

# MACRO-ELEMENTS AND TRACE ELEMENTS IN CEREAL GRAINS CULTIVATED IN LATVIA

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*Cereal-based foods have great importance in the compensation of micro- and trace element deficiency, because 50% of the foods produced worldwide are made up of cereal grains. The aim of the research was to determine the concentration of macro-elements and trace elements in different cereals cultivated in Latvia. Various cereals were used in the research: rye (n = 45), barley (n = 54), spring wheat (n = 27), winter wheat (n = 53), triticale (n = 45) and oats (n = 42). 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 = 266). Macro-elements and trace elements varied significantly ( $p < 0.01$  or  $p < 0.001$ ). The highest concentrations of macro- and trace elements were found in oats and the lowest in rye. The obtained data will expand the opportunity for food and nutrition scientists to evaluate content of the examined elements in grain products, and dietary consumption (bioavailability) of the examined macro-elements and trace elements.*

**Key words:** cereals, rye, wheat, barley, oats, triticale, macro-elements, trace elements.

## INTRODUCTION

World cereal production is high. In terms of quantity and area, wheat is by far the most popular cereal grown in the EU, making up nearly half the total. Of the remaining 50%, about one-third is maize and one-third is barley. Other cereals grown in smaller quantities include triticale, rye, oats, and spelt. Nearly two-thirds of EU's cereal crop is used for animal feed, with around one-third for human consumption. Only 3% is used for biofuels (Anonymous, 2015).

Cereal grains have been a primary source of nourishment for humans for thousands of years (Awika, 2011). Cereal group provide significant amounts of most nutrients and form an important part of a balanced diet in many countries (Dewettinck *et al.*, 2008; Poutanen, 2012).

In daily consumption, cereal grains like barley, wheat, oats, rye, and triticale are used. Triticale (*Triticosecale* Whitm.) is a hybrid of wheat (*Triticum* sp.) and rye (*Secale* sp.). It contains high levels of nutritionally beneficial compounds (Rakha *et al.*, 2011). Each crop plays an important role in different food industry areas: barley is commonly used for beer production, wheat and rye in bakery products, and oats for oatmeal and musli. Triticale is mainly used as an ingredient in animal feed, but also on a smaller scale is used as a food ingredient, for example in bread, cookies, cakes (Doxastakis *et al.*, 2002; McKeivith, 2004).

Cereals are the major staple food crop, contributing most of the human daily calorie intake in many cultures, as well as relevant quantities of minerals (Lombardi-Boccia, 2003).

Today, cereal grains are the single most important source of calories to a majority of the world population (Awika, 2011). However, other nutrients than protein, carbohydrates, fats and fibre are available — cereal grains are important source of mineral elements as well. Macro-elements and trace elements are essential not only for optimal plant growth and development, but also for human and animal nutrition (Underwood and Smitasiri, 1999).

The mineral and trace element contents of plants are known to be affected by the cultivar of plant, soil conditions, weather conditions during the growing season, use of fertilisers and the state of plant maturity at harvest (Pietola and Salo, 2000; Bılınt *et al.*, 2001; Hattori and Chino, 2001).

The demand for organic agriculture and environmentally-friendly agricultural products is increasing. In this respect it is not known whether and how different agriculture techniques and/or cultivation systems affect the nutrient composition of the final product. Comparison of organically and conventionally grown crops 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).

Previous studies of micro- and macroelement concentrations in Latvia, since 2000, for example, by Klavins and Vircavs (2001), Gilucis (2007), Cekstere and Osvalde (2013), Nikodemus *et al.* (2004) and Tabors (2004) have been focused on soil, water quality and air pollution. Stapkevica *et al.* (2013) studied metal uptake from contaminated soils by some plant species (radish, lettuce and dill). Vincevica-Gaile *et al.*, (2011) determined the geographical distribution of trace and major elements in honey. Only very few studies have been related to food composition, for example, on potatoes (Murniece *et al.*, 2011), cranberries (Osvalde and Karlsons, 2010), honey (Dimins, 2006) and cereal meals (rice meal, buckwheat meal and wheat containing meal), i.e. on cereal mixtures for porridge preparation (Vincevica-Gaile, 2014). The literature lacks information on macroelement and trace element concentrations in cereal grains, depending on type of grain, agronomic practice and climatic conditions.

The aim of the study was to determine the concentrations of macro- and trace elements in cereals cultivated in Latvia.

## MATERIALS AND METHODS

In the State Stende Cereal Breeding Institute, the following cultivated cereal grains were used in the research: rye ( $n = 45$ ), barley ( $n = 54$ ), spring wheat ( $n = 27$ ), winter wheat ( $n = 53$ ), triticale ( $n = 45$ ) and oats ( $n = 42$ ). Thirteen macro- and trace elements (Cd, Pb, Ni, Cr, Al, Cu, K, Na, Mn, Fe, Zn, Mg, Ca) were determined in cereal grain samples ( $n = 266$ ) collected in the time period 2011–2013 at the State Stende Cereal Breeding Institute.

**Organic field.** The soil type was sod-podzolic (PVv), sandy loam and loamy sand. Organic matter content in soil was 20.2–21.6 mg·kg<sup>-1</sup>, soil pH<sub>KCl</sub> was 5.27–5.89, content of plant available phosphorus P<sub>2</sub>O<sub>5</sub> 138–164 mg·kg<sup>-1</sup>, and potassium K<sub>2</sub>O 130–175 mg·kg<sup>-1</sup>. The common agronomic practices for organic management were used during the vegetation period.

**Conventional field.** The soil type in the conventional field was sod-podzolic (PVv), with the following characteristics: sandy loam, content of organic substances 21–24 mg·kg<sup>-1</sup>, soil pH<sub>KCl</sub> 5.4–5.8, available phosphorus P<sub>2</sub>O<sub>5</sub> 137.0–158.8 mg·kg<sup>-1</sup>, and potassium K<sub>2</sub>O 211.0–175.7 mg·kg<sup>-1</sup>. The experimental treatment consisted of three N application rates (N80, N120, and N160) in the conventional growing conditions. Complex mineral fertiliser was used as a basic fertiliser at the rate 725 kg·ha<sup>-1</sup> (pure matter N – 80 kg·ha<sup>-1</sup>, P – 28.6, K – 112.4 kg·ha<sup>-1</sup>). The N application was split between two times: part of the N was applied at the time of sowing and the remaining half at the end of tillering stage (growing stage/GS 29) of the crop. Ammonium nitrate (N 34%) was used a top-fertiliser in the following amount: 40 kg of N per ha (N120) and 80 kg of N per ha (N160). The

treatments were laid out in a randomised complete block design; plot size was 10 m<sup>2</sup>, four replicates.

**Weather conditions.** The average air temperature from April to August differs annually. The most significant differences ( $p < 0.05$ ) in temperature were noticed in June: 13 °C in 2011 and 2013 and 17 °C in 2012. August mean temperature was similar during the period of study (from 15.5 to 17 °C). Precipitation in July significantly differed ( $p < 0.05$ ) between years: 35 mm in 2013 to 165 mm in 2011. The weather conditions were warmer than the long-term average with a few heavy rainfalls during the growing period of 2011. In August, the air temperature was similar to the long-term average.

**Sample preparation.** For dry digestion grains were ground and 0.5–1.0 g was placed into a crucible. The crucible were placed into a muffle furnace with a programmable heating: grain samples were dried for 1 h at 110 °C; then temperature was increased (50 °C h<sup>-1</sup>) until 450 °C and held for eight hours. After that the crucible was removed from the muffle furnace and cooled down, and 1–3 ml of water was added to the residue in the crucible. This procedure was repeated until light gray or white ash was obtained. Then 6 M HCl was added and evaporated. The residue was re-dissolved in 25 ml 0.1 M HNO<sub>3</sub> and this solution obtained was used for element determination.

**Determination of the mineral and trace elements.** Five elements (Cd, Cr, Al, Pb, and Ni) were determined by electrothermal atom absorption spectrometry (ETAA; Perkin Elmer AAnalyst 600, Zeeman background correction was applied) after dry digestion, and eight elements (K, Na, Zn, Cu, Ca, Mg, Mn and Fe) by flame atom absorption spectrometry (FAAS; Perkin Elmer AAnalyst 800). Absorption measurements were carried out in accordance with manufacturer instructions on wavelengths, lamp and other specifications.

For data analysis the following methods were used: descriptive statistics — indicators of central tendency or location and indicators of variability, non-parametric statistics — Kolmogorov-Smirnov test, Kruskal Wallis test, Mann-Whitney test, and Levene test for equality of variance.

## RESULTS

The Cd, Cr, Cu, and Zn concentrations were very variable in barley (respectively, 0.0011–0.0670 mg·kg<sup>-1</sup>; 0.021–.921 mg·kg<sup>-1</sup>; 1.71–5.9 mg·kg<sup>-1</sup>; and 16–53 mg·kg<sup>-1</sup>), while the lowest ranges in concentrations occurred in spring wheat (respectively, 0.008–0.041 mg·kg<sup>-1</sup>; 0.053–0.295 mg·kg<sup>-1</sup>; 3.1–5.8 mg·kg<sup>-1</sup>; 18–35 mg·kg<sup>-1</sup>). The highest Cd concentration was in winter wheat 0.0306 ± 0.0124 mg·kg<sup>-1</sup>, the highest Cr, Cu, and Zn concentrations were in oats (respectively, 0.490 ± 0.726 mg·kg<sup>-1</sup>; 5.65 ± 4.954 mg·kg<sup>-1</sup>, and 28.680 ± 4.710 mg·kg<sup>-1</sup>). The lowest Cd concentration was in barley 0.0095 ± 0.0101 mg·kg<sup>-1</sup>, while the lowest Cr, Cu, and Zn concentrations were in rye (respectively, 0.086 ±

0.066 mg·kg<sup>-1</sup>; 1.915 ± 0.907 mg·kg<sup>-1</sup>; and 18.140 ± 4.876 mg·kg<sup>-1</sup>). The statistics of the Cd, Cr, Cu, and Zn concentration in cereal grains are shown in Table 1.

Table 1

STATISTICAL INDICATORS OF THE MACRO-ELEMENTS AND TRACE ELEMENTS CONCENTRATION IN CEREAL GRAINS, mg·kg<sup>-1</sup>

Ele- ments	Statistical indicators	Barley	Oats	Spring wheat	Winter wheat	Triticale	Rye
1	2	3	4	5	6	7	8
Cd	N	54	42	27	53	45	45
	Mean	0.0095	0.0180	0.0231	0.0306	0.0206	0.0132
	Median	0.0048	0.0130	0.0240	0.0290	0.0180	0.0080
	SD	0.0101	0.0146	0.0084	0.0124	0.0105	0.0124
	Minimum	0.0011	0.0045	0.0080	0.0045	0.0045	0.00450
	Maximum	0.0670	0.0550	0.0410	0.0600	0.0540	0.05600
Pb	Mean	0.0234	0.0343	0.0346	0.0218	0.0220	0.0210
	Median	0.0180	0.0240	0.0320	0.0160	0.0180	0.0200
	SD	0.0206	0.0319	0.0208	0.0170	0.0141	0.0121
	Minimum	0.0090	0.0095	0.0095	0.0095	0.0095	0.0095
	Maximum	0.1400	0.1510	0.0890	0.0970	0.0620	0.0540
Cr	Mean	0.2150	0.4900	0.1307	0.1028	0.1384	0.0861
	Median	0.1700	0.2150	0.1180	0.0950	0.0920	0.0680
	SD	0.1655	0.7263	0.0639	0.0647	0.11902	0.06643
	Minimum	0.021	0.005	0.053	0.026	0.005	0.005
	Maximum	0.921	3.210	0.295	0.425	0.529	0.334
Ni	Mean	0.7105	1.0888	0.2449	0.1065	0.1184	0.0982
	Median	0.104	0.8515	0.131	0.091	0.083	0.084
	SD	1.5307	0.6482	0.3152	0.0532	0.1373	0.0451
	Minimum	0.045	0.171	0.045	0.025	0.031	0.045
	Maximum	9.014	2.400	1.470	0.229	0.808	0.268
Al	Mean	3.242	5.6460	3.675	5.212	2.964	1.915
	Median	2.98	3.835	2.82	2.12	2.46	1.72
	SD	2.087	4.954	2.231	9.933	2.217	0.907
	Minimum	0.89	0.62	1.42	0.45	0.45	0.45
	Maximum	12.72	17.28	11.79	46.01	11.8	3.68
Cu	Mean	3.607	3.794	4.471	3.987	4.225	3.478
	Median	3.50	3.735	4.55	3.90	4.30	3.30
	SD	0.863	0.577	0.670	0.831	0.804	0.684
	Minimum	1.71	2.70	3.10	2.60	2.60	2.10
	Maximum	5.90	5.00	5.80	5.78	6.00	4.83
K	Mean	4431.6	3803.4	5115.5	4004.3	5244.4	4510.6
	Median	4430	3833	5270	4120	5520	4670
	SD	459.5	520.2	683.6	789.8	874.0	868.7
	Minimum	3494	2500	3480	1940	3450	2320
	Maximum	5260	4790	6718	5640	6813	6164
Na	Mean	107.4	83.9	58.4	51.8	91.8	84.5
	Median	64	63.5	29.5	30	95	43
	SD	109.7	77.0	70.7	52.1	76.1	107.4
	Minimum	15.8	10.8	17.0	10.1	10.2	10.3
	Maximum	387	382	297	249	296	629
Ca	Mean	375.6	766.8	436.0	473.3	412.0	394.6
	Median	339	686	405	460	371	373
	SD	100.5	224.7	93.7	142.7	140.6	81.7

Table 1 (continued)

1	2	3	4	5	6	7	8
Mn	Minimum	260	475	302	216	215	243
	Maximum	688	1272	684	815	1046	596
	Mean	12.4	38.8	26.2	27.1	24.7	22.6
	Median	12	39	26	26	23.6	21
	SD	2.7	10.1	6.7	6.6	8.1	5.6
	Minimum	7	20	14	15	13	13
Mg	Maximum	18	54	37	43	44	32
	Mean	1157.1	1365.5	1334.3	1230.1	1262.6	978.0
	Median	1172	1301	1301	1193	1217	975
	SD	89.3	120.3	120.4	253.8	212.7	100.2
	Minimum	907	1070	1149	539	1015	770
	Maximum	1385	1630	1626	1945	1887	1165
Fe	Mean	37.8	43.6	26.0	29.9	27.5	32.1
	Median	36.6	44.5	23.8	31	26.8	31.4
	SD	8.5	6.8	8.8	8.4	4.5	4.5
	Minimum	25	28	14	15	17	25
	Maximum	66	59	54	50	40	45
Zn	Mean	26.4	28.7	22.8	22.3	24.1	18.1
	Median	23.9	28.2	21.9	20	22	17
	SD	8.9	4.7	4.9	6.6	6.1	4.9
	Minimum	16	19	18	15	17	11
	Maximum	53	40	35	44	38	35

SD, standard deviation

Cd, Cr, Cu, and Zn concentrations differed significantly between the type of grains ( $p < 0.0010$ ), shown by the Kruskal Wallis test (respectively,  $\chi^2 = 103.486$ ,  $p = 0$ ;  $\chi^2 = 72.837$ ,  $p = 0$ ,  $\chi^2 = 41.119$ ,  $p = 0$ , and  $\chi^2 = 70.233$ ,  $p = 0$ ). Cd concentration differed statistically significantly in barley where it was lowest and in oats, in spring wheat, winter wheat, triticale, rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ). Cr concentration differed statistically significantly in oats and in barley, spring wheat, winter wheat, triticale, rye; Cr concentration differed statistically significantly also in barley and in spring wheat, winter wheat, triticale, rye, also in spring wheat and in winter wheat, rye, and in winter wheat and in rye, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ). Cu concentration differed statistically significantly in barley and in spring wheat, winter wheat, triticale, also in oats and in spring wheat, triticale, rye, and in spring wheat and in winter wheat, rye, in winter wheat and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ). Zn concentration differed statistically significantly in oats and in barley, spring wheat, winter wheat, triticale, rye, also in barley and in winter wheat, rye, in spring wheat and in rye, in winter wheat and in rye, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The range in Pb concentration was highest in oats (0.0095–0.1510 mg·kg<sup>-1</sup>) and lowest in rye (0.0095–0.0540 mg·kg<sup>-1</sup>). The highest Pb concentration was in spring wheat  $0.0346 \pm 0.0208$  mg·kg<sup>-1</sup> and the lowest Pb concentration in

rye  $0.0210 \pm 0.0121 \text{ mg}\cdot\text{kg}^{-1}$  (see Table 1). Pb concentrations significantly differed between cereal crops (Kruskal Wallis test,  $\chi^2 = 13.395$ ,  $p = 0.020$ ). The Pb concentration differed statistically significant in rye and in spring wheat, in triticale and in spring wheat, in winter wheat and in spring wheat; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest range in Ni concentration was in barley ( $0.045\text{--}9.014 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in winter wheat ( $0.025\text{--}0.229 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Ni concentration was in oats ( $1.109 \pm 0.648 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $0.098 \pm 0.045 \text{ mg}\cdot\text{kg}^{-1}$ , Table 1). Ni concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 97.071$ ,  $p = 0$ ). The Ni concentration differed statistically significant in oats and in barley, spring wheat, winter wheat, triticale, rye, the Ni concentration differed statistically significant also in barley and in winter wheat, triticale, and also in spring wheat and in winter wheat, triticale, rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest range in Ca concentration was in triticale ( $215\text{--}1046 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $243\text{--}596 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Ca concentration was in oats ( $766.75 \pm 224.69 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in barley ( $375.60 \pm 100.50 \text{ mg}\cdot\text{kg}^{-1}$ ; Table 1). Ca concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 108.043$ ,  $p = 0$ ). The Ca concentration differed statistically significant in barley and in oats, spring wheat, winter wheat, and also in oats and in spring wheat, winter wheat, triticale, rye, and in spring wheat and in rye, in winter wheat and in triticale, rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest range of Mn concentration was in oat ( $20\text{--}54 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in barley ( $7\text{--}18 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Mn concentration was in oats ( $38.760 \pm 10.140 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in barley ( $12.390 \pm 2.660 \text{ mg}\cdot\text{kg}^{-1}$ ; Table 1). Mn concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 157.175$ ,  $p = 0$ ). Mn concentration differed statistically significantly in barley and in oats, spring wheat, winter wheat, triticale, rye, and also in oats and in spring wheat, winter wheat, triticale, rye, and in spring wheat and in rye, in winter wheat and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest range of Mg concentration was in winter wheat ( $539\text{--}1945 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $770\text{--}1165 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Mg concentration was in oats ( $1365.54 \pm 120.26 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $977.98 \pm 100.16 \text{ mg}\cdot\text{kg}^{-1}$ , Table 1). Mg concentration significantly differed between cereal crops (Kruskal Wallis test ( $\chi^2 = 119.829$ ,  $p = 0$ ). Mg concentration differed statistically significantly in barley and in oats, spring wheat, triticale, rye, and also in oats and in winter wheat, triticale, rye, and in spring wheat and in winter wheat, triticale, rye, in winter wheat and in rye, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

Fe concentration had the widest range in barley ( $25\text{--}66 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $25\text{--}45 \text{ mg}\cdot\text{kg}^{-1}$ ). The high-

est Fe concentration occurred in oats ( $43.550 \pm 6.756 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in spring wheat ( $26.000 \pm 8.839 \text{ mg}\cdot\text{kg}^{-1}$ , Table 1). Fe concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 114.964$ ,  $p = 0$ ). The Fe concentration differed statistically significant in barley and in oats, spring wheat, triticale, rye, and also in oats and in spring wheat, winter wheat, triticale, rye, and in spring wheat and in winter wheat, rye, in winter wheat and in triticale, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest Al concentration range occurred in winter wheat ( $0.45\text{--}46.01 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $0.45\text{--}3.68 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Al concentration occurred in oats ( $5.650 \pm 4.954 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in rye ( $1.915 \pm 0.907 \text{ mg}\cdot\text{kg}^{-1}$ ; Table 1). Al concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 24.990$ ,  $p = 0$ ). Al concentration differed statistically significant in oats and in rye, in barley and in winter wheat, rye, also in spring wheat and in winter wheat, rye, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The widest Na concentration range occurred in rye, ( $10.3\text{--}629 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in winter wheat ( $10.1\text{--}296 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest Na concentration was in barley ( $107.41 \pm 109.73 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in winter wheat ( $51.78 \pm 52.14 \text{ mg}\cdot\text{kg}^{-1}$ ; Table 1). Na concentration did not significantly differ between cereal crops (Kruskal Wallis test  $\chi^2 = 10.798$ ,  $p > 0.05$ ).

K concentration had the widest range in rye ( $2320\text{--}6164 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in barley ( $3494\text{--}5260 \text{ mg}\cdot\text{kg}^{-1}$ ). The highest K concentration was in triticale ( $5244.40 \pm 873.98 \text{ mg}\cdot\text{kg}^{-1}$ ) and the lowest in oats ( $3803.38 \pm 520.12 \text{ mg}\cdot\text{kg}^{-1}$ ). K concentration significantly differed between cereal crops (Kruskal Wallis test  $\chi^2 = 84.627$ ,  $p = 0$ ). The K concentration differed statistically significantly in barley and in oats, spring wheat, winter wheat, triticale, also in oats and in spring wheat, triticale, rye, and in spring wheat and in winter wheat, rye, in winter wheat and in triticale, rye, in triticale and in rye; it was proved by the results of the Mann-Whitney tests ( $p < 0.05$ ).

The Cd, Pb, Ni, Al, Cu, K, Na, Mn, Mg, and Zn concentrations differed significantly within harvesting year ( $p < 0.05$ ). The Cd, Ni, Mn, and Zn concentrations significantly differed between years, being higher in 2011 (Mann-Whitney test,  $p < 0.05$ ). In 2011, the concentrations of Cd, Ni, and Zn were higher than in 2012 and 2013 while the Mn concentration was lower in 2011. Pb, Mg, Fe, and Al concentrations in cereal grains significantly differed between years (Mann-Whitney test,  $p < 0.05$ ). The Cu and Ca concentrations were significantly lower in 2012 (Mann-Whitney tests  $p < 0.001$ ) than in 2011 and 2013. Na and K concentrations in cereal grains significantly differed in 2013 (Mann-Whitney tests  $p < 0.01$ ): lower Na concentration and higher K concentration. The arithmetic means and standard deviations of the macro-element and trace element concentrations in cereal grains, in 2011, 2012, and 2013 are shown in Table 2.



Table 2

MEANS AND STANDARD DEVIATIONS OF MACRO-ELEMENT AND TRACE ELEMENT CONCENTRATIONS IN CEREAL GRAIN CROPS IN 2011, 2012, 2013, mg·kg<sup>-1</sup> (n = 266)

Elements	2011	2012	2013
Cd	0.0235 ± 0.0146*	0.0120 ± 0.0094	0.0131 ± 0.0128
Pb	0.0440 ± 0.0289*	0.0208 ± 0.0098*	0.0138 ± 0.0078*
Cr	0.222 ± 0.167	0.341 ± 0.692	0.177 ± 0.169
Ni	0.854 ± 0.820*	0.286 ± 0.485	0.213 ± 0.257
Al	6.32 ± 4.31*	2.92 ± 0.91*	1.44 ± 0.74*
Cu	4.10 ± 0.84	3.52 ± 0.60***	3.95 ± 0.74
K	4436 ± 654	4361 ± 718	4673 ± 888**
Na	121.6 ± 101.6	87.9 ± 71.8	17.4 ± 6.0**
Ca	618 ± 291	411 ± 129***	477 ± 139
Mn	23 ± 12*	24 ± 12	28 ± 13
Mg	1255 ± 145*	1135 ± 165*	1281 ± 200*
Fe	34 ± 11*	36 ± 10*	36 ± 7*
Zn	29 ± 7*	22 ± 6	22 ± 5

\*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$

## DISCUSSION

From a nutritional point of view, attention mainly has been focused on essential trace elements, e.g., Fe, Ca, Cu, and Zn (Kashian and Fathivand, 2015). Another important issue is food safety, which is a major public health concern worldwide and food consumption has been identified as the major pathway for human exposure to environmental contaminants; accounting for over 90% of intake compared to inhalation or dermal routes of exposure (Fries, 1995). Micronutrients may become harmful when their ingestion rates are too high. In contrast, trace elements such as Cd and Pb are well known as toxic if their intake through ingestion or inhalation is excessive (Al-Gahri and Almussali, 2008). The levels of some elements can vary in a large scale.

Shar *et al* (2013) reported mineral element and trace element concentrations in barley cultivars of Pakistan that had higher concentrations comparing to barley cultivated in Latvia. These differences might be due to growing area, climate, cultivation practise and cultivar, as significant difference due to these factors were shown within Pakistan.

Al-Gahri and Almussali (2008) reported mineral (Fe, Zn, Mn, Cu, Cd, and Pb) concentrations in wheat cultivated in three Yemen regions. In comparison with levels in wheat samples cultivated in Latvia, all minerals had higher concentration, excepting Zn, which was in twice higher concentration in Latvian wheat samples. These differences might be explained by climate — wheat in Yemen is mainly cultivated in northern regions at altitude more than 2000 m above sea level or elsewhere with irrigation (Al-Gahri and Almussali, 2008).

Sager and Hoesch (2005) determined Ca, Fe, Mn, Cu, S, and P concentrations in various cereal grains (wheat, rye, barely, and maize) of Austria. Fe concentration in barley was in the range from 31.1 to 54.1 mg·kg<sup>-1</sup>, in wheat samples from 19.1 to 44.5 mg·kg<sup>-1</sup> and in rye from 15.6 to 36.8 mg·kg<sup>-1</sup>, which are similar to the ranges of these elements

in Latvia. Cu and Mn concentrations were also similar, excepting Mn concentration in rye samples, which was higher in Latvia. Concentrations of Zn in grains cultivated in Austria were higher than in Latvia, except for wheat samples, which had similar concentrations.

Ciołek *et al.* (2012) determined macro- and trace element concentrations (K, Ca, Mg, Cu, Mn, Fe and Zn) in oats, wheat, hulled barley, and hull-less barley cultivated in Poland. Concentrations of K in barley and oats were similar to those in Latvia, but lower in wheat. Ca concentrations were higher in oats and barley in Latvia, Mg concentrations were higher in all studied grains cultivated in Latvia, Cu concentration was twice as higher in wheat samples from Latvia, and Mn concentration was twice as higher in oats. Fe and Zn concentrations were similar between the countries.

Kan (2015) determined macro- and trace element concentrations (K, P, Ca, Mg, Fe, Mn, Ni, Pb, Cr, Zn, Cu, and Na) in wheat, rye, oat, barley and triticale (cultivated in Turkey). K concentration was the highest in wheat samples (6490 mg·kg<sup>-1</sup>), while in the present research the highest K concentration was in triticale (5244.4 mg·kg<sup>-1</sup>). Ca concentration was the highest in wheat samples (1133 mg·kg<sup>-1</sup>), which was much higher than in cereal crops cultivated in Latvia. The highest Ca concentration was observed in oats (803.14 mg·kg<sup>-1</sup>). Also Mg concentration in cereal grains of Turkey was the highest in wheat (2766 mg·kg<sup>-1</sup>), while in Latvia it was highest in oats (1361 mg·kg<sup>-1</sup>). In Turkey, Na concentration was the highest in wheat (19 mg·kg<sup>-1</sup>), and Zn concentration in rye (28 mg·kg<sup>-1</sup>) and oats (28.68 mg·kg<sup>-1</sup>). In general, in Turkey wheat grains were richest in micro- and trace elements (Kan, 2015), while in Latvia oat grains had the highest levels.

In conclusion, the highest concentrations of the macro-element and trace elements were found in oat grains, while the lowest were observed in rye. There were large differences in macro-element and trace element concentrations between Latvia and Asian countries, while the level were rather similar to those in Austria, Poland, and Turkey.

The determined element concentrations have supplemented the state database with information on composition of food and its raw materials in Latvia. The observed concentrations did not exceed admissible upper limits. For food and nutrition scientists, the obtained data will expand the opportunity to evaluate the content of the examined elements in grain products, and dietary consumption (bioavailability) of macro-elements and trace elements.

The obtained results will be provided to the National Food Composition database — information will be available for stakeholders involved in the area of nutrition and health making policy.

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## MAKROELEMENTU UN MIKROELEMENTU DAUDZUMS DAŽĀDOS LATVIJĀ AUDZĒTOS GRAUDAUGOS

Makroelementiem un mikroelementiem ir liela nozīme cilvēku ikdienas uzturā. Pasaulē 50% pārtikas produktu ikdienas uzturā sastāda tieši graudaugi. Pētījuma mērķis bija noteikt makroelementu un mikroelementu daudzumu dažādos graudos, kas selekcionēti un audzēti Latvijā Valsts Stendes graudaugu selekcijas institūtā. Pētījumā tika izmantoti dažādi graudaugu veidi: rudzi ( $n = 45$ ), mieži ( $n = 54$ ), vasaras kvieši ( $n = 27$ ), ziemas kvieši ( $n = 53$ ), tritikāle ( $n = 45$ ) un auzas ( $n = 42$ ); kopā  $n = 266$ . Graudos tika noteikti šādi makroelementi un mikroelementi (minerālvielas): Cd, Pb, Ni, Cr, Al, Cu, K, Na, Mn, Fe, Zn, Mg, Cu. Minerālvielu saturs graudos bija būtiski atšķirīgs ( $p < 0,01$  vai  $p < 0,001$ ). Dominējoši augstākais minerālvielu saturs tika konstatēts auzu un zemākais — rudzu graudos. Iegūtie pētījuma rezultāti paplašinās iespēju pārtikas un uztura zinātniekiem izvērtēt graudu pārstrādes produktos esošo un ar uzturu uzņemto makroelementu un mikroelementu daudzumu un to biopieejamību organismam.