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ANTAGONISTIC RELATIONS OF LEAD AND CADMIUM WITH SELECTED MICRONUTRIENTS

ANTAGONISTYCZNE ODDZIAŁYWANIE OŁOWIU I KADMU Z WYBRANYMI MIKRONUTRIENTAMI

Słowa kluczowe: ołów, kadm, cynk, jęczmień jary.

Key words: lead, cadmium, zinc, spring barley.

Aktualnie zwraca się szczególną uwagę na zanieczyszczenie środowiska z uwzględnieniem metali ciężkich w aspekcie łańcucha pokarmowego. Coraz więcej naukowców zajmuje się zagadnieniami zanieczyszczenia środowiska oraz wynikającymi z niego konsekwencjami dla łańcucha pokarmowego. Metale ciężkie stanowią znaczącą grupę zanieczyszczeń gleby, które są źródłem ryzyka dla zdrowia człowieka ze względu na swoje właściwości teratogenne, mutagenne oraz rakotwórcze. Również badania dotyczące działania synergicznego i antagonistycznego pomiędzy poszczególnymi pierwiastkami prowadzą do pogłębienia wiedzy w zakresie ich oddziaływania. W pracy prezentowane są wyniki wpływu wybranych metali ciężkich – ołowiu, kadmu i cynku – na ilościowe i jakościowe parametry plonu jęczmienia jarego. Uzyskane rezultaty sugerują, że pojedyncze wprowadzenie ołowiu do gleby w ilości 200 mg/kg i kadmu w ilości 10 mg/kg ma negatywny wpływ nie tylko na plon jęczmienia jarego, ale także na parametry jakościowe. Spadek plonu wynosił ok. 43%, po dodaniu kadmu natomiast spadek ten wynosił 26,3%. W przypadku mieszanin ołowiu i cynku (200 mg/kg + 80 mg/kg) oraz kadmu i cynku (10 mg/kg Cd + 80 mg/kg Zn) dodanych do gleb, był obserwowany tylko nieznaczny spadek plonu/zbioru – odpowiednio 21,4% i do 19,9%, co można wytłumaczyć pozytywnym wpływem jonów cynku. Zawartość metali w mieszaninie kadmu i ołowiu w suchej masie jęczmienia jarego była porównywalna do zawartości w suchej masie po zastosowaniu mieszanin cynku i ołowiu, kadmu i cynku, i wynosiła odpowiednio dla

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Pb (1,32 mg/kg) i Cd (0,74 mg/kg). Przy pojedynczych dawkach zawartość w suchej masie jonów poszczególnych metali była wyższa – dla Pb (2,0 mg/kg) i Cd (1,2 mg/kg).

1. INTRODUCTION

Cereals have still been remaining the most important agricultural commodity. Spring barley is the second most frequent cultivated cereal; it is crop with short vegetation period, with weak and shallow root system and thus requires quality soil for its cultivation. This crop belongs among economic important cereals from the reasons of low cost on unit of cultivation area, higher purchase cost of raw material (malting barley) and also from the standpoint of raw material export possibilities as grain, malt or as final product – beer [Statistical Office SR 2004].

Changes of soil traits in negative and positive way, such as soil contamination caused by various human activities lasting long period, affect biological components of land and human health of population very intensively during last decades [Tóth et al. 2006].

Heavy metals, nitrogen and sulphur oxides, as well as many organic compounds belong among the main contaminants that negatively affect environment.

Heavy metals occur in soils in various concentrations and in various forms. They can derive directly from weathering of parent rock, where their concentration and distribution is directly influenced by processes in soil or they enter into the soil as direct consequence of human activities [Árvay et al. 2007]. The content of element in soil solution, uptake of soil solution by root system and affinity of elements to root system determine the amount of heavy metal taken by root system. The values of pH, cation exchangeable capacity and the content of CaCO₃ in soil belong to the most important parameters that affect adsorption of heavy metals in soil. The uptake of heavy metals by plants can be affected by interaction with other elements. Many authors [Lombi et al. 2000, Adiloglu 2002, Yassen et al. 2007] refer about possible efficiency of these relations (synergic and antagonistic) and of minimising of risky elements enter into food chain. Mutual synergism of numerous elements of macro- and microbio-genic character and of toxic elements provide knowledge that increasing doses of cadmium do not affect uptake of compounds of Ni, Cu, Mo and Cr, but on the other hand, they activate salts of Zn, Mn and Sr, that are also accumulated in enhanced rate in dry matter [Kulich 1989].

The objective of our work was to evaluate the influence of selected heavy metals (Pb, Cd and Zn) added as individual and gradual common doses on quantitative and qualitative parameters of spring barley (*Hordeum vulgare* L.).

2. MATERIAL AND METHODS

The tested crop was spring barley (*Hordeum vulgare* L.) variety Jubilant. Priority of this variety is high malting quality, high grain yield and good adaptability. Experiment was carried out as trial experiment, variants of observation A, B, C, D, E, are shown in Table 1.

Six kilograms of soil was weighted into plastic pots bowl-shaped with average of 20 cm and height of 25 cm with foraminated bottom. Basic nutrients were added in the form of NPK fertilizer. Heavy metals were added in the form of solutions:

- lead in the form of $\text{Pb}(\text{NO}_3)_2$,
- cadmium in the form of $\text{CdCl}_{2.2} \cdot \frac{1}{2} \text{H}_2\text{O}$,
- zinc in the form of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Then the seeds of tested crop were sown into soil after applying of basic nutrients of NPK and heavy metals in the form of empiric solution. After the emergence the plants were thinned to twenty per pot.

Table 1. Characteristics of pot trial variants

Tabela 1. Charakterystyka kombinacji w doświadczeniu wazonowym

Variants	Characteristic	Repetition
A	NPK – control	1 – 4
B	NPK + 200 mg $\text{Pb} \cdot \text{kg}^{-1}$ soil	5 – 8
C	NPK + 200 mg Pb + 80 mg $\text{Zn} \cdot \text{kg}^{-1}$ soil	9 – 12
D	NPK + 10 mg $\text{Cd} \cdot \text{kg}^{-1}$ soil	13 – 16
E	NPK + 10 mg Cd + 80 mg $\text{Zn} \cdot \text{kg}^{-1}$ soil	17 – 20

Table 2. Agrochemical characteristics of soil substrate

Tabela 2. Agrochemiczna charakterystyka podłoża glebowego

Soil reaction pH		C_{ox}	Hum.	Content of nutrients ($\text{mg} \cdot \text{kg}^{-1}$)				
H_2O	KCl	%	%	N	P	K	Ca	Mg
5.98	4.63	1.527	2.633	2979.0	19.86	215.5	1459.5	265.0

Table 3. Content of potentially available heavy metals in tested soil (in solution of HNO_3 , $c=2 \text{ mol} \cdot \text{dm}^{-3}$)

Tabela 3. Zawartość potencjalnie dostępnych metali ciężkich w badanej glebie

Cu	Fe	Zn	Mn	Cr	Pb	Cd	Ni	Co
9.54	1645.0	51.5	398.5	2.34	13.18	0.37	7.30	4.54

The weights of yield of spring barley after adding of heavy metals into the soil and its qualitative grain composition from the standpoint of risky elements content were evaluated. Content of risky elements was assessed after mineralization by dry way method AAS atomic absorption spectrophotometry on apparatus Varian AA 240 FS.

3. RESULTS AND DISCUSSION

Environmental pollution has various forms and one of them is also soil contamination by heavy metals. Heavy metals through food chain get into plants, animals and then also into human body. Their threat lies not only in their acute intoxication, which is scarce, but these substances

also tend to accumulate and organism is gradually changed by their effects. They cause apparently not noticeable disorders, but these can result in metabolic disorders [Vollmannová et al. 2006].

While agricultural production is the main source of foodstuffs, it is important to evaluate mainly negative influences of risky elements on quality of agricultural products.

Many works have referred about interaction Cd–Zn, especially with regard to their chemical relation. The results have showed that zinc addition into the substrate lowers uptake of cadmium by plants, but there are also some opinions about mechanisms of uptake of both elements under conditions of their excessive accumulation in soil [Fargašová 2001, Sharma et al. 1999]. Also Lombi et al. [2000] reported that uptake of Cd–Zn is not mutually dependent and carried out through various mechanisms.

Generally, it is suggested that interaction Cd–Zn is based on principle of competitive inhibition, when cadmium and zinc compete with similar active centres of carriers [Cibuľka 1991].

The yield of spring barley after treatment with heavy metals (Pb, Cd) in soil as single doses also in combination with zinc cations was evaluated in our work. Results are shown on Figure 1 and 2.

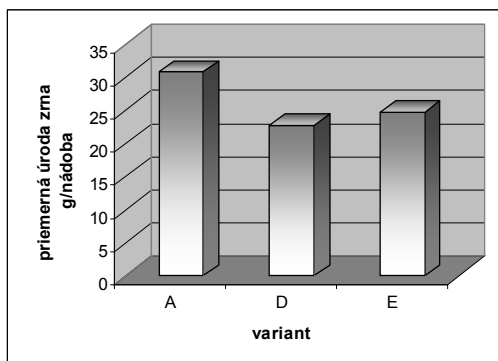


Fig. 1. Application of cadmium and zinc cations

Rys. 1. Zastosowanie kationów kadmu i cynku

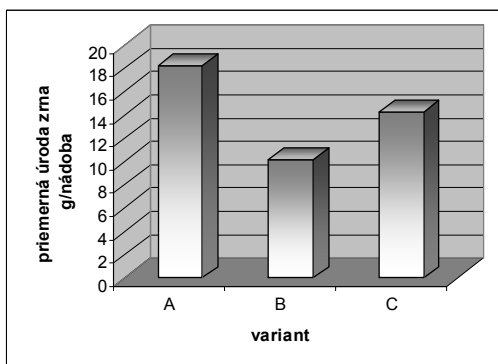


Fig. 2. Application of lead and zinc cations

Rys. 2. Zastosowanie kationów ołowiu i cynku

According to the authors [Poongothai et al. 1997], the addition of zinc into the environment lowers the uptake of cadmium by plants. Others [Lombi et al. 2000] reported that mechanisms of the uptake of zinc and cadmium are mutually dependent and thus equal uptake of both elements under conditions of their accumulation in soil. Our gained results showed that the dose of 10 mg Cd on 1 kg soil (variant D) lowered average yield of spring barley by 26.3% when compared to variant A (control variant). The combination of zinc and cadmium (variant E) caused only slight decline in yield of grain of spring barley when compared to control variant, but in comparison to variant D there was an enhancement in yield by 8.8%, what can be positively evaluated.

Zinc and cadmium can compete in bond places in soil system. Due to changing of mechanisms, in which cadmium and zinc can be involved, the final effect of zinc addition in system soil-plant is changing, in dependence on concentration of cadmium and zinc, on soil traits and plant species. Figure 1 showed that the addition of bivalent cations of Zn in amount of 80 mg/kg was manifested positively on yield of grain of spring barley in comparison with variant D, when the negative effect of bivalent cations of Cd was eliminated.

Lead was another toxic heavy metal that was surveyed in our work. Lead has high affinity to the formation of complex compounds with both oxidant numbers 2 and 4. It does not belong to essential elements and is highly toxic for animal and plant organisms [Makovníková et al. 2006].

Similar results were obtained after treatment of soil with bivalent cation of lead. Individual dose of lead cation into soil (variant B) also had negative influence on yield of spring barley and the yield decline was recorded in comparison with control variant (A) by 44.30%. The combination of lead and cadmium treatment was only slight decline (by 21.40%) in comparison to control variant, what could be also positively evaluated.

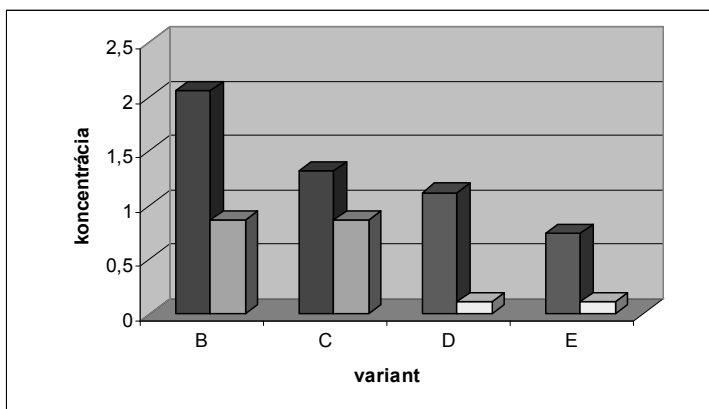


Fig. 3. Content of Pb and Cd (mg·kg⁻¹) in grain of spring barley

Rys. 3. Zawartość ołowiu i kadmu (mg·kg⁻¹) w ziarnie jęczmienia jarego

Also contents of heavy metals in dry matter of plants of spring barley were assessed, while bivalent cations of heavy metals (Pb, Cd) and Zn^{2+} were applied into soil on elimination of negative effects of lead and cadmium cations. Gained results are shown on Figure 3.

Positive effect of added bivalent cations of zinc into soil was confirmed when monitoring this qualitative parameter. The addition of bivalent cations of Zn was positively manifested on cadmium content in spring barley grain in comparison to variant D, when adsorption of Cd^{2+} was partly eliminated into grain structure. Decline of cadmium content in grain of barley was observed in variant E (10 mg Cd + 80 mg Zn) by 34% in comparison with variant D (10 mg Cd), what is positive statement.

Similar results were achieved by combination of treatment of zinc and lead. Lower content values of lead ($1.32 \text{ mg}\cdot\text{kg}^{-1}$) in dry matter of spring barley were assessed by treatment with combination variant C (200 mg Pb + 80 mg Zn) and by single dose of lead, variant B this value was $2.0 \text{ mg}\cdot\text{kg}^{-1}$.

4. CONCLUSION

Few methods concerning minimising or eliminating of enter of foreign substances, especially heavy metals into food chain are known. Individual effect of combination of Cd^{2+} and Pb^{2+} ions in relation to synergic or antagonistic effect of cations of zinc on yield and qualitative parameters of spring barley were evaluated in this work. Our gained results showed that addition of zinc in dose of 80 mg/kg (variant C, variant E) was positively manifested on height of yield of spring barley and also on observed qualitative parameters, what eliminated negative effect of risky elements (Cd, Pb).

Our obtained results can not be uniformly associated with the effect of bivalent zinc cations, because reaction of plants on presence of zinc is individual and affected by plant species, lead and cadmium content in soil, mutual combination of mentioned risky elements with zinc as well as by many other factors.

Acknowledgement: The work was supported by grants VEGA 1/0030/09 and KEGA 3/5081/07.

REFERENCES

- ADILOGLU A. 2002. The effect of zinc application on uptake of cadmium in some cereal species. In *Agricultural and Forest Science*, vol. 48, No. 6: 553–556.
- ÁRVAY J., ČÉRY J., HARANGOZO L., TREBICHALSKÝ P., JOBBÁGY J. 2007. Actual situation of the agricultural land contamination on the agricultural lands with heavy metals in different environmental loaded areas of Slovak Republic. In: *Bioclimatology and natural hazards*. International scientific conference, Poľana nad Detvou, Slovakia.

- CIBULKA J., DOMAŽLICKÁ E., KOZÁK J. 1991. Pohyb olova, kadmia a ortuti v biosfére. Praha. Academia: 432.
- FARGAŠOVÁ A. 2001. Effect of Cd in combination with Cu, Zn, Pb and Fe on root prolongation and metal accumulation in the roots and cotyledons of muslard (*Sinapis ulbä*) seedings. In Rostlinná výroba, vol. 43, No. 3: 97–103.
- KULICH J. 1989. Príspevok k poznatkom o fytotoxicite kadmia. In Poľnohospodárstvo, vol. 35, 1989, No. 2: 114–121.
- LOMBI E., ZHAO F.J., DUNHAM S.J. 2000. Cadmium accumulation in populations of *Thlaspi caerulescens* and *Thlaspi geosingense*. In New Phytologist, vol. 145, No. 1: 11–20.
- MAKOVNÍKOVÁ J., BARANČÍKOVÁ G., DLAPA P., DERCOVÁ K. 2006. Anorganické kontaminanty v pôdnom ekosystéme. In Chemické listy, vol. 100, No. 6: 424–432.
- POONGOTHAI S., MATHAN K., KRISHNASWAMY R. 1997. Effect of zinc and cadmium on the dry mater yield and nutrient uptake of Sorghum. In Madras Agricultural Journal, vol. 84, No. 5: 290–293.
- STATISTICAL OFFICE SR. 2004. dostupné na <http://www.google.sk>
- SHARMA S., SCHAT H., VOOIJS R. 1999. Combination toxicology of copper, zinc and cadmium in binary mixtures: concentration-dependent antagonistic, nonadditive, and synergistic effects on root growth in *Silene vulgaris*. In Environ. Toxicol. Chem., No. 2: 348–355.
- TÓTH T., LAZOR P., TOMÁŠ J., MELICHÁČOVÁ S. 2006. Obsah kadmia a olova v obilnách pestovaných v environmentálne zaťažených oblastiach Slovenska vo vzťahu k hygienickej kvalite potravín. In XXXVI. Lenfeldovy a Höklovy dny. Brno: Veterinárna a farmaceutická univerzita, No. 48–52.
- VOLLMANNOVÁ A., TIMORACKÁ M., MELICHÁČOVÁ S., HARANGOZO L., JOMOVÁ K. 2006. The relationship of heavy metal contents in soils to content of chemoprotective compounds in soya bean. In Zem v pasci? Analýza zložiek životného prostredia. Zvolen : TU, p: 744–748.
- YASSEN A.A., BADRAN N.M., ZAGHLOUL S.M. 2007. Role of some organic residues as tools for reducing heavy metals hazard in plant. In World Journal of Agricultural Sciences, vol. 3, No. 2: 204–209.