ISSN 1392-3196 / e-ISSN 2335-8947
Zemdirbyste-Agriculture, vol. 106, No. 1 (2019), p. 21–28
DOI 10.13080/z-a.2019.106.003

Macro and trace elements in oat cultivars bred in Latvia

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Abstract

The aim of the research was to quantify 13 macro and trace elements in different oat (*Avena sativa* L.) genotypes depending on the year of cultivation (2011, 2012 and 2013) and crop management practice (conventional or organic), agronomic practice (different N supply) and evaluate the risks regarding Cd, Pb, Cr, Ni, Cu, Zn and Al concentrations and nutritional aspects regarding K, Na, Ca, Mn, Mg, Fe, Cu, Zn and Cr concentrations in oat grain. Elements Cd, Pb, Cr, Ni and Al were detected by electrothermal atomic absorption spectrometry, and K, Na, Zn, Cu, Ca, Mg, Mn and Fe were analysed by flame atomic absorption spectrometry. Cluster analysis showed that genotype and agronomic / crop management practice play an important role in the concentration of macro and trace elements in oat grain. Statistically different concentrations of elements were noticed for Cr, Ni, Zn, K and Mg among the genotypes: for Mn and Fe in grains, grown conventionally or organically, for Cr, Ni, Zn, K and Mg in hulled and naked grain, and for Cd, Pb, Ni, Cu, Al, K, Na and Mg among the study years. The concentrations of potentially hazardous elements were low: Cd 0.008–0.023, Pb 0.014–0.060, Cr 0.117–1.460, Ni 0.447–1.834, Cu 3.2–4.1 and Zn 22.0–32.3 mg kg^{-1}. Oat products can contribute to the consumption of necessary macro and trace elements, especially of Mn, Mg and Fe: 30.0–49.3, 1166–1486 and 33.5–48.9 mg kg^{-1}, respectively, as well as Cr and Zn.

Key words: *Avena sativa*, conventional farming, macro and trace elements, nutritional aspects, organic agriculture, risk assessment, statistical indicators.

Introduction

Cereal products are included in the base of food pyramid. They provide significant amounts of nutrients and minerals, and therefore are important for balanced diet. According to Poutanen (2012), the average annual consumption of cereals in the European Union (EU) is 131 kg per capita. Human consumption of oats is rather low. According to the EU Cereals balance sheet for marketing year 2016–2017, the human use of oats in EU countries is 1.1 million tonnes, from the total use of 8.2 million tonnes (EU, 2017).

Due to their particular biochemical composition, oats are considered as ideally suited for the production of healthy products (Martínez-Villaluenga, Peñas, 2017). Whole grains of oats are rich in dietary fibres and therefore are an excellent raw material for healthy foods. The consumption of oats in Nordic and Baltic countries is rather low compared to wheat; however, in Latvia this figure has increased during the last decades (Sahlstrom, Knutsen, 2010). According to FAOSTAT data (FAOSTAT, 2017, http://faostat.fao.org), Latvia has one of the highest consumption of oats in the world (7.0 kg per capita), followed by Denmark (5.0 kg per capita) and Finland (4.0 kg per capita), Lithuania (3.0 kg per capita) and Estonia (2.0 kg per capita). In the EU, human consumption of oats is 2.8 kg per capita, which is 3.5 times higher than that of barley.

The prerequisite for the production of high quality foodstuffs is a high quality raw material – grain. The results of studies on oats in Latvia confirmed that grain quality indices can be affected by the weather conditions during the growing season, location and genotypes (Bleidere et al., 2012), meteorological conditions (Zute et al., 2010) and nitrogen management (Brunava et al., 2015). Therefore development of oat cultivars adaptable to changing climatic conditions and capable of ensuring both stable yields and corresponding grain quality from year to year is the most significant task for oat breeders in Latvia. In the last decade, oat researchers from the AREI have worked in several research projects to clarify which oat cultivars should be recommended for growing in Latvia and which technological elements ought to be applied in oat cultivation to satisfy the requirements of

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Please use the following format when citing the article:
Jakobsone I., Zute S., Bleidere M., Kantane I., Ece L., Bartkevics V. 2019. Macro and trace elements in oat cultivars bred in Latvia. Zemdirbyste-Agriculture, 106 (1): 21–28. DOI 10.13080/z-a.2019.106.003

both farmers and processors of oats. The investigation of chemical composition of cultivars and promising breeding lines is the priority of food oat research (Sterna et al., 2015 a).

Naked, less creatively called "hull-less oats", lose their hulls in the field, returning nutrients directly to the soil. They can be rolled without any industrial heat treatment, giving raw, unprocessed and naturally tasty product. The naked oat is now becoming more wide-spread in Latvia because of the opportunity for its different uses. Naked oats are used by small processors to produce a wide range of niche products. 'Stendes Emilija', included in this study, is the first local naked oat cultivar registered in Latvia. Other studies showed that grains of naked cultivars have an excellent biochemical composition – high levels of soluble fibres such as beta-glucan (Brunava et al., 2015), crude protein (Sterna et al., 2016) and high content of α-tocopherol (Sterna et al., 2014) – traits, determining dietary quality of products.

In breeding of cereal cultivars it is important to pay attention both to the characteristics essential for the processing industry and the ability of the cultivars to adapt to the growing conditions. Nitrogen (N) is the most limiting nutrient for cereal production; therefore adoption of good N management strategies often results in significant economic benefits to farmers. In the breeding process it is important to identify genotypes providing high productivity and ensuring grain quality at lower N rates. Organic farming system is best placed to respond to the challenges of effective nitrogen management (Hirel et al., 2011). It was found that chemical composition of oat grain such as content of proteins and amino acids, β-glucans, lipids, α-tocopherol and total dietary fibres can fluctuate due to different N levels and crop management practices (conventional or organic) applied (Vilmane et al., 2015; Sterna, 2015 b).

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 are mostly found in the aleurone layer (Lui et al., 2007; Poutanen, 2012). Mineral and vitamin deficiencies affect a greater number of the world's population than does protein energy malnutrition. Even though these 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; Teklić et al., 2013).

Some of the trace elements, including Fe, Mg, Zn and Co, are essential micronutrients for 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).

The concentration and influence on human health of toxic heavy metals (Pb, Cd and Cr) and essential heavy metals (Ni, Cu and Zn) in agricultural products was briefly analysed in the articles of Pirsaheb et al. (2015) and Teklić et al. (2013). Pb and Cd have been characterized as very toxic even at low concentrations, Cr is a carcinogen, but it is essential at low concentrations, Ni can be toxic, but normally occurs at very low concentrations, Zn and Cu are needed for human organism.

Zinc (Zn) deficiency causes growth failure and weakened immunity in young children. It also is linked to a higher risk of diarrhoea and pneumonia, resulting in nearly 800,000 deaths per year (World Food Programme, 2017, https://www.wfp.org/hunger/malnutrition/types). Aluminium (Al) is sometimes mentioned as a harmful element too. According to WHO (1996), tolerable daily intake of Al is 1 mg.

The aim of the research was to determine the concentration of 13 macro and trace elements in different oat genotypes depending on the year of cultivation (2011, 2012 and 2013), crop management practice (conventional or organic) and agronomic practice (different N supply), and evaluate risks regarding Cd, Pb, Cr, Ni, Cu, Zn and Al concentration and nutritional aspects regarding K, Na, Ca, Mn, Mg, Fe, Cu, Zn and Cr concentration in oat grain.

Materials and methods

Description of experimental conditions. Field trials were carried out during 2011–2013 at the Institute of Agricultural Resources and Economics (AREI), Stende Research Centre (57°11′35″ N, 22°33′19″ E, 78 m a. s. l.), Latvia under conventional and organic crop management systems.

Organic field trials. Trials were arranged in the organically certified fields. The soil type was *Stagnic Retisol* (loamic), content of organic matter was 20.2–21.6 mg kg^{-1}, pH$_{KCl}$ 5.27–5.89, the content of plant-available phosphorus (P_2O_5) – 138–164 mg kg^{-1} and potassium (K_2O) – 130–175 mg kg^{-1}. The common organic management practices were used during the vegetation period.

Conventional field trials. The soil type in the conventional field was *Stagnic Retisol* (loamic), content of organic matter 21–24 mg kg^{-1}; pH$_{KCl}$ s 5.4–5.8, available phosphorus (P_2O_5) – 137.0–158.8 mg kg^{-1} and potassium (K_2O) – 175.7–211.0 mg kg^{-1}. Soil characteristics met the requirements for oat cultivation. The experimental treatment consisted of three mineral nitrogen (N) rates – N80, N120 and N160 in the conventional growing conditions. Complex mineral fertilizer was used as a basic fertilizer at the rate 725 kg ha^{-1} (N – 80, P – 28.6, K – 112.4 kg ha^{-1}). Nitrogen was split-applied at sowing and at the end of tillering stage (GS 29) of the crop. Ammonium nitrate (N 34%) was used as top-fertilizer: 40 kg of N per ha (N120) and 80 kg of N per ha (N160). The treatments were laid out in a randomized complete block design with four replicates, he plot size was 10 m^2.

Weather conditions. The average air temperature from April to August differed annually (Table 1). The most significant differences ($p < 0.05$) in temperature were noticed in June, it varied from 13°C (2012) to 17°C (2011 and 2013), while similar temperature in all study years was in August (from 15.5 to 16.6°C). Rainfall differences between the study years were most significant ($p < 0.05$) in July – it ranged from 36 (2013) to 165 mm (2011). The weather conditions were warmer than the long term average (norm) with occasional heavy rainfalls during the growing period of 2011.

Description of the studied oats. In cooperation with the AREI Stende Research Centre the following oat (*Avena sativa* L.) cultivars or genotypes from oat breeding program were used in the research: hulled 'Lizete' and naked 'Stendes Emilija' (in previous publications breeding line S-156) and naked breeding line No. 33793 ('Nos nacht' / 'Stmara'). 'Lizete' is one of the newest oat cultivars bred in Latvia characterized by specific plant morphological traits suitable for growing in crop mixtures. From the dietary point of view, under Latvian conditions 'Lizete' grain showed heightened content of soluble dietary fibre (Sterna et al., 2016). Both naked genotypes had particularly high protein (Vilmane et al., 2015) and α-tocopherol content (Sterna et al., 2014).

Table 1. The average monthly air temperatures and sum of precipitation (Stende, Latvia, 2011–2013)

Month	Average air temperature °C				Sum of precipitation mm			
	2011	2012	2013	norm	2011	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*

Oat genotypes were sown with a plot seeder ‘Hege 80’ (Germany) in a well prepared seedbed at a rate of 500 viable seeds per m^2. The plot size was 10 m^2, four replicates. The grain was harvested by a combine harvester ‘Hege 140’. Sampling procedure was done according to the ISO 950 Cereals-Sampling (as grain).

Analysis of macro and trace elements. Thirteen macro and trace elements (Cd, Pb, Ni, Cr, Al, Cu, K, Na, Mn, Fe, Zn, Mg and Ca) were analysed in the cereal grain samples (n = 36), provided by the Stende Research Centre and collected during the period of 2011–2013.

Sample mineralization. Grains were ground and 0.5–1.0 g was weighed into the crucible. The crucible was placed into the muffle furnace with a programmable heating. Grain samples were dried for 1 h at 110°C; then the temperature was increased (50°C h^{-1}) to 450°C and maintained for eight hours. After that 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 hydrogen chloride (HCl) was added and evaporated. The residue was dissolved in 25 ml 0.1 M nitric acid (HNO_3) (AOAC, 1999 - Determination of lead, cadmium, copper, iron and zinc in foods. Atomic absorption spectrophotometry after dry ashing). The obtained solutions were used for element detection.

Sample analysis. Five elements (Cd, Cr, Al, Pb and Ni) were detected by electrothermal atomic absorption spectrometry (ETAAS) with Zeeman background correction (Perkin Elmer AAnalyst 600, USA) after dry digestion, and eight elements (K, Na, Zn, Cu, Ca, Mg, Mn and Fe) were detected by flame atomic absorption spectrometry (FAAS) (Perkin Elmer AAnalyst 800, USA).

Quality assurance. Analytical performance of the applied procedure was checked by the intra laboratory validation procedure in accordance with the Commission Regulation (EC) No. 333/2007. Relative standard deviation <20% and accuracy within the interval 70–115% was obtained for all elements measured within the current research. Quantification limits of the applied analytical procedure varied between 0.005 mg kg^{-1} (Cd) and 1 mg kg^{-1} (K and Na). In addition, the analytical procedure has been successfully checked (z-score below 2) by participation in the proficiency testing rounds organized by the European Union Reference Laboratory.

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 about consumption of flour, dough, flakes, bread, pasta, pizza, pastry, etc. per capita in 2015 (CSB, 2015). The calculated human consumption was ~130 g per day per capita. To assess the potential health risk from intake of potentially harmful elements (Cd, Cr, Pb, Ni, Cu, Zn and Al) the values of estimated weekly intake (EWI) were calculated using the formula from ATSDR (2005) in modified version used by Reinholds et al. (2017):

$$\mathrm{EWI} = \mathrm{C} \times 130 \times \frac{\mathrm{T}}{60},$$

where EWI is exposure dose in μg kg^{-1} per week per kg of body weight, C – element concentration mg kg^{-1} grain, 130 – human intake of grain products g per capita per day, T – 7 days per week and 60 – theoretical weight of human body 60 kg. The results were compared with published data and recommendations.

Statistical analysis. The data were processed using the software *IBM SPSS Statistics* for *Windows*, version 22.0 (IBM Corp., USA). For data analysis the following methods were used: descriptive statistics – indicators of central tendency or location and indicators of variability, non-parametric statistics – Kruskal-Wallis test, pairwise comparisons with Bonferroni correction and Mann-Whitney test.

Results and discussion

Concentration of macro and trace elements in oat genotypes depending on agronomic / crop management practice. Concentrations of macro and trace elements in three oat genotypes depending on agronomic practice (conventional growing with three different nitrogen rates) and organic practice are shown in Table 2 (macro elements) and Table 3 (trace elements). The highest and lowest average concentrations for each element are marked in bold, and no visible regularities were noticed. In many cases a standard deviation was very high.

Potassium (K). The highest K concentration was in No. 33793 + BIO and ‘Stendes Emilija’ + BIO samples (4307 mg kg^{-1}), the lowest – in ‘Lizete’ + 160 (3277mgkg^{-1}). The distribution of K concentration differed statistically significantly in oat genotypes (Kruskal-Wallis test, $p = 0.023$). The K concentration differed statistically significantly in No. 33793 and ‘Lizete’ (pairwise comparisons with Bonferroni correction $p = 0.018$).

Sodium (Na). The highest Na concentration was in ‘Lizete’ + 120 sample (171 mg kg^{-1}), the lowest – in No. 33793 + 120 sample (29 mg kg^{-1}). The distribution of Na concentration did not differ statistically significantly between the oat genotypes (Kruskal-Wallis test, $p = 0.088$).

Calcium (Ca). The highest Ca concentration was in No. 33793 + 160 sample (835 mg kg^{-1}), the lowest – in ‘Lizete’ + BIO sample (664 mg kg^{-1}). The distribution of Ca concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, $p = 0.521$).

Magnesium (Mg). The highest Mg concentration was in No. 33793+ 80 sample (1486 mg kg^{-1}), the lowest – in ‘Lizete’ + BIO sample (1166 mg kg^{-1}). The distribution of Mg concentration differed statistically significantly in oat genotypes (Kruskal-Wallis test, $p < 0.0005$). The Mg concentration differed statistically significantly in No. 33793 and ‘Lizete’, ‘Stendes Emilija’ and ‘Lizete’ (pairwise comparisons with Bonferroni correction $p = 0.002$, $p < 0.0005$, respectively).

Iron (Fe). The highest Fe concentration was in ‘Lizete’ + 160 sample (48.9 mg kg^{-1}), the lowest – in ‘Stendes Emilija’ + BIO sample (33.5 mg kg^{-1}). The distribution of Fe concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, $p = 0.501$).

Cadmium (Cd). The highest Cd concentration was in ‘Stendes Emilija’ + 120 sample (0.023 mg kg^{-1}), the lowest – in ‘Stendes Emilija’ + BIO sample (0.008 mg kg^{-1}). The distribution of Cd concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, $p = 0.986$).

Table 2. The concentration (mg kg^{-1}) of macro elements in oat grain depending on the agronomic / crop management practice

Element	Sample of oat grain	Conventional, N80		Conventional, N120		Conventional, N160		Organic	
		$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range
K	No. 33793	4072 ± 320	3858–4440	4299 ± 327	3940–4580	4091 ± 285	3792–4360	**4307** ± **428**	3972–4790
	‘Stendes Emilija’	4004 ± 238	3733–4180	3979 ± 272	3666–4160	4083 ± 361	3740–4460	**4307** ± **188**	3720–4070
	‘Lizete’	3659 ± 756	2830–4310	3751 ± 825	2930–4580	**3277** ± **695**	2500–3841	3688 ± 494	3150–4120
Na	No. 33793	38 ± 24	15–62	**29** ± **18**	13–49	45 ± 30	13–73	46 ± 32	12–76
	‘Stendes Emilija’	88 ± 78	12–94	51 ± 41	13–94	62 ± 46	15–107	54 ± 40	11–89
	‘Lizete’	56 ± 41	15–97	**171** ± **190**	14–382	98 ± 89	15–191	167 ± 131	16–258
Ca	No. 33793	824 ± 264	647–1127	761 ± 221	584–1009	**835** ± **346**	591–1231	805 ± 180	642–998
	‘Stendes Emilija’	787 ± 199	635–1012	776 ± 335	498–1148	796 ± 211	633–1034	770 ± 179	628–971
	‘Lizete’	698 ± 118	613–832	769 ± 222	623–1025	805 ± 254	630–1097	**664** ± **247**	475–943
Mg	No. 33793	1407 ± 126	1278–1529	1412 ± 102	1303–1504	1393 ± 108	1304–1513	1517 ± 87	1454–1616
	‘Stendes Emilija’	**1486** ± **90**	1394–1573	1472 ± 147	1311–1600	1481 ± 142	1348–1630	1458 ± 101	1365–1566
	‘Lizete’	1191 ± 149	1071–1358	1259 ± 53	1227–1320	1276 ± 92	1209–1381	**1166** ± **85**	1070–1233
Fe	No. 33793	44.2 ± 3.0	42.0–47.7	45.8 ± 1.4	45.0–47.5	44.5 ± 4.4	41.0–49.4	36.5 ± 3.5	33.0–40.0
	‘Stendes Emilija’	45.2 ± 2.0	43.0–47.0	46.5 ± 1.9	45.0–48.6	48.0 ± 3.6	44.0–51.0	**33.5** ± **5.1**	28.0–38.0
	‘Lizete’	44.0 ± 8.6	35.0–52.0	48.7 ± 6.3	45.0–56.0	**48.9** ± **9.6**	40.0–59.0	41.2 ± 10.4	33.6–53.0

Note. N80 – mineral N rate 80 kg ha^{-1}, N120 – mineral N rate 120 kg ha^{-1}, N160 – mineral N rate 160 kg ha^{-1}; average value ± SD and range presents results from the year 2011, 2012 and 2013; bold – highest and lowest average concentrations for particular element.

Table 3. The concentration (mg kg^{-1}) of trace elements in oat grain depending on agronomic / crop management practice

Element	Sample of oat grain	Conventional, N80		Conventional, N120		Conventional, N160		Organic	
		$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range	$\bar{x}$ ± SD	range
Cd	No. 33793	0.014 ± 0.010	<0.005–0.024	0.023 ± 0.022	<0.005–0.048	0.021 ± 0.022	<0.005–0.046	0.012 ± 0.007	<0.005–0.019
	‘Stendes Emilija’	0.014 ± 0.013	<0.005–0.029	**0.023** ± **0.020**	0.009–0.046	0.021 ± 0.018	<0.005–0.040	**0.008** ± **0.003**	<0.005–0.010
	‘Lizete’	0.010 ± 0.004	<0.005–0.013	0.018 ± 0.018	<0.005–0.038	0.020 ± 0.014	<0.005–0.031	0.013 ± 0.007	<0.005–0.018
Pb	No. 33793	**0.060** ± **0.079**	<0.010–0.151	0.027 ± 0.030	<0.010–0.062	0.027 ± 0.030	<0.010–0.062	0.021 ± 0.013	<0.010–0.035
	‘Stendes Emilija’	0.047 ± 0.045	0.015–0.098	0.033 ± 0.030	0.011–0.067	**0.014** ± **0.008**	<0.010–0.024	0.017 ± 0.007	<0.010–0.024
	‘Lizete’	0.027 ± 0.017	<0.010–0.043	0.028 ± 0.021	<0.010–0.051	0.035 ± 0.016	0.025–0.053	0.025 ± 0.026	<0.010–0.055
Cr	No. 33793	0.240 ± 0.043	0.192–0.276	0.164 ± 0.052	0.111–0.215	0.140 ± 0.041	0.095–0.176	0.227 ± 0.036	0.191–0.262
	‘Stendes Emilija’	0.282 ± 0.237	0.121–0.555	**0.117** ± **0.051**	0.083–0.176	0.164 ± 0.064	0.094–0.218	0.151 ± 0.078	0.076–0.232
	‘Lizete’	1.174 ± 0.945	0.540–2.260	1.354 ± 1.175	0.646–2.710	1.307 ± 1.181	0.588–2.670	**1.460** ± **1.522**	0.441–3.210
Ni	No. 33793	0.619 ± 0.279	0.298–0.809	0.900 ± 0.785	0.274–1.780	0.864 ± 0.497	0.439–1.410	0.620 ± 0.406	0.230–1.040
	‘Stendes Emilija’	0.989 ± 0.398	0.568–1.360	0.845 ± 0.483	0.471–1.390	0.815 ± 0.378	0.434–1.190	**0.447** ± **0.260**	0.171–0.687
	‘Lizete’	1.291 ± 0.570	0.703–1.840	1.564 ± 0.769	0.852–2.380	**1.834** ± **0.854**	0.851–2.400	1.397 ± 0.889	0.371–1.920
Cu	No. 33793	4.0 ± 0.7	3.5–4.8	**4.1** ± **0.5**	3.7–4.7	3.9 ± 0.9	3.1–4.9	3.7 ± 0.4	3.4–4.1
	‘Stendes Emilija’	3.3 ± 0.2	3.2–3.6	3.3 ± 0.5	2.7–3.7	3.6 ± 0.4	3.2–3.8	**3.2** ± **0.6**	2.8–3.9
	‘Lizete’	3.4 ± 0.5	3.0–3.9	3.8 ± 0.9	3.2–4.8	3.8 ± 0.6	3.1–4.3	3.9 ± 0.6	3.2–4.4
Zn	No. 33793	26.8 ± 3.0	24.0–30.0	28.9 ± 1.1	27.8–30.0	31.1 ± 2.9	28.3–34.0	29.7 ± 6.5	23.0–36.0
	‘Stendes Emilija’	29.6 ± 5.5	25.9–36.0	27.0 ± 1.0	26.0–28.0	**32.3** ± **6.5**	26.0–39.0	31.3 ± 4.6	26.0–34.0
	‘Lizete’	**22.0** ± **3.0**	19.0–24.9	25.8 ± 2.8	24.0–29.0	27.7 ± 4.9	22.1–31.0	26.6 ± 3.8	24.0–31.0
Al	No. 33793	6.14 ± 7.78	0.77–15.06	5.67 ± 5.85	0.63–12.08	5.86 ± 7.10	0.68–13.95	4.94 ± 6.56	0.82–12.50
	‘Stendes Emilija’	3.60 ± 2.94	1.06–6.82	3.70 ± 2.86	0.62–6.28	4.13 ± 3.03	1.01–7.06	4.63 ± 5.86	1.14–11.40
	‘Lizete’	**2.32** ± **1.96**	1.05–4.58	**7.27** ± **8.75**	1.06–17.28	6.01 ± 5.71	1.21–12.33	5.77 ± 5.88	1.42–12.46
Mn	No. 33793	36.0 ± 8.7	30.0–46.0	45.5 ± 3.9	41.0–48.0	48.1 ± 3.7	46.0–52.4	32.0 ± 7.9	26.0–40.9
	‘Stendes Emilija’	35.8 ± 9.2	26.0–44.3	46.1 ± 9.0	36.0–53.4	49.0 ± 7.8	40.0–53.9	31.6 ± 9.0	25.0–41.9
	‘Lizete’	**30.0** ± **15.6**	20.0–48.0	45.4 ± 10.4	34.0–54.3	**49.3** ± **4.5**	45.0–53.9	30.1 ± 4.5	25.0–33.3

Note. N80 – mineral N rate 80 kg ha^{-1}, N120 – mineral N rate 120 kg ha^{-1}, N160 – mineral N rate 160 kg ha^{-1}; average value ± SD and range presents results from the year 2011, 2012 and 2013; bold – highest and lowest average concentrations for particular element.

Lead (Pb). The highest Pb concentration was in No. 33793 + 80 sample (0.060 mg kg^{-1}), the lowest – in ‘Stendes Emilija’ + 160 sample (0.014 mg kg^{-1}). The distribution of Pb concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, $p = 0.802$).

Chromium (Cr). The highest Cr concentration was in ‘Lizete’ + BIO sample (1.460 mg kg^{-1}), the lowest – in ‘Stendes Emilija’ + 120 sample (0.117 mg kg^{-1}). The distribution of Cr concentration differed statistically significant between oat genotypes (Kruskal-Wallis test, $p < 0.0005$). The Cr concentration differed statistically significantly in No. 33793 and ‘Lizete’, ‘Stendes Emilija’ and ‘Lizete’ (pairwise comparisons with Bonferroni correction $p < 0.0005$, $p = 0.001$, respectively).

Nickel (Ni). The highest Ni concentration was in ‘Lizete’ + 160 sample (1.834 mg kg^{-1}), the lowest – in ‘Stendes Emilija’ + BIO sample (0.447 mg kg^{-1}). The distribution of Ni concentration differed statistically significantly between the genotypes (Kruskal-Wallis test, p = 0.007). The Ni concentration differed statistically significantly in No. 33793 and 'Lizete', 'Stendes Emilija' and 'Lizete' (pairwise comparisons with Bonferroni correction p = 0.014, p = 0.025, respectively).

Copper (Cu). The highest Cu concentration was in No. 33793 + 120 sample (4.1 mg kg^{-1}), the lowest – in 'Stendes Emilija' + BIO sample (3.2 mg kg^{-1}). The distribution of Cu concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, p = 0.096).

Zinc (Zn). The highest Zn concentration was in 'Stendes Emilija' + 160 sample (32.3 mg kg^{-1}), the lowest – in'Lizete' + 80 sample (22.0 mg kg^{-1}). The distribution of Zn concentration differed statistically significantly in the genotypes (Kruskal-Wallis test, p = 0.039). The Zn concentration differed statistically significantly in 'Stendes Emilija' and 'Lizete' (pairwise comparisons with Bonferroni correction p = 0.05).

Aluminium (Al). The highest Al concentration was in 'Lizete' + 120 sample (7.27 mg kg^{-1}), the lowest – in 'Lizete' + 80 sample (2.32 mg kg^{-1}). The distribution of Al concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, p = 0.833).

Manganese (Mn). The highest Mn concentration was in 'Lizete' + 160 sample (49.3 mg kg^{-1}), the lowest – in 'Lizete' + 80 sample (30.0 mg kg^{-1}). The distribution of Mn concentration did not differ statistically significantly between the genotypes (Kruskal-Wallis test, p = 0.971).

Concentration of macro and trace elements in oat grain as influenced by conventional or organic cultivation. The statistical indicators of the concentration of macro and trace elements in oat grain depending on crop management practice are reflected in Table 4. Higher Cd, Pb, Ni, Cu, Ca, Mn and Fe concentrations were observed in the oat grain grown conventionally.

Table 4. The concentration (mg kg^{-1}) of trace and macro elements in oat grain as influenced by conventional and organic crop management practice

	Conventional (with different N supply) (n = 27)	Organic (n = 9)
Cd	0.018 ± 0.015	0.011 ± 0.006
Pb	0.033 ± 0.032	0.021 ± 0.015
Cr	0.549 ± 0.754	0.613 ± 0.993
Ni	1.080 ± 0.622	0.821 ± 0.669
Cu	3.70 ± 0.59	3.60 ± 0.55
Zn	27.91 ± 4.4	29.2 ± 4.9
Al	4.97 ± 4.92	5.11 ± 5.32
K	3913 ± 512	3950 ± 439
Na	70.9 ± 78.6	88.8 ± 91.7
Ca	784 ± 212	747 ± 188
Mn	42.8* ± 10.0	31.2* ± 6.4
Mg	1375 ± 141	1380 ± 181
Fe	46.2* ± 4.8	37.1* ± 6.9

Note. * – p < 0.003; average value ± SD presents results from the years 2011, 2012 and 2013.

The variability of Cd, Pb, Ca and Mn concentration in the conventionally grown oat grain was higher than in the organically grown grain. The average concentration of Mn and Fe differed statistically significantly in the organically and conventionally (with different N supply) grown oats, which was proved by the results of the Mann-Whitney test (p < 0.003). Higher Cr, Zn, Al, K, Na and Mg concentrations were revealed in the organically grown grain, the variability of Cr and Al concentrations was. The average concentration of Cd, Pb, Cr, Ni, Cu, Zn, Al, K, Na, Ca and Mg did not differ statistically significantly in the organically and conventionally (with different N supply) grown oat grain (Mann-Whitney test, p > 0.176).

Concentration of macro and trace elements in hulled and naked oat grain. Higher Cr, Ni, Cu, Al, Na and Fe concentrations were in hulled grains ('Lizete'), the concentrations of Cd, Pb, Zn, K, Ca, Mn and Mg were higher in naked grain (No. 33793 and 'Stendes Emilija') (Table 5). The concentration of Cr, Ni, Zn, K, Na and Mg differed statistically significantly in hulled and naked grain, which was proved by results of Mann-Whitney test (p = 0.000, p = 0.001, p = 0.010, p = 0.024, p = 0.049 and p = 0.000, respectively).

Table 5. The concentration (mg kg^{-1}) of trace and macro elements in the grain of naked and hulled oats

	Naked oats: No. 33793, 'Stendes Emilija' (n = 24)	Hulled oats 'Lizete' (n = 12)
Cd	0.017 ± 0.015	0.015 ± 0.011
Pb	0.031 ± 0.035	0.029 ± 0.018
Cr	0.186** ± 0.098	1.324** ± 1.049
Ni	0.762** ± 0.423	1.521** ± 0.699
Cu	3.64 ± 0.57	3.73 ± 0.60
Zn	29.6* ± 4.1	25.5* ± 3.9
Al	4.83 ± 4.74	5.34 ± 5.53
K	4086* ± 298	3594* ± 631
Na	51.5* ± 39.1	123.1* ± 118.2
Ca	794 ± 210	734 ± 194
Mn	40.5 ± 9.5	38.7 ± 12.5
Mg	1453** ± 105	1223** ± 98
Fe	43.0 ± 5.7	45.7 ± 8.3

Note. * – p < 0.05; ** – p < 0.001; average value ± SD presents results from the years 2011, 2012 and 2013.

Concentration of macro and trace elements in oat grain depending on year of cultivation and crop management practice. The concentration of Cd, Pb, Ni, Cu, Al, K, Na and Mg in oat grains between the study years varied statistically significantly (Kruskal-Wallis test, p < 0.016) – the concentration range of elements is wide, which means that the weather conditions (air temperature and rainfall, Table 1) had an influence on it (Table 6). The distributions of Cd and Na concentrations differed statistically significantly in 2011 and 2013, 2012 and 2013 (pairwise comparisons with Bonferroni correction p < 0.01 and p < 0.0005, respectively). The distribution of Pb, Ni and Ca concentrations differed statistically significantly in 2011 and 2012, 2011 and 2013 (pairwise comparisons with Bonferroni correction p < 0.010 and p < 0.020, respectively). The distribution of Al concentration differed statistically significantly in all years (p < 0.014). The distributions of Cu and K concentration differed statistically significantly in 2011 and 2012, 2012 and 2013 (pairwise comparisons with Bonferroni correction p < 0.031 and p < 0.034, respectively). The distribution of Mn and Mg concentrations differed statistically significantly in 2012 and 2013 (pairwise comparisons with Bonferroni correction p < 0.016).

Comparison with the data from other countries. The mean and median data for all 36 oat samples, as well as main literature data regarding the data from different regions are reflected in Tables 7 and 8. In many cases, the concentrations of elements in oat grain samples from different regions are similar to our data. In some cases, the differences are significant. For example, samples from the United Kingdom (UK) contain significantly lower concentrations of Cd, Pb, Cr and Ni, and higher concentrations of Cu (Chapell et al., 2017). Samples from East regions of Turkey have higher concentrations of Cu and K (Dembiras, 2005), in samples from Poland the content of Na is significantly lower (Rybicka, Gliszczyńska-Świgło, 2017) than in our samples.

Table 6. The concentration (mg kg^{-1}) of trace and macro elements in oat grain in 2011, 2012 and 2013 as influenced by the conventional and organic crop management practice

	Conventional with different mineral N rates (n = 9)	Organic (n = 3)	Conventional with different mineral N rates (n = 9)	Organic (n = 3)	Conventional with different mineral N rates (n = 9)	Organic (n = 3)
	2011		2012		2013	
	$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD	$\bar{x}$ ± SD
Cd	0.035 ± 0.012	0.015 ± 0.006	0.014 ± 0.006	0.012 ± 0.003	0.005 ± 0.002	0.005 ± 0.000
Pb	0.068 ± 0.037	0.036 ± 0.019	0.019 ± 0.008	0.018 ± 0.007	0.012 ± 0.006	0.010 ± 0.000
Cr	0.324 ± 0.249	0.288 ± 0.134	0.973 ± 1.187	1.194 ± 1.746	0.350 ± 0.266	0.356 ± 0.337
Ni	1.565 ± 0.536	1.216 ± 0.635	0.941 ± 0.734	0.767 ± 0.982	0.734 ± 0.097	0.481 ± 0.110
Cu	4.02 ± 0.87	3.67 ± 0.75	3.34 ± 0.26	3.20 ± 0.20	3.72 ± 0.19	3.92 ± 0.45
Zn	29.7 ± 3.9	29.3 ± 5.7	28.22 ± 5.9	28.7 ± 6.4	25.8 ± 1.9	29.6 ± 4.5
Al	10.60 ± 4.51	12.12 ± 0.62	3.40 ± 1.06	2.09 ± 1.16	0.90 ± 0.22	1.13 ± 0.30
K	3696 ± 509	3677 ± 506	4166 ± 646	4327 ± 402	3877 ± 216	3847 ± 109
Na	123.6 ± 106.8	130.3 ± 83.1	75.1 ± 43.1	123.0 ± 117.1	13.9 ± 1.0	12.9 ± 2.9
Ca	1057 ± 113	971 ± 28	625 ± 68	626 ± 151	669 ± 25	643 ± 68
Mn	40.6 ± 9.4	29.7 ± 2.1	37.4 ± 10.8	25.3 ± 0.6	50.4 ± 3.9	38.7 ± 4.7
Mg	1351 ± 124	1331 ± 227	1285 ± 112	1392 ± 212	1490 ± 111	1418 ± 169
Fe	43.1 ± 3.7	38.3 ± 1.5	48.0 ± 6.4	38.0 ± 13.2	47.5 ± 2.0	34.9 ± 1.5

Table 7. Comparison of the concentrations of macro elements (mg kg^{-1}) in oat grain and oat product samples from different regions

Sample	K	Na	Ca	Mg	Fe	Reference
Latvia, mean ± SD	3922 ± 489	75 ± 81	774 ± 204	1377 ± 150	43.9 ± 6.6	This research
Latvia, median	3956	53	690	1373	45.0	This research
UK, Orkney	4431 ± 373	117 ± 17	508 ± 49	1099 ± 35	40.2 ± 3.4	Chapell et al., 2017
UK, Berwik	4107 ± 315	41 ± 16	552 ± 70	960 ± 85	34.4 ± 5.3	Chapell et al., 2017
Finland, oat flakes	3900	–	430	1300	32	Ekholm et al., 2007
Finland, oat bran	5500	–	630	2110	61	Ekholm et al., 2007
Turkey, East	18400 ± 2100	–	1200 ± 400	1600 ± 500	26.4 ± 2.4	Demirbas, 2005
Sweden, hulled	–	44 ± 20	461 ± 32	–	49 ± 10	Xin-Zhong et al., 2014
Denmark, hulled	–	42 ± 16	529 ± 142	–	38 ± 8	Xin-Zhong et al., 2014
China, naked	–	200 ± 88	520 ± 178	–	29 ± 9	Xin-Zhong et al., 2014
Polish market, oat flour	3510 ± 40	4 ± 1	403 ± 22	1330 ± 40	54.9 ± 1.1	Rybicka, Gliszczyńska-Świgło, 2017
Polish market, oat flakes	3210 ± 110	<0.1	344 ± 16	1210 ± 20	48.5 ± 2.1	Rybicka, Gliszczyńska-Świgło, 2017

Table 8. Comparison of the concentrations of trace elements (mg kg^{-1}) in oat grain and oat product samples from different regions

Sample	Cd	Pb	Cr	Ni	Cu	Zn	Al	Mn	Reference
Latvia, mean ± SD	0.016 ± 0.013	0.030 ± 0.029	0.565 ± 0.805	1.015 ± 0.635	3.7 ± 0.6	28.2 ± 4.4	5.003 ± 4.944	39.9 ± 10.5	This research
Latvia, median	0.011	0.195	0.225	0.815	3.7	27.9	3.190	41.5	This research
UK, Orkney	n.a.	n.a	<0.02	<0.02	44.8 ± 4.4	21.2 ± 5.5	–	35.3 ± 0.2	Chapell et al., 2017
UK, Berwik	n.a.	n.a.	<0.02	<0.02	40.6 ± 19	20.5 ± 5.5	–	41.1 ± 6.9	Chapell et al., 2017
Finland, oat flakes	0.02	0.05	–	1.39	4	33	6	45	Ekholm et al., 2007
Finland, oat bran	0.03	0.05	–	1.86	5	43	4	57	Ekholm et al., 2007
Turkey, East	–	–	–	–	14.8 ± 1.3	26.4 ± 2.1	–	16.9 ± 1.7	Demirbas, 2005
Sweden, hulled	–	–	–	–	–	29 ± 2.7	–	–	Xin-Zhong et al., 2014
Denmark, hulled	–	–	–	–	–	29 ± 6	–	–	Xin-Zhong et al., 2014
China, naked	–	–	–	–	–	32 ± 8	–	–	Xin-Zhong et al., 2014
Polish market, oat flour	–	–	–	–	4.4 ± 0.4	30.3 ± 0.6	–	37.2 ± 1.2	Rybicka, Gliszczyńska-Świgło, 2017
Polish market, oat flakes	–	–	–	–	3.5 ± 0.1	30.5 ± 1.2	–	36.8 ± 1.6	Rybicka, Gliszczyńska-Świgło, 2017

n.a. – negligible amount

Risk assessment and nutritional aspects regarding element concentration in oats. To evaluate the health risk regarding Cd, Pb, Cr, Ni, Cu and Zn concentrations in oat grain, the mean concentrations were used for all 36 samples (Table 9). The estimated weekly intake (EWI) was calculated presuming that all weekly consumption of grain (130 g day^{-1} per 7 days) consists of oat products. Such approach seems acceptable as in the article of Jākobsone et al. (2015) it has been shown that the concentration of heavy elements is low in all grain species grown in Latvia and used for human consumption.

The calculated values of EWI were compared with PTWI of Cr, Ni, Cu and Zn reported in the article of Pirsaheb et al. (2015) or EU Regulations (in case of Cd and Pb). Results of Table 10 indicate that using 130 g oat grain products per day gives little influence on possibility to achieve a limit of PTWI in the case of Cd, Pb, Cr, Ni and Cu. In the case of Zn, the calculated 102% of EWI:PTWI should be significantly lower, if bioavailability of Zn was taken in account. According to WHO/FAO (2004), in the case of cereal grains the assumed bioavailability for Zn from cereal grains is 15–30% only. To evaluate nutritional aspects due to K, Na, Ca, Mn, Mg, Fe, Cu, Zn and Cr concentration in oat grain, the mean concentration was calculated for all 36 samples. Daily consumption was calculated presuming that all grain products (130 g) consist only of oat products.

Table 9. The mean concentration, estimated (EWI) and potential tolerable (PTWI) weekly intake of trace elements

Element	Cd	Pb	Cr	Ni	Cu	Zn	Al
Mean concentration, mg kg^{-1}	0.016	0.030	0.565	1.015	3.7	28.2	5.0
EWI, µg kg^{-1} of body weight	0.24	0.46	8.57	15.4	56.1	428	76
PTWI, µg kg^{-1} of body weight	2,5[1]	25[2]	23.3[3]	35[3]	500[3]	420[3]	117[4]
EWI:PTWI 100%	9.6	1.8	36.8	44	11.2	102	65

[1] – EC Regulation No. 488/2014, [2] – EC Regulation No. 1881/2006; [3] – Pirsaheb et al., 2015; [4] – calculated from tolerable daily intake 1 mg day^{-1} (WHO, 1996)

Table 10. Possible contribution of oat grain in the recommended daily intake of macro elements and Mn

	K	Na	Ca	Mn	Mg	Fe	Cu	Zn	Cr
Mean concentration, mg kg^{-1}	3922	75	774	39.9	1377	43.9	3.7	28.2	0.565
Recommended intake (mg) by:									
Latvian Ministry of Health (LMH)	4000[1]	3300[1]	1000–1200[1]	3[2]	350[1]	10–18[2]	3[2]	14[2]	0.2[2]
European Food Safety Authority (EFSA), 2006	3000	1500	900–1200	–	250	25	5	25	1
Daily consumption, present work, in:									
mg	510	9.8	101	5.2	179	5.7	0.48	3.7	0.073
% from LMH	13	0.3	8–10	173	51	32–57	16	26	36.5
% from EFSA	17	0.7	8–11	–	72	23	10	15	7

[1] – 2013, [2] – 2014

The calculated data of consumption were compared with recommendations for daily intake issued by the LMH (2013; 2014) and tolerable daily intakes of EFSA (2006). The highest contribution of oat grain in the recommended intake is remarkable in the cases of Mn, Mg, Fe, Zn and Cr (173, 51, 32–57, 26 and 36.5 % from recommendations of LMH, respectively).

Conclusions

1. Element concentrations in the studied oat grain samples grown in Latvia were mainly similar to those reported by other authors. However, in some cases (Cd, Pb, Cr, Ni, Cu, Na and K) the concentrations were significantly different.
2. The concentrations of Cr, Ni, Zn, K and Mg in oat grain differed statistically significantly between the genotypes.
3. Higher Cd, Pb, Ni, Cu, Ca, Mn and Fe concentrations were determined in oat grain grown conventionally, higher Cr, Zn, Al, K, Na and Mg concentration were in oat grain grown organically. The concentration of Mn and Fe differed statistically significantly in the organically and conventionally (with different N supply) grown oat grain.
4. Higher Cr, Ni, Cu, Al, Na and Fe concentrations were in hulled grain ('Lizete'), the concentrations of Cd, Pb, Zn, K, Ca, Mn and Mg were higher in naked grain (No. 33793 and 'Stendes Emilija'). The concentration of Cr, Ni, Zn, K, Na and Mg differed statistically significantly in hulled and naked grain.
5. The concentration of Cd, Pb, Ni, Cu, Al, K, Na and Mg in oat grain differed statistically significantly between the study years.
6. The concentrations of potentially hazardous elements were low: Cd 0.008–0.023, Pb 0.014–0.060, Cr 0.117–1.460, Ni 0.447–1.834, Cu 3.2–4.1 and Zn 22.0–32.3 mg kg^{-1}. Oat products can contribute to the consumption of necessary macro and trace elements, especially Mn, Mg and Fe: 30.0–49.3, 1166–1486 and 33.5–48.9 mg kg^{-1}, respectively, as well as Cr and Zn.

Acknowledgments

The authors acknowledge financial support from the European Social Fund project No. 2013/0072/1DP/1.1.1.2.0/13/APIA/VIAA/032.

Received 16 04 2018
Accepted 26 11 2018

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ISSN 1392-3196 / e-ISSN 2335-8947
Zemdirbyste-Agriculture, vol. 106, No. 1 (2019), p. 21–28
DOI 10.13080/z-a.2019.106.003

Makro- ir mikroelementų kiekis Latvijoje išvestų veislių avižose

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Santrauka

Tyrimo metu siekta nustatyti trylikos makro- ir mikroelementų kiekį įvairiuose sėjamosios avižos (*Avena sativa* L.) genotipuose, priklausomai nuo auginimo metų (2011, 2012 ir 2013), auginimo sistemos (tradicinės bei ekologinės) ir taikytų agrotechnikos priemonių (skirtingo aprūpinimo azotu (N)), taip pat įvertinti riziką, susijusią su cheminių elementų Cd, Pb, Cr, Ni, Cu, Zn bei Al koncentracijomis avižų grūduose, ir mitybinius K, Na, Ca, Mn, Mg, Fe, Cu, Zn bei Cr koncentracijos avižų grūduose aspektus. Elementų Cd, Pb, Cr, Ni ir Al kiekiai buvo nustatyti elektrotermine atominės absorbcijos spektrometrija, o K, Na, Zn, Cu, Ca, Mg, Mn ir Fe kiekiai buvo tirti taikant atominę absorbcijos spektrometriją. Klasterinė analizė parodė, kad makro- ir mikroelementų kaupimuisi avižų grūduose didelę reikšmę turi genotipas, auginimo sistema ir taikytos agrotechnikos priemonės. Nustatyta Cr, Ni, Zn, K ir Mg koncentracijų esminiai skirtumai tarp genotipų: Mn ir Fe skirtumai grūduose, augintuose tradiciškai ir ekologiškai, Cr, Ni, Zn, K ir Mg skirtumai tarp avižų su lukštais ir be lukštų grūdų ir Cd, Pb, Ni, Cu, Al, K, Na bei Mg skirtumai tarp tyrimų metų. Potencialiai žalingų elementų koncentracijos buvo mažos: Cd 0,008–0,023, Pb 0,014–0,060, Cr 0,117–1,460, Ni 0,447–1,834, Cu 3,2–4,1 ir Zn 22,0–32,3 mg kg^{-1}. Vartojant iš avižų pagamintus produktus mitybą galima papildyti būtinais makro- ir mikroelementais, ypač Mn, Mg ir Fe, atitinkamai 30,0–49,3, 1166–1486 ir 33,5–48,9 mg kg^{-1}, taip pat ir Cr bei Zn.

Reikšminiai žodžiai: *Avena sativa*, ekologinė žemdirbystė, makro- ir mikroelementai, mitybiniai aspektai, rizikos įvertinimas, statistiniai rodikliai, tradicinis ūkininkavimas.