

## THE IMPACT OF AGROTECHNICAL FACTORS ON THE CONTENTS OF CHROMIUM AND NICKEL IN GRITS OF SELECTED VARIETIES OF SPRING BARLEY

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### ABSTRACT

Fertilization and soil tillage have an important position in agriculture, because the modification and availability of nutrients from the soil to plants, as well as heavy metals are related to these mentioned treatments. The main negative impact of heavy metals on the environment is their non-degradability. In our study, the samples of barley grits were analysed, where chromium and nickel contents were determined depending on different agrotechnical methods of growing cereal plants. The field trials were based on a plot of land in the cadastral territory of Dolná Malanta near the city of Nitra in the Slovak Republic. The plot area was 14 m<sup>2</sup>. In the experiment, three different dosages of macroelements into the soil were applied, and two methods of soil treatment by ploughing were also performed. Barley grits were obtained by grinding of grains of four varieties of spring barley: *KM2084*, *Lédi*, *Xanadu* and *Marthe*. The lowest content of chromium and nickel in barley grits was determined in the *KM2084* variety. The amounts of chromium in the barley grits of our tested samples were in the range 0.17-0.77 mg.kg<sup>-1</sup> dry matter and nickel 0.05-0.76 mg.kg<sup>-1</sup> dry matter, respectively. According to the Food Code of the Slovak Republic, the maximum permissible amount of chromium (0.77 mg.kg<sup>-1</sup>) was exceeded, mainly in the *Lédi* variety, in the case of nickel, its exceeding of the maximum permissible amounts (0.76 mg.kg<sup>-1</sup>) was not determined in any variety. NPK fertilization in the ratio 16:1:4 (70 kg N ha<sup>-1</sup>) in combination with minimization ploughing, as well as fertilization in the ratio 2.5:1:1.5 (60 kg N ha<sup>-1</sup>) in combination with conventional ploughing had an effect on an increase in chromium contents in barley grain in all varieties, but at the same time caused a decrease in nickel contents, except for the *Xanadu* variety. The same values were determined in the fertilized variant with the addition of limestone after the application of conventional ploughing. The application of conventional ploughing on unfertilized areas had an effect on the increase of nickel contents in all varieties and the decrease of chromium contents in three varieties of spring barley.

**Keywords:** fertilization, tillage, barley, chromium, nickel

### INTRODUCTION

Chemical composition of barley grain is determined not only genetically, but also by ecological factors, such as soil, fertilizing, tillage or also physical and chemical influences during storage and processing. Present tendency forward to increasing of foodstuffs quality requires greater emphasis on quality of products from agricultural first-production (Fecenko and Ložek, 2000; Mühlbachová et al., 2018).

The nutrients in soil have an important role in the crop nutrition to achieve higher yield, better growth and plant development. Fertilization is one of the most important parts of the crop growing technology and has the highest dynamic effect on the grain barley yield economically (Gülser and Kizilkaya, 2019). To provide a high yield-forming effectiveness of fertilizers, one shall maintain the adequate ratios between the nutrients applied (Kostadinova, 2014). The right fertilization should be based on the balance of nutrients, considering their uptake from soil as well as from fertilizers (Mandic et al., 2015).

Tillage affects different soil properties and soil processes, resulting in a complex system with various feedbacks on processes related to soil water, temperature, carbon, and nitrogen (Lutz et al. 2019). The combination of reasonable tillage practices and fertilization methods not only affects changes in soil nutrients but is also the most important measure for sustainable agricultural development and utilization (Li et al., 2020). Different tilling of the soil can influence incorporating of used fertilizers in soil profiles.

Nickel is recognized as a heavy metal micronutrient required for proper plant growth and development. It is a key component of the enzyme urease, which catalyzes the hydrolysis of urea in carbon dioxide (CO<sub>2</sub>) and ammonium (NH<sub>4</sub>) in plant tissues (Kumar et al., 2017). At level of dynamics in soil, Ni is abundant metal in the earth crust with about 3% of the composition of the earth. Soil pH plays an important role in the availability of Ni, and at pH > 6.7 Ni exists in form of poorly soluble hydroxides, while at pH < 6.5 increases the presence of relatively soluble compounds (Brown, 2006). The metabolism of this element is crucial for maintaining a proper cellular redox state and various other biochemical, physiological, and growth responses. Besides involvement in nitrogen (N) metabolism and iron absorption, nickel is required for viable seed production and germination (Poonkothai and Vijayavathi, 2012). Soil acidity is one of the main

factors that affect the nickel solubility in soil solution, its availability for plants. Nickel is required by plants in trace amounts, although it does not play any remarkable metabolic functions. It can be counted as a nutrient, although a few plant species present negative symptoms during its deficiency (Singh et al. 2011). During the last few decades, a significant increase in environmental contamination with Ni has been observed; hence, a phytotoxic effect of this element, rather than deficiency, is much more commonly found. The increasing Ni pollution of the environment is mainly caused by various anthropogenic activities (Matraszek et al., 2016).

Chromium is a naturally occurring element, elemental chromium does not occur in nature. Rather, it is found complexed with oxygen, iron, or lead, forming oxides such as chromite (FeOCr<sub>2</sub>O<sub>3</sub>), chromitite (Fe<sub>2</sub>O<sub>3</sub>·2Cr<sub>2</sub>O<sub>3</sub>), and crocitate (PbCrO<sub>4</sub>). Although chromium can exist in nine different oxidation (valence) states, trivalent (III) and hexavalent (VI) chromium are the two most common species (Shupack, 1991). Chromium is a natural component of plant tissues, although concentrations vary considerably between different plant species, plant tissues, and soil types. In our study, the samples of barley grits were analysed, where chromium and nickel contents were determined depending on different agrotechnical methods of growing cereal plants.

### MATERIAL AND METHODS

#### Description of experimental site

Field polyfactorial experiments were established under agroecological conditions of a warm maize production area on the research and experimental base of the Slovak University of Agriculture in Nitra, in the cadastral area of Dolná Malanta. This model territory lies in the lower part of the Selenec basin and its tributaries, which belong to the central part of the Nitra River basin. It is located east of the town of Nitra on the Žitavská hill. From a regional point of view, the territory is located in the area of the geological interface of the crystalline-mountain massif of Tribeč and the Danube Lowland (Tobiášová and Šimanský, 2009). The agrochemical soil properties are shown in table 1.

**Table 1** Agrochemical soil properties of research plots

Soil reaction (pH/KCl)	Humus content (%)	Nutrients		
		Nan	P	K
		mg.kg <sup>-1</sup>	mg.kg <sup>-1</sup>	mg.kg <sup>-1</sup>
6.4	2.88	10.7	63.9	204.2

**Experiment establishment**

Four varieties of spring barley were used in our work: KM2084, Lédi, Xanadu, and Marthe. Experiments were based on the method of split blocks, observing randomness. The area of the individual research plot was 14 m<sup>2</sup>. The number of rows on the plot was 16 and the distance between rows was 0.125 m. In this experiment, four levels of fertilization were applied: 1) unfertilized (control variant), 2) fertilization by the fertilizer Condit mineral batched 1 t.ha<sup>-1</sup> (applied to soil 70 kg N ha<sup>-1</sup>, 4.4 kg P ha<sup>-1</sup> and 16.6 kg K ha<sup>-1</sup>), 3) application of the following fertilizers: Amofos batched in 150 kg, KCl (60 %) 60 kg ha<sup>-1</sup>, Hakofyt 150 dm<sup>3</sup> ha<sup>-1</sup> and NH<sub>4</sub>NO<sub>3</sub>, in total, we added to the soil 60 kg N ha<sup>-1</sup>, 22.7 kg P ha<sup>-1</sup>, 36 kg K ha<sup>-1</sup>, 4) same level of fertilization as in the previous case, however, instead of the last applied separate fertilizer NH<sub>4</sub>NO<sub>3</sub> we used mixture of NH<sub>4</sub>NO<sub>3</sub> + CaCO<sub>3</sub> and so we added 60 kg N ha<sup>-1</sup> and 25 kg Ca ha<sup>-1</sup> to the soil. We realized two methods of tillage: conventional tillage (tillage up to the depth of 0.18 – 0.20 m) and minimalization – disc ploughing (up to the depth of 0.10 – 0.12 m). Barley was harvested using a Claas Dominator 38 harvester (Kupeček, 2011). The grain from individual plots was separately bagged and marked with a number according to the trial establishment plan.

**Analysis of nickel and chromium in plant samples**

Ground samples of barley grits were mineralized by ‘wet way’ method using microwave digestion in a MARS X-press oven from CEM (USA). 1 g of ground barley grits was weighed into Teflon boats, which was filled with 10 cm<sup>3</sup> of concentrated HNO<sub>3</sub>. The mineralization took place according to the program shown in Table 2. After cooling, the mineralizate was filtered into a measuring flask with a volume of 50 cm<sup>3</sup> and filled up to the mark with distilled water. The contents of nickel and chromium were measured in the obtained liquid solution by the AAS method on a flame spectrophotometer VARIAN AA 240 FS at the Institute of Food Sciences at SUA in Nitra. The obtained results were compared with the Food Codex of the Slovak Republic. All data were processed statistically in program Statgraphics.

**Table 2** Program of mineralization in microwave oven MARS X-press

Phase	Power (W)	Input (min)	Temperature (°C)	Process time (min)
1. Initialization	800	15	–	–
2. Mineralization	800	–	180	15
3. Cooling	–	–	–	20

**RESULTS AND DISCUSSION**

Nowadays, soil pollution with heavy metals is causing larger problems that has been related to heavy metals accumulation in plants and could directly or indirectly enter the animals and humans’ organisms. The hygienic safety of foods of plant

origin can be disturbed during their formation, by the passage of some contaminants from the soil to the root system and plant tissues. All the fertilizers must meet the requirements for maximum content of heavy metals. The threshold of heavy metals in the fertilizers must not be exceeded. The highest value of chromium in ground barley grits (0.77 mg.kg<sup>-1</sup>) was determined in the second variant by *Xanadu* variety (Tab. 3) and in the third variant by *Lédi* variety grown on the area where minimization ploughing was applied. Conversely, the lowest value of chromium in grits (0.17 mg.kg<sup>-1</sup>) was determined by *Marthe* variety in the control (unfertilized) variant growing on the area where minimization ploughing was performed. According to the Food Codex of the Slovak Republic, the maximum permissible amount of chromium in cereals is 0.5 mg.kg<sup>-1</sup> in grain - in our examined cereals of the *Lédi* variety (in all variants where minimization ploughing was applied), the maximum permissible amount of this contaminant in grits was exceeded. Likewise, further exceeding of the maximum permissible amount of chromium was recorded in four cases by *Marthe* and *Xanadu* varieties. The amounts of nickel in barley grits ranged from 0.05 to 0.76 mg.kg<sup>-1</sup>. Both of these extremes were evaluated by the variety *KM2084*, which was grown on an area with conventional ploughing. The highest permissible content of this heavy metal is 1 mg.kg<sup>-1</sup> in grain according to the Food Codex of the Slovak Republic and it was not exceeded in our analyses (Tab. 3).

After the arithmetic averaging of the values of all four variants (i.e., the control with the remaining three fertilized variants) in individual varieties of spring barley (graph 1), the following order of chromium uptake into the grain was found: *Marthe* > *Xanadu* > *Lédi* > *KM2084* in cereals where conventional ploughing was performed and in cereals that grew on the area where minimization ploughing was carried out, the following order of varieties was found: *Lédi* > *Xanadu* > *KM2084* > *Marthe* (graph 2).

When all four variants in the nickel contents in barley grits were averaged in the same way, the following order of the varieties was found (graph 3): *Xanadu* > *Marthe* > *KM2084* > *Lédi* (conventional ploughing) and *Xanadu* ≈ *Lédi* > *KM2084* > *Marthe* (minimization ploughing) (graph 4). From the exact comparisons, it can be seen that particularly the *Xanadu* variety accumulated the most nickel in the grain, and conversely, the relatively smallest accumulation of chromium was recorded in the barley grain of the *KM2084* variety. Brunetti et al. (2012) found that barley and wheat do not act as metal accumulators under tested field conditions. As part of a phytoremediation project in the Apulia region (Italy), they conducted a field experiment in soils contaminated by more metals, where they studied the accumulation and distribution of metals in different parts of barley and wheat. Through the experiment, the authors found that phytoextraction with these cereals would not be recommended as an alternative to soil remediation, and thus also concluded that there is a low health risk for humans and animals consuming straw and grain from these plants grown on contaminated soils. Similar research was also conducted by Mussarat et al. (2021). The authors found that irrigation of plants with wastewater increased Ni, Pb and Cd contents in the grain of wheat variety cv. *Atta Habib 2010* compared to the control variants, but fertilization with NPK had an effect only on the increase of Pb in the grain. Lavado et al. (2001) in a research study state that Cr and Ni accumulation in plant was not related to their concentration level in the soil.

Fertilization in the dose of N<sub>70</sub>+P<sub>4.4</sub>+K<sub>16.6</sub> (2<sup>nd</sup> variant) compared to the control resulted in an increase in chromium contents in the grits obtained from all varieties of barley plants (Tab. 3) that grew on the plots where the minimization ploughing (statistically significant by three varieties) was applied and, on the contrary, its statistically significant decrease by *Xanadu* and *Marthe* varieties growing on areas with conventional ploughing. In the remaining two varieties (*KM2084* and *Lédi*), this ratio of nutrients did not affect the Cr contents in their barley grits.

**Table 3** Content of chromium and nickel in grits (mg.kg<sup>-1</sup>) of different varieties of barley

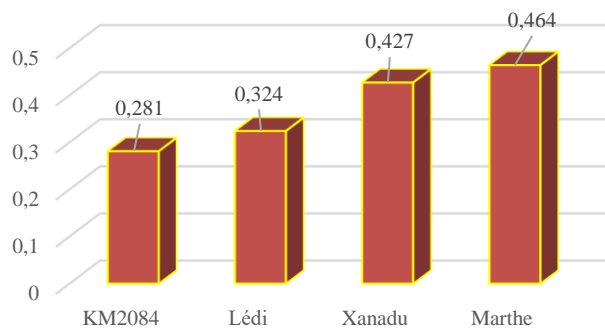
Level of fertilization	Tillage	Contents of Cr (mg.kg <sup>-1</sup> grits)				Contents of Ni (mg.kg <sup>-1</sup> grits)			
		<i>KM2084</i>	<i>Lédi</i>	<i>Xanadu</i>	<i>Marthe</i>	<i>KM2084</i>	<i>Lédi</i>	<i>Xanadu</i>	<i>Marthe</i>
1	unfertilized	0.33 <sup>a</sup>	0.55 <sup>a</sup>	0.44 <sup>c</sup>	0.17 <sup>a</sup>	0.27 <sup>b</sup>	0.33 <sup>b</sup>	0.27 <sup>a</sup>	0.33 <sup>b</sup>
2	N <sub>70</sub> +P <sub>4.4</sub> +K <sub>16.6</sub>	0.49 <sup>ab</sup>	0.60 <sup>b</sup>	0.77 <sup>ab</sup>	0.28 <sup>b</sup>	0.16 <sup>a</sup>	0.17 <sup>a</sup>	0.28 <sup>a</sup>	0.22 <sup>a</sup>
3	N <sub>60</sub> +P <sub>22.7</sub> +K <sub>36</sub>	0.27 <sup>a</sup>	0.77 <sup>a</sup>	0.38 <sup>b</sup>	0.50 <sup>c</sup>	0.27 <sup>a</sup>	0.33 <sup>ab</sup>	0.16 <sup>a</sup>	0.17 <sup>a</sup>
4	N <sub>60</sub> +P <sub>22.7</sub> +K <sub>36</sub> +Ca <sub>25</sub>	0.44 <sup>b</sup>	0.66 <sup>a</sup>	0.27 <sup>a</sup>	0.55 <sup>ac</sup>	0.22 <sup>a</sup>	0.17 <sup>a</sup>	0.27 <sup>a</sup>	0.17 <sup>ab</sup>
1	unfertilized	0.27 <sup>a</sup>	0.27 <sup>a</sup>	0.38 <sup>a</sup>	0.44 <sup>b</sup>	0.76 <sup>b</sup>	0.38 <sup>a</sup>	0.33 <sup>a</sup>	0.50 <sup>a</sup>
2	N <sub>70</sub> +P <sub>4.4</sub> +K <sub>16.6</sub>	0.27 <sup>a</sup>	0.27 <sup>a</sup>	0.33 <sup>b</sup>	0.39 <sup>a</sup>	0.27 <sup>a</sup>	0.33 <sup>b</sup>	0.33 <sup>a</sup>	0.22 <sup>b</sup>
3	N <sub>60</sub> +P <sub>22.7</sub> +K <sub>36</sub>	0.27 <sup>b</sup>	0.33 <sup>a</sup>	0.45 <sup>b</sup>	0.49 <sup>c</sup>	0.11 <sup>a</sup>	0.16 <sup>b</sup>	0.60 <sup>b</sup>	0.22 <sup>bc</sup>
4	N <sub>60</sub> +P <sub>22.7</sub> +K <sub>36</sub> +Ca <sub>25</sub>	0.33 <sup>b</sup>	0.44 <sup>a</sup>	0.55 <sup>c</sup>	0.53 <sup>bc</sup>	0.05 <sup>b</sup>	0.11 <sup>b</sup>	0.38 <sup>a</sup>	0.28 <sup>c</sup>

NOTE: Letters in table stand for statistical significance in columns (p < 0.05). Their conformity means that the values are statistically non-significant and different letters characterize statistical significance

Nickel contents in the grits in the 2<sup>nd</sup> variant compared to the control had a statistically significant decreasing tendency in all varieties, regardless of the applied ploughing, except for the *Xanadu* variety - in this variety, this ratio of nutrients in the soil did not have a significant effect on the decrease or increase of this metal in the barley grits (Tab. 3). When cereals were fertilized with a dose of N<sub>60</sub>+P<sub>22.7</sub>+K<sub>36</sub> (3<sup>rd</sup> variant), there was an increase in the chromium content in the

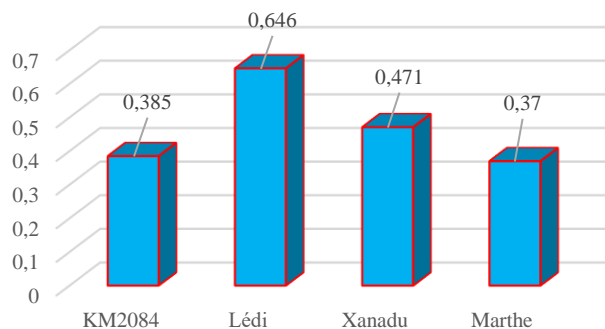
barley grits of the *Lédi* and *Marthe* varieties and its decrease compared to the control variant in the *KM2084* and *Xanadu* varieties grown on areas where minimization ploughing was implemented.

Cr - conventional ploughing



**Graph 1** Average chromium contents in barley varieties

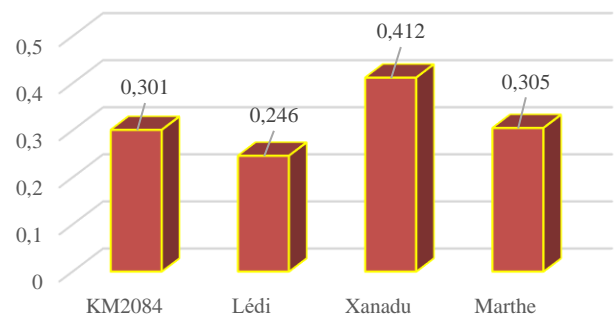
Cr - minimization ploughing



**Graph 2** Average chromium contents in barley varieties

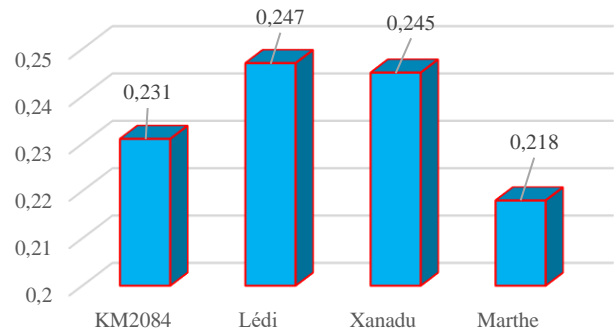
monitored metals in barley grits from cereal grains that grew on the plot where minimal tillage was applied.

Ni - conventional ploughing



**Graph 3** Average nickel contents in barley varieties

Ni - minimization ploughing



**Graph 4** Average nickel contents in barley varieties

On soils where conventional tillage was performed, the amounts of chromium in the barley grits in the given variant in all varieties increased compared to the control variant (except for the *KM2084* variety where no significant difference was observed). The second investigated metal, nickel, in the third variant had lower content values compared to the control in the varieties *Xanadu* and *Marthe*, or this fertilization had a negligible effect on the accumulation of Ni in barley grits (minimization ploughing). On plots where conventional tillage was carried out, a statistically significant decrease of this element was recorded in the barley grain of this variant compared to the control in all varieties, except for the *Xanadu* variety. The conclusions of the authors Dolijanović et al. (2019) show that Ni concentration in the grain of winter wheat cultivar *Azra* was the lowest in the variant with the highest rate of nitrogen application (120 kg. ha<sup>-1</sup>), which can be the consequence of soil acidity, organic matter content and sorption capacity (Shaheen et al., 2017; Wlasniewski et al., 2019). The study of Wlasniewski et al. (2019) did not record a significant impact of mineral nutrition on the varying of nickel quantities in the wheat and barley grain, but there was a certain tendency of reducing the content of this metal in the wheat grain with the increase of NPK dose (Wlasniewski et al., 2019). A decrease in nickel contents in grain was recorded by Dolijanović et al. (2019) also in cereals fertilized with a dose of 60 kg. ha<sup>-1</sup> of nitrogen compared to the unfertilized (control) variant, which is also in moderate agreement with our findings. Similarly, the authors Nazarkiewicz et al. (2018) state that mineral fertilization (regardless of liming) had no statistically significant influence on the nickel concentration in grain of the test cereals. However, there was usually a tendency towards a decreasing content of this metal in winter wheat grain in response to the increasing NPK doses at a constant N:P:K ratio. No univocal trend in the nickel content of spring barley grain shaped under the influence of increasing NPK doses was observed according to Nazarkiewicz et al. (2018). The effect of fertilizers on the elements contents in the grain is also the result of different things – e.g. synergism or antagonism of ions, changes in soil reaction (pH). In a study by Chen et al. (2020) the characteristics of heavy metals in soil, straw and wheat grain in response to long-term application of phosphorus in different doses were carried out. The authors investigated the transport capabilities of heavy metals from soil to straw and wheat grain. They concluded that by increasing the amount of phosphorus in the soil, the amounts of Zn, Cu, Pb and Ni in wheat grain decreased, while the amounts of Cd and As increased. Similarly, the amount of Cr in the grain had a decreasing character with the increase of P doses to the soil, but at the maximum dose of phosphorus (400 kg P ha<sup>-1</sup>) there was a slight increase of this element.

From the values shown in Table 3 it can be seen that liming in combination with NPK application compared to the non-limed variant (with the same nutrient dosage) did not have a clearly noticeable effect on the accumulation of both

In the case of conventional tillage, statistically non-significant increased Cr contents were recorded in the barley grits from plants that grew on limed and fertilized soil compared to cereals growing on the same fertilized soil. Increased contents of this element in the grain were also recorded in the comparison of the fourth variant with the control. On the contrary, in the last variant (conventional ploughing), a decrease in the amount of nickel in barley grits was observed compared to the penultimate variant in all varieties of spring barley, except for the variety *Marthe* (statistically significant only in the varieties *KM2084* and *Xanadu*). Compared to the control variant, a decrease in Ni in grits was also recorded in the variant with additive liming (except for the *Xanadu* variety). In similar consistency with our results, Nazarkiewicz et al. (2018) refer in their work that the interaction of liming with mineral fertilization showed a statistically significant impact on the nickel concentration in winter wheat grain, making its several-fold lower in grain of the cereal plants from limed than from non-limed treatments. No statistically confirmed interaction between these two agrotechnical procedures on the nickel content in the grain of spring barley was recorded, instead, a tendency towards a decreasing nickel content in grain from limed treatments was observed.

Ploughing itself with the absence of NPK macroelements in the soil also had an effect on the change in the contents of both monitored heavy metals in the barley grits obtained from the grain of our cereal varieties. Different soil tillage systems can influence some physical or chemical or biological soil processes (aeration, more CO<sub>2</sub> production via microorganisms, soil pH changes) (Vilček et al., 2019). The application of conventional ploughing compared to minimization ploughing caused an increase in nickel contents in grain in all varieties of spring barley and at the same time a decrease in chromium contents, except for the *Marthe* variety. Similarly, in the work of Dolijanović et al. (2019) reported that the highest concentrations of trace elements Co, Cu and Ni were observed in the grain of winter wheat cultivar *Azra* produced in areas where conventional tillage was performed. After applying conventional ploughing, Lavado et al. (2001) presented the statistically non-significant reducing of nickel content and relatively minimal reduction of chromium in wheat grain grown on soils at the site of Pergamino, Argentina.

## CONCLUSION

The influence of the spring barley variety on the accumulation of both monitored heavy metals (chromium and nickel) in the grain was observed. The lowest content of chromium and nickel in barley grits was determined in the *KM2084* variety. The first place in the intake of nickel in grain was in the *Xanadu* variety. The application of macroelements N<sub>70</sub>+P<sub>4,4</sub>+K<sub>16,6</sub> in combination with minimal ploughing had an



effect on the increase of chromium contents in barley grain in all varieties, but at the same time caused a decrease in nickel contents, except for the *Xanadu* variety where minimal effect of agrotechnical factors was observed in relation to the accumulation of this element in barley grits. The supply of nutrients  $N_{60}+P_{22.7}+K_{36}$  in combination with the same ploughing had no clear effect on the intake of both investigated metals in the grits of our tested spring barley varieties. Conventional tillage and  $N_{70}+P_{4.4}+K_{16.6}$  fertilization resulted in a decrease of nickel in spring barley grits (except for *Xanadu* variety). This agrotechnical procedure did not have a clearly characterized effect on the chromium contents in the grain grits. Fertilization  $N_{60}+P_{22.7}+K_{36}$  in combination with conventional ploughing caused an increase in chromium content in spring barley grits (except for variety *KM2084*) and a decrease in nickel (again except for variety *Xanadu*). The addition of  $CaCO_3$  together with NPK had no clear effect on the amounts of both observed heavy metals in cereals growing on the area with performed minimization ploughing. In the case of conventional ploughing followed by additive liming, an increase in chromium and a decrease in nickel in barley grits were evaluated. The application of conventional ploughing on unfertilized areas had an effect on the increase of nickel contents in all varieties and the decrease of chromium contents in three varieties of spring barley.

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