹ in '1185'+160 to 33.7 mg·kg⁻¹ in 'Kornelija'+120 (see Table 4). Zn concentration significantly differed between barley genotypes (Kruskal–Wallis test $\chi 2 = 8.441$, p = 0.038). Zn concentration significantly differed between barley genotypes '1185' and 'Kornelija', between '1165' and 'Kornelija', and also between 'Kornelija' and 'Ansis' (Mann– Whitney test, z = -2.250, p = 0.024; z = -2.195, p = 0.028; z = -2.139, p = 0.032, respectively).

Aluminium (Al) concentration was from 1.62 mg·kg⁻¹ in '1165'+160 to 6.09 mg·kg⁻¹ in 'Kornelija'+BIO (see Table

4). Al concentration did not significantly differ between barley genotypes (Kruskal–Wallis test, p > 0.05).

Manganese (Mn) concentration was from 7.8 mg·kg⁻¹ in '1165'+BIO to 16.1 mg·kg⁻¹ in 'Kornelija'+120 (see Table 4). Mn concentration significantly differed between barley genotypes (Kruskal—Wallis test, $\chi 2 = 11.306$, p = 0.010). Mn concentration significantly differed between barley varieties 'Kornelija' and '1185' (pairwise comparisons with Bonferroni correction, adjusted *p*-value = 0.010). Eriksson (2001) reported concentration of Mn in barley to range from 12–34 mg·kg⁻¹ (average 18 mg·kg⁻¹).

Concentration of macro and trace elements in barley depending on conventional or organic practices. The average concentrations of Cd, Pb, Cr, Ni, Cu, and Zn did not significantly differ (Mann–Whitney test, p > 0.220) between organically or conventionally (with different N supply) grown barley genotypes (Table 5).

The highest Cd, Pb, Cr, Ni, and Zn concentrations were in barley genotypes grown conventionally. The variability of Cd, Pb, Cr, and Ni concentration in barley genotypes grown conventionally was also high. The highest Cu concentration with low variability was in barley genotypes grown organically.

The highest K and Mg concentrations with lowest variability were in barley genotypes grown organically. The highest Mn concentration with lower variability occurred in barley genotypes grown conventionally. The variability of Al and Na concentration was high in barley genotypes grown conventionally and grown organically. The variability of K, Ca, Mn, Mg, and Fe concentration was low in barley genotypes grown conventionally and grown organically. In general, the variability of Al, K, Na, Ca, Mn, Mg, and Fe concentration was lower in barley genotypes grown organically than in genotypes grown conventionally.

 $\label{table 5} Table\ 5$ CONCENTRATIONS OF MACRO AND TRACE ELEMENTS IN BARLEY DEPENDING ON CONVENTIONAL OR ORGANIC GROWING CONDITIONS, $mg\cdot kg^{-1}$

	Conventional (with different N supply) (n = 36)	Organic (n = 12)
Cd	0.011 ± 0.012	0.006 ± 0.002
Pb	0.025 ± 0.024	0.017 ± 0.006
Cr	0.214 ± 0.140	0.178 ± 0.128
Ni	0.412 ± 0.765	0.277 ± 0.278
Cu	3.53 ± 0.90	3.82 ± 0.63
Zn	25.1 ± 9.1	24.3 ± 4.3
Al	3.02 ± 1.84	3.52 ± 3.05
K	4414 ± 509	4447 ± 331
Na	96 ± 104	81 ± 79
Ca	371 ± 89	323 ± 67
Mn	13.1 ± 2.0	9.4 ± 2.7
Mg	1143 ± 91	1196 ± 76
Fe	39.3 ± 8.0	32.0 ± 4.8

Average value \pm SD represents results from the years 2011, 2012, and 2013

The concentrations of Ca, Mn, and Fe significantly differed between organically or conventionally (with different N supply) grown barley genotypes (Mann–Whitney test p < 0.005). The concentrations of Al, K, Na, and Mg did not significantly differ between organically or conventionally grown barley genotypes (Mann–Whitney test, p > 0.140).

Concentration of macro and trace elements in hulled and hull-less barley. The highest Cd, Cr, and Ni concentrations were in hulled grains ('Ansis'); Pb, Cu, and Zn concentrations were higher in hull-less grains (Table 6). In hulled barley grains the variability of Cd, Pb, Cr, Ni, Cu, and Zn was lower than in hull-less grains. The variability of Cd, Cr, and Ni concentration in barley genotypes was high. The variability of Pb concentrations was high in hull-less barley grains but low in hulled grains. The variability of Cu and Zn concentration in barley genotypes was moderate.

The concentrations of Cd, Pb, Cu, and Zn did not significantly differ between hulled and hull-less grains (Mann–Whitney test, p=0.113). The concentrations of Cr and Ni significantly differed between hulled and hull-less grains (Mann–Whitney test, p=0.012; p=0.045, respectively).

In hulled barley grains the variability of Al, K, Na, Mn, Mg, and Fe was lower than in hull-less grain although the variability of Al and Na concentrations in hulled grains and in hull-less grains was high. The variability of Ca was higher in hull-less barley grains. The highest K, Mn, and Fe concentrations with lower variability were in hulled grains than in hull-less grains. The concentrations of Al, K, Na, Ca, Mn, Mg, and Fe did not significantly differ between hulled and hull-less grain (Mann-Whitney test, p > 0.116).

Concentration of macro and trace elements in barley depending on year. The concentration range of some elements is rather wide (Table 7). Weather conditions (air tem-

 $\label{thm:concentrations} Table~6$ Concentrations of Macro and Trace elements in Hulled and Hull-less barley, $mg\cdot kg^{-1}$

	Hull-less barley (1185, Kornelija, 1165) (n = 36)	Hulled barley (Ansis) $(n = 12)$
Cd	0.009 ± 0.011	0.011 ± 0.008
Pb	0.025 ± 0.023	0.018 ± 0.001
Cr	0.174 ± 0.113	0.297 ± 0.164
Ni	0.318 ± 0.627	0.559 ± 0.810
Cu	3.69 ± 0.93	3.33 ± 0.45
Zn	25.3 ± 8.6	23.6 ± 6.5
Al	3.22 ± 2.39	2.92 ± 1.45
K	4382 ± 507	4544 ± 313
Na	102 ± 109	65 ± 43
Ca	337 ± 45	425 ± 138
Mn	12.2 ± 2.9	12.2 ± 2.3
Mg	1164 ± 99	1132 ± 49
Fe	37.2 ± 8.7	38.4 ± 5.0

Average value \pm SD represents results from the years 2011, 2012, and 2013

CONCENTRATIONS OF MACRO AND TRACE ELEMENTS IN BARLEY IN 2011, 2012, AND 2013 DEPENDING ON ORGANIC OR CONVENTIONAL GROWING CONDITIONS, $mg \cdot kg^{-1}$

	20	11	20	12	2013		
	Conventional (with different N supply) (n = 12)	Organic (n = 4)	Conventional (with different N supply) (n = 12)	Organic (n = 4)	Conventional (with different N supply) (n = 12)	Organic (n = 4)	
	$\overline{\mathbf{x}} \pm \mathbf{SD}$	$\overline{\mathbf{x}} \pm \mathbf{SD}$	$\overline{\mathbf{x}} \pm \mathbf{SD}$	$\overline{\mathbf{x}} \pm \mathbf{SD}$	$\overline{\mathbf{x}} \pm \mathbf{SD}$	$\overline{\mathbf{x}} \pm \mathbf{SD}$	
Cd	0.021 ± 0.017	0.008 ± 0.004	0.005 ± 0.002	0.005 ± 0.000	0.006 ± 0.002	0.005 ± 0.001	
Pb	0.041 ± 0.034	0.016 ± 0.005	0.024 ± 0.011	0.019 ± 0.004	0.012 ± 0.005	0.017 ± 0.008	
Cr	0.296 ± 0.128	0.243 ± 0.058	0.234 ± 0.159	0.205 ± 0.195	0.111 ± 0.037	0.087 ± 0.028	
Ni	1.053 ± 1.085	0.590 ± 0.093	0.105 ± 0.101	0.177 ± 0.265	0.078 ± 0.013	0.064 ± 0.010	
Cu	4.03 ± 0.94	3.58 ± 0.71	$3,58 \pm 0.79$	4.18 ± 0.68	3.00 ± 0.69	3.71 ± 0.48	
Zn	35.4 ± 7.9	28.0 ± 4.9	19.7 ± 3.6	20.5 ± 1.9	20.2 ± 2.7	24.3 ± 1.9	
Al	4.54 ± 2.07	5.48 ± 4.83	3.21 ± 0.83	3.49 ± 0.75	1.31 ± 0.24	1.57 ± 0.15	
K	4798 ± 396	4605 ± 410	4543 ± 361	4448 ± 276	3902 ± 271	4288 ± 300	
Na	209 ± 106	138 ± 83	60 ± 39	87 ± 80	20 ± 1	20 ± 4	
Ca	444 ± 123	353 ± 115	347 ± 33	292 ± 16	324 ± 23	323 ± 23	
Mn	13.5 ± 1.5	8.6 ± 1.4	12.1 ± 2.0	8.0 ± 0.9	13.7 ± 2.2	11.6 ± 3.7	
Mg	1157 ± 112	1206 ± 53	1103 ± 85	1162 ± 58	1167 ± 62	1221 ± 111	
Fe	39.2 ± 10.9	29.8 ± 4.3	39.0 ± 7.3	29.3 ± 3.8	39.7 ± 5.4	37.1 ± 0.7	

perature and rainfall, see Table 1) evidently had an effect. It has previously been reported that bioavailability of trace elements depends on conditions of the environment (moisture, temperature) (Pinto *et al.*, 2014).

In 2011, the grain from organic farming contained less Cd, Pb, Cr, Ni, and Zn than grain from conventional farming, but the reverse occurred in other years (excepting for Cr).

Cd, Pb, Cr, Ni, Ca, Zn, Al, K, and Na concentrations in barley grains significantly differed (Kruskal–Wallis test, *p* 0.011) between years (see Table 7). Cd, Ni, Zn, Na, and Ca concentrations in grain significantly differed between 2011 and 2012 and also between 2011 and 2013 (pairwise comparisons with Bonferroni correction, adjusted *p*-value < 0.011). Pb, Cr, Al, and K concentrations in grain significantly differed between 2011 and 2013 and also between 2012 and 2013 (pairwise comparisons with Bonferroni correction, adjusted *p*-value < 0.022).

DISCUSSION

The mean and median data for all 48 barley samples, compared with values from Finland, Austria, Bulgaria, Pakistan, and north of Saudi Arabia, as well as data from soil analyses in Latvia and in Pakistan, are shown in Table 8. Element concentrations in samples from European countries (Finland, Austria, and Bulgaria) are in the same range as in our study. In many cases soil of Pakistan contains higher concentrations of macro and trace elements than in Latvia (with the exception of Pb), and correspondingly the grain from Pakistan contains higher levels of macro and trace elements (with the exception of Cu, Zn, K, Na, Ca, Mn, and Mg). In grain samples from Saudi Arabia only Cd and Pb had higher concentrations then in samples from Latvia and other European countries (Table 8).

Other studies, not reflected in Table 8, showed different ranges of Cd concentration in barley samples: Cd concentration 0.013–0.022 mg·kg⁻¹ in barley (Kabata-Pendias, 2011); Cd concentration 0.014 to 0.084 mg·kg⁻¹ (mean 0.039 mg·kg⁻¹, concentration of Cd in the soil was 0.0–0.295 mg·kg⁻¹) in barley grown adjacent to roadways in Poland (Wieczorek *et al.*, 2005)

According to European Commission Regulation 488/2014 (Anonymous, 2014a) the maximum allowed concentration of Cd in grain is 0.10 mg·kg⁻¹. This value was exceeded in barley samples from Pakistan and Saudi Arabia (see Table 8).

A linear relationship between Cd concentrations in plant material and growth media has been reported. In many publications, soil pH is listed as the major soil factor controlling both total and relative uptake of Cd. Soil type also affects uptake of Cd by plants. For soils with the same total Cd concentration, Cd has been found to be more soluble and more plant-available in sandy soil than in clay soil (He and Singh, 1994).

Eriksson (2001) reported a concentration range of 0.007–0.028 mg·kg⁻¹ Pb (mean 0.013 mg·kg⁻¹) in barley. Pb concentration in grains grown adjacent to roadways in Poland was from 0.16 to 0.76 mg·kg⁻¹ (mean 0.27 mg·kg⁻¹, concentration of Pb in the soil was 3–68 mg·kg⁻¹) (Wieczorek *et al.* 2005).

According to European Commission Regulation 2015/1005 (Anonymous, 2015b) the maximum allowed concentration of Pb in grain is 0.20 mg·kg⁻¹; this value was exceeded in most samples from Poland (near roadways), and in Pakistan and Saudi Arabia (see Table 8).

						M	acro and ti	ace elemen	ıts					
	Cd	Pb	Cr	Ni	Cu	Zn	Al	K	Na	Ca	Mn	Mg	Fe	Reference
Grain														
Latvia, mean ± SD	0.0092 ± 0.010	0.023 ± 0.021	0.205 ±0.136	0.378 ±0.676	3.60 ±0.85	24.9 ±8.1	3.14 ±2.18	4422 ±468	95.5 ±97.6	359 ±86	12.2 ±2.7	1156 ±90	37.5 ±7.9	This re- search
Latvia, median	0.0055	0.018	0.164	0.079	3.62	23.1	2.91	4388	53	337	12	1171	36.5	This re- search
Finland (flour)	0.01	0.07		0.06	4.0	18.0	7	3400		190	10.0	780	19.0	Ekholmet al., 2007
Austria					2.8-6.4	14.7–21.7				336–469	9.0–15.0		31.1–38.5	Sager, Hoesch, 2005
Bulgaria					1.746	4.996			31.51	106.9		395.02	14.9	Markova Ruzdiket al., 2016
Pakistan	0.23 ±0.04	1.27 ±0.02	1.22 ±0.09	28.9 ±0.33	7.72 ±0.81	39.19 ±4.86	14.35 ±2.22	7884 ±375	1328 ±43	826 ±12	23.9 ±3.0	2687 ±55	505 ±51	Sharet al., 2007
Saudi Arabia (North)	1.05 ±0.14	3.77 ±0.11			3.61 ±0.15	16.52 ±1.44					12.35 ±1.35		60.9 ±1.49	Ali, Al-Qahta ni, 2012
Soil														
Latvia (1)					2.6-2.9	1.9-3.1			10-75	820–1090	111–173	73–189	1135–145 9	Unpub- lished data, SRC*
Latvia (2)	0.05	5	1.3–51	1.2–2.8	1.5–2	5–12	1500–37 00	300–700	70	1200	27–109	300-800	1400–390 0	Gilucis, 2007
Pakistan	1.95 ±0.17	5.64 ±0.51	13.6 ±1.4	16.7 ±2.3	25.65 ±3.10	90.8 ±9.6	35964 ±4301	12457 ±249	8284 ±248	3204 ±231	536 ±39	41519 ±4042	5732 ±112	Sharet al., 2007

^{*} SRC, Stende Research Centre

The great variation of Pb content in plants is caused by several environmental factors, like geochemical anomalies, pollution, seasonal variation, and genotype accumulation ability. Genotype factors cause distinctive differences in the concentrations (Alexander *et al.*, 2006).

Kabata-Pendias (2011) summarised information on the concentration range (4–15 mg·kg⁻¹) and mean (5.5 mg·kg⁻¹) of Cu in barley. Phytobioavailability and toxicity of Cu differs between chemical species. Several soil variables control Cu solubility and thus its bioavailability; these factors include pH, oxidation and reduction potential, soil texture, mineral composition, temperature, and water regime (Kabata-Pendias and Sadurski, 2004).

The immobilisation of Zn in soils is highly controlled by phosphorous and clays (Kumpiene *et al.*, 2008). Zn toxicity and tolerance in plants have recently been of special concern because of the prolonged use of Zn fertilisers, as well as its input from industrial pollution causing raised Zn concentration of surface soils. Several plant species and genotypes are known to have high tolerance to Zn and a great selectivity in absorbing Zn from soils (Kabata-Pendias, 2011).

Ciołek *et al.* (2012) reported K concentration of 4912 mg·kg⁻¹ in barley and Ca concentration of 306 mg·kg⁻¹ in

barley. Cereals frequently do not respond to K fertilisation and wheat is more sensitive to K deficiency than barley (Askegaard *et al.*, 2004). Cultivars of the same species may differ in ability to exploit soil K resources.

Kan (2015) reported Na concentration in barley to be 124 mg·kg⁻¹ (in the range of our data), and observed slightly little higher Ca concentration — 487 mg·kg⁻¹.

Mn is one of the most abundant trace elements in the lithosphere. Several soil factors influence Mn availability to plants. The solubility of soil Mn is of significance since the plant supply of Mn depends mainly on the soluble Mn pool in the soil. In well-drained soils, the solubility of Mn always increases with increase of soil acidity. However, the ability of Mn to form anionic complexes and to complex with organic ligands may contribute to increased Mn solubility in the alkaline pH range. Mn mobility and its availability to plants increase at pH 5.5 (Kabata-Pendias, 2011).

Other studies (Ciołek *et al.*, 2012) have found lower Mg concentration (802 mg·kg⁻¹) or higher Mg concentration (1667 mg·kg⁻¹) (Kan 2015).

Kabata-Pendias (2011) summarised data on Fe concentration in various grains and roots. Fe concentrations in barley

grains were in the range $33-218 \text{ mg} \cdot \text{kg}^{-1}$ (mean 98 $\text{mg} \cdot \text{kg}^{-1}$).

Risk assessment regarding Cd, Cr, Pb, Ni, Cu, and Zn concentration in barley. To evaluate the health risk due to Cd, Cr, Pb, Ni, Cu, and Zn concentration in barley, the mean concentration was calculated for all 48 samples (Table 9). The Estimated Weekly Intake (EWI) was calculated presuming that the weekly consumption of grain (130 g day⁻¹ per 7 days) consisted only of barley. Such approach seems acceptable, as previously (Jakobsone *et al.*, 2015) it was shown that concentrations of heavy elements are low in all grain species grown in Latvia and used for human consumption.

The calculated values of EWI were compared with the Potential Tolerable Weekly Intake (PTWI) reported previously (Pirsaheb *et al.*, 2015).

Consumption of 130 g barley grain products per day did not reach the limit of PTWI for Cd, Pb, Cr, Ni, and Cu. In the case of Zn, the calculated 90% of EWI/PTWI should be significantly lower, if bioavailability of Zn is taken in account (Table 9). According to WHO/FAO (Anonymous, 2004) in the case of cereal grains the assumed bioavailability for Zn from cereal grains is only 15–30%.

Nutritional aspects associated with Al, K, Na, Ca, Mn, Mg, Fe, Cu, Zn, and Cr concentration in barley. To evaluate nutritional aspects associated with Al, K, Na, Ca, Mn, Mg, Fe, Cu, Zn, and Cr concentrations in barley, the mean concentration was calculated for all 48 samples (Table 10). Daily consumption was calculated presuming that all grain products (130 g) consist only of barley.

Calculated consumption data were compared with recommendations for daily intake given by the Latvian Ministry of Health (Anonymous, 2013; 2014b), tolerable daily intakes or upper limit of safe range of WHO (Anonymous, 1996) and tolerable daily intakes reported by EFSA (Anonymous, 2006). The highest contribution of barley grain in the recommended intake was for Mn, Mg, Fe, and Zn (53, 43, 27–49, and 23% of values given in recommendations of Latvian Ministry of Health, respectively).

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Table 9
MEAN CONCENTRATIONS, ESTIMATED WEEKLY INTAKE (EWI) AND POTENTIAL TOLERABLE WEEKLY INTAKE (PTWI) OF Cd, Pb, Cr, Ni, , and Zn

Element	Cd	Pb	Cr	Ni	Cu	Zn
Mean concentration, mg·kg ⁻¹	0.0093	0.0234	0.205	0.378	3.60	24.9
EWI, μg·kg ⁻¹ of body weight	0.14	0.35	3.1	5.7	54	378
PTWI, µg⋅kg ⁻¹ of body weight*	7	25	23.3	35	500	420
EWI/PTWI100%	2	1.4	13.3	16.3	10.8	90

^{*} Pirsaheb et al. (2015)

Table 10

POSSIBLE CONTRIBUTION OF GRAIN IN THE RECOMMENDED (OR TOLERABLE) DAILY INTAKE OF SOME ELEMENTS											
Element	Al	K	Na	Ca	Mn	Mg	Fe	Cu	Zn	Cr	
Mean concentration, mg·kg ⁻¹	3.1	4422	92.5	359	12.2	1156	37.5	3.6	24.9	0.205	
Recommended (or tolerable) intake (mg) by:											
Latvian Ministry of Health (MoH)		4000^{1}	3300^{1}	$1000 - 1200^1$	3^2	350^{1}	$10-18^2$	3^2	14^{2}	0.2^{2}	
TDI ³ or USF ⁴ of WHO, 1996	1^3							$10-12^4$	35-45 ⁴	0.25^{4}	
TDI ³ of EFSA, 2006		3000	1500	900-1200		250	25	5	25	1	
Daily consumption, present work, in:											
mg	0.40	575	12	47	1.6	150	4.9	0.47	3.2	0.027	
% from recommendations of MoH		14.4	0.4	3.9-4.7	53	43	27-49	16	23	13.5	
% from limits of WHO	40							3.9-4.7	7–9	11	
% from TDI of EFSA		19	0.4	1.9		60	19.6	9.4	13	2.7	

¹ MoH, 2014, recommended daily intake

² MoH, 2013, recommended daily intake

³ USF, upper limit of safe range

⁴ TDI, tolerable daily intake

REFERENCES

- Alexander, P. D., Alloway, B. J., Dourado, A. M. (2006). Genotypic variation in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environment Pollution*, 144, 736–745.
- Ali, Mohamed, H. H., Al-Qahtani, K. M. (2012). Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets. *Egypt. J. Aquatic Res.*, 38, 31–37.
- Anonymous (1996). Trace Elements in Human Nutrition and Health. WHO, 343 pp.
- Anonymous (1999). AOAC official method 999.11. Determination of lead, cadmium, copper, iron and zinc in foods. Atomic absorption spectrophotometry after dry ashing. First action 1999.
- Anonymous (2004). Vitamin and Mineral Requirements in Human Nutrition. 2nd ed. WHO and FAO. 341 pp. Available at: http://apps.who.int/iris/bitstream/10665/42716/1/9241546123.pdf (accessed at 03.03.2017).
- Anonymous (2005). Public Health Assessment Guidance Manual. Appendix G: Calculating Exposure Doses. Agency of Toxic Substances and Disease Registry. Available at:
- https://www.atsdr.cdc.gov/hac/phamanual/appg.html (accessed at 09.01.2017).
- Anonymous (2013). FAO Statistical Year Book. World Food and Agriculture, Food and Agriculture Organisation of the United Nations, Rome. 289 pp. Available at: (http://www.fao.org/docrep/018/i3107e/i3107e.PDF) (accessed 03.03.2017).
- Anonymous (2006). *Tolerable Upper Intake Levels for Vitamins and Minerals*. European Food Safety Authority, Brussels. 480 pp.
- Anonymous (2013). Ministry of Health of the Republic of Latvia, Healthy Food, Microelements, 2013 (in Latvian). Available at http://www.vm.gov.lv/lv/tava_veseliba/veseligs_uzturs/mikroelementi/(accessed 17.02.2017).
- Anonymous (2014a). Commission Regulation (EU) No 488/2014 amending Regulation (EC) No. 1881/2006 as regards maximum levels of cadmium in foodstuffs. Available at: http://data.europa.eu/eli/reg/2014/488/oj (accessed 4 April 2018).
- Anonymous (2014b). Ministry of Health of the Republic of Latvia. Healthy Food, Mineral Substances (in Latvian). Available at http://www.vm.gov.lv/lv/tava_veseliba/veseligs_uzturs/mineralvielas/(accessed 17.02.2017).
- Anonymous (2015a). Central Statistical Bureau (CSB) of the Republic of Latvia, MBG161. Consumption of food products average per household member per year (ECOICOP), 2015. Available at: http://data.csb.gov.lv/pxweb/en/Sociala/Sociala_ikgad_mb/MB0161.p
- http://data.csb.gov.lv/pxweb/en/Sociala/Sociala_ikgad_mb/MB0161.p x/?rxid=e2bfcd92-a7dc-43cf-961d-e4c8b9ff5eef (accessed at 25.01.2017).
- Anonymous (2015b). Commission Regulation (EU) 2015/1005 amending Regulation (EC) No. 1881/2006 as regards maximum levels of lead in certain foodstuffs. Available at: http://data.europa.eu/eli/reg/2015/1005/oj (accessed 4 April 2018).
- Anonymous (2016). Barley by area, production and humidity. Eurostat. Available at:
- http://ec.europa.eu/eurostat/tgm/refreshTableAction.do?tab=table&plugin=1&pcode=tag00051&language=en (accessed at 03.03.2017).
- Anonymous (2017). EU Cereals Balance sheet 2016/2017 and forecast 2017/2018; Committee for the Common Organisation of Agricultural Markets, 28th February, 2017. Available at: https://ec.europa.eu/agriculture/sites/agriculture/files/cereals/presentations/-oilseeds/balance-sheets-and-forecasts_en.pdf (accessed at 11.03.2017).
- Askegaard, M., Eriksen, J., Johnston, A. E. (2004). Sustainable management of potassium. In: *Managing Soil Quality: Challenges in Modern Agriculture*. Schjønning, P., Elmholt, S., Christensen, B. T. (eds.). CABI Publishing, pp. 85–102.

- Baik, B.-K., Ullrich, S. E. (2008). Barley for food: Characteristics, improvement, and renewed interest. J. Cereal Sci., 48, 233–242.
- Bleidere, M., Zute, S., Brunava, L., Bobere, N., Jakobsone, I. (2013a). Yield and grain quality of hulless spring barley in field trials under different nitrogen management conditions. *Proc. Latvian Acad. Sci., Section B*, **67** (3), 229–235.
- Bleidere, M., Zute, S., Jakobsone, I. (2013b). Characterisation of physical and biochemical traits of hulless spring barley grain in Latvian breeding program. *Proc. Latvian Acad. Sci.*, *Section B*, **67** (4/5), 399–404.
- Bourn, D., Prescott, J. (2002). A comparison of the nutritional value, sensory qualities, and food safety of organically and conventionally produced foods. *Crit. Rev. Food Sci. Nutr.*, **42**, 1–34.
- Ciołek, A., Makarska, E., Wesołowski, M., Cierpiała, R. (2012). Content of selected nutrients in wheat, barley and oat grains from organic and conventional farming. *J. Elementol.*, 2, 181–189.
- Ekholm, P., Reinivuo, H., Mattila, P., Pakkala, H., Koponen, J., Happonen, A., Hellström, J., Ovaskainen, M.-L. (2007). Changes in the mineral and trace element contents of cereals, fruit and vegetables in Finland. *J. Food Compos. Anal.*, **20**, 487–495.
- Eriksson, J. E. (2001). Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. *Swedish EPA. Rep 5159*. Stockholm. 69 pp. Available at: http://swedishepa.se/Documents/publikationer/620-6246-8.pdf (accessed 4 April 2018).
- Gilucis, A. (2007). Relevancies of Content and Distribution of Trace and Major Elements in the Latvian Topsoils. Doctoral Thesis. University of Latvia, Riga, 88 pp. (in Latvian). Available at: http://www3.acadlib.lv/greydoc/Gilucis_disertacija/Gilucis.pdf (accessed at 17.02.2017).
- Graham, R., Welch, R., Bouis, H. (2001). Addressing micronutrient malnutrition through the nutritional quality of staple foods: Principles, perspectives, and knowledge gaps. *Adv. Agron.*, **70**, 77–142.
- He, Q. B., Singh, B. R. (1994). Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. *Eur. J. Soil Sci.*, **44** (4), 641–650.
- Jäkobsone, I., Kantāne, I., Zute, S., Jansone, I., Bartkevičs, V. (2015).
 Macro-elements and trace elements in cereal grains cultivated in Latvia.
 Proc. Latvian Acad. Sci., Section B, 69 (4), 152–157.
- Kabata-Pendias, A., Sadurski, W. (2004). Trace elements and compounds in soil. In: *Elements and Their Compounds in the Environment*. 2nd ed. Merian, E., Anke, M., Ihnat, M., Stoeppler, M. Wiley-VCH, Weinheim, pp. 79–99.
- Kabata-Pendias, A. (2011). *Trace Elements in Soils and Plants*. Taylor and Francis Group, LLC, CRC Press. 534 pp.
- Kabata-Pendias, A., Mukherjee, A.B. (2007). *Trace Elements from Soil to Human*. Springer-Verlag, Berlin. 550 pp.
- Kan, A. (2015). Characterization of the fatty acid and mineral composition of selected cereal cultivars from Turkey. Rec. Nat. Prod. J., 9 (1), 124–134.
- Korkmaz, K., Kara, S. M., Ozkutlu, F., Gul, V. (2010). Monitoring of heavy metals and selected micronutrients in hempseeds from north-western Turkey. Afr. J. Agricult. Res., 5, 463–467.
- Kumpiene, J., Lagerkvist, A., Naurice, C. (2008). Stabilization of As, Cr, Cu, Pb, and Zn in soil using amendments: Review. *Waste Management*, **28**, 215–225.
- Lui, K., Peterson, K. L., Raboy, V. (2007). Comparison of the phosphorus and mineral concentrations in bran and abraded kernel fractions of a normal barley (*Hordeum vulgare*) cultivar versus four low phytic acid isolines. *J. Agricult. Food Chem.*, **55** (11), 4453–4460.
- Markova Ruzdik, N., Mihajlov, Lj., Llieva, V., Ivanovska, S., Valcheva, D., Balabanova, B., Lievski, M. (2016). Determination of some macro and mi-

- cro elements in grain of winter barley genotypes. *Agricult. Science Technol.*, **8** (1), 51–57.
- Pinto, E., Aguiar, A. A. R. M., Ferreira, I. M. P. L. V. O. (2014). Influence of soil chemistry and plant physiology in the phytoremediation of Cu, Mn and Zn. *Crit. Rev. Plant Sci.*, **33**, 351–373.
- Pirsaheb, M., Fattahi, N., Sharafi, K., Khamotian, R., Atafar, Z. (2015). Essential toxic heavy metals in cereals and agricultural products marketed in Kermanshan, Iran, and human health risk assessment. *Food Add. Contamin.*, *B*, **9** (1). Available at:
- http://dx.doi.org/10.1080/19393210.2015.1099570 (accessed at 17.02.2017).
- Poutanen, K. (2012). Past and future of cereal grains as food for health. *Trends Food Sci. Technol.*, **25**, 58–62.
- Reinholds, I., Pugajeva, I., Bavrins, K., Kuckovska, G, Bartkevics, V. (2017). Mycotoxins, pesticides and toxic metals in commercial spices and herbs. *Food Add. Contamin, B*, **10** (1) Available at:

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- http://dx.doi.org/10.1080/19393210.2016.1210244 (accessed at 15.03.2017).
- Sager, M., Hoesch, J. (2005). Macro- and micro element levels in cereals grown in lower Austria. *J. Centr. Eur. Agricult.*, **6** (4), 461–472.
- Schjønning, P., Elmholt, S., Christensen, B. T. (2003). *Managing Soil Quality: Challenges in Modern Agriculture*. CABI Publishing. 368 pp.
- Shar, G. Q., Shar, L. A., Kazi, T. G., Afridi, H. I., Arain, M. B., Jamali, M. K. (2007). Multielement analysis of Pakistani barley (*Hordeum vulgare L.*) varieties by flame atomic absorption spectrometry. *Journal of Research (Science), Bahauddin Zakariya University* (Pakistan), **18** (2), 69–77.
- Welch, R. M., Graham, R. D. (2005). Agriculture: The real nexus for enhancing bioavailable micronutrients in food crops. *J. Trace Elem. Med. Biol.*, **18**, 299—307.
- Wieczorek, J., Wieczorek, Z., Bieniaszewski, T. (2005). Cadmium and lead content in cereal grains and soil from cropland adjacent to roadways. *Polish J. Environ. Studies*, 14 (4), 535–540.

MAKRO- UN MIKROELEMENTI LATVIJĀ AUDZĒTOS MIEŽOS (*HORDEUM VULGARE* L.) ATKARĪBĀ NO ŠĶIRNES, VIDES UN LAUKSAIMNIECĪBAS PRAKSES

Pētījuma mērķis bija noteikt 13 makro- un mikroelementu koncentrāciju dažādos miežu šķirņu genotipos atkarībā no audzēšanas gada (2011, 2012, 2013) un lauksaimniecības prakses (konvencionālā un bioloģiskā). Cd, Pb, Cr, Ni un Al noteica ar elektrotermisko atomu absorbcijas spektrometru, K, Na, Zn, Cu, Ca, Mg, Mn, Fe noteica ar liesmas atomu absorbcijas spektrometru. Statistiski atšķirīgas elementu koncentrācijas tika konstatētas Cr, Cu un Zn gadījumā starp dažādiem genotipiem; Ca, Mn un Fe starp konvencionāli un bioloģiski audzētiem miežu graudiem; Cr un Ni starp plēkšņgraudu un kailgraudu miežu graudiem un Cd, Cr, Ni, Cu, Zn, Al, K un Na starp pētījumu gadiem. Potenciāli bīstamo elementu koncentrācijas bija zemas (Cd 0,005–0,027; Pb 0,013–0,066; Cr 0,111–0,327; Ni 0,161–1,264; Cu 2,8–4,7 un Al 1,62–6,09 mg·kg⁻¹). Miežu produkti var dot ieguldījumu nepieciešamo makro- un mikroelementu patēriņā, īpaši Mn, Mg, Fe un Zn nodrošinājumam (attiecīgi 7,8–16,1; 1024–1249; 29,2–52,9 un 20,5–33,7 mg·kg⁻¹).