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THE CONTENT OF MERCURY IN VARIOUS TYPES OF CEREALS GROWN IN THE MODEL CONDITIONS

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ABSTRACT

The consumption of cereals in Slovakia but also worldwide is increasing by every year. From 30000 to 50000 tons of mercury circulates throught the biosphere that gets into the atmosphere degassing of the earth's crust and world oceans. Mercury affects CNS and causes its disorders. The high doses of mercury causes a lot of different changes of personality as well as increased agitation, memory lossorinsomnia. It can also affect other organ systems such as the kidney. The exposure level is reflected in the concentration of mercury in blood and urine. The aim of our work was the evaluation of transfer of mercury from sludge to edible part of chosen cereals. The objectives were achieved in simulated conditions of growing pot experiment. We used agricultural soil from the location of Výčapy – Opatovce for the realization of the experiment. The sludge, which was added atvarious doses, was taken from Central Spiš area from locality of Rudňany near the village where minedironore that contains mainly copperand mercury during last few decades was. We used three types of cereals: barley (*Hordeum sativum L.*) variety PRESTIGE, spring wheat (*Triticum aestivum L.*) variety ISJARISSA and oat (*Avena sativa L.*) variety TATRAN. The length of growing season was 90 days. From the obtained results of two years can be concluded that the accumulation of mercury by seed follows wheat < barley < oat. Even though that the oat is characterized by the highest accumulation of mercuryin the seeds, the content did not exceed the maximum level sspecified by The Codex Alimentarius of Slovak Republic. The results shows that the suitable cultivation of the cereals in localities, which are contaminated with heavy metals, especially by mercury, that the high content of mercury in soil do not pose a risk of accumulation of the metal into the cereal grain.

Keywords: cereals; plants; mercury; heavy metals

INTRODUCTION

The cereals are probably the most important source of food for humans and feed foranimals. Consequently, the low level of contamination can affect the health of consumers. Chemical contamination can occur from growing of cereals to their processing and storage **(Alldrick, 2012)**.

The cereals are the most common crops that are grown on arable land of EU. The fifty percent of cereal production in Southern Europe consists of wheat and than barley and maize. Other cereals as oat and rye are grown to a limited amounth **(Finch et al., 2014)**. The consumption of cereals in Slovakia but also worldwide is increasing by every year. The cereals are particularly very important for its nutritional value. The opinion of many experts is that cereals should constitute from 40 to 60 percent of well - balanced diet. Cereals provide most of the calories and proteins consumed worldwide. The current annual world production is more than 2.5 billion tons. This out put is either directly channeled to the food industry or used as animal feed to provide meats, dairy, and poultry products. Among cereals, rice, wheat, and maize yield approximately 89% ofthe total production and constitute the main stay of practically all cultures. The otherless important cereals are barley, oats, sorghum, rye, triticale, and millets. All cereals are strachy foods and contain protein that does not meet the essential aminoacid balance required by growing infants. They are considered a good source of energy, most B vitamins, and dietary fiber when consumed as whole grains **(Serna Saldivar, 2016)**.

The cereals and cereal products are the main sources of carbohydrates in food for humans and feed for animals. Cereal grains are an important source of energy and nutrients in the form of protein, fat, fiber, minerals and vitamins **(Beverly, 2014)**.

The cereals are as well as the most important source of fructans in our daily diet. Nowadays are hotly discussed and compared a lot of different cereals in the terms of fructans structure. Their degradation during processing of food is considered as a potential health benefit. Recent published data suggest that they may also have a prebiotic effect **(Verspreeta et al., 2015)**.

The cereals and cereal bran obtained a significant position as a functional food. They are a source of carbohydrates (arabinoxylan, beta – glucan), phenolic acids (ferulic acid), flavonoids (anthocyanins), oil (γ - oryzanol), vitamins, carotenoids, folates and sterols. Their physico – chemical properties makes them a necesssary ingredient for food fortification. The bran of rice, wheat, oat, barley, millet, rye and corn contain a huge amount of health-promoting ingredients. The anti-atherogenic, anti-hypertensive and hypoglycemic properties were verified. Further, it was found the effect against oxidative stress. They reduce insulin resistance, prevent the risk of obesity by inducing the feel of fullness **(Patel, 2015)**.

The importance of fiber as a part of a well - balanced diet, has been known for a decades. Soluble fiber such as β-glucan has a significant glycemic effect. The cereals, especially barley and oat are a perfect source of these functional components. Current research suggests that the efficacy of the beta-glucans is also appreciable in the immune system. They have a positive effect as prebiotics **(Koutinas et al., 2014)**. Recent large-scale epidemiological studies have shown that regular consumption of whole grain cereals can reduce the risk of heart disease and certain cancers by 30 percent. One of the factors that increase the functionality of foods is theso-called in digestible resistant starch **(Duchoňová and Šturdík, 2010)**.

The most common toxic heavy metals include Hg, Cd and Pb. The current state of the environment significantly influences gene pool of plants and animals and through food chain and population health and animals **(Cimboláková and Nováková, 2009)**.

Food consumption has been identified as a major source of contaminants income. There are a lot of elements which have a pathological effect on the organism, and are characterized by high toxicity. These contaminants are mercury and arsenic too **(Melo et al., 2008)**. Lead, mercury and cadmium are the elements which have a harmfule ffects on the central nervous system in the development of the child **(Kippler et al., 2012)**. Mercury, as well as other trace elements, moves between different media (i.e. atmospheric aerosol, dust, soil, plants, sediment, in the gas phase, in aqueous solution and solids **(Charlesworth et al., 2011)**.

Mercury mining and its use in products continue to the present. Consumer products containing mercury are batteries, fluorescent lamps, and some cosmetics **(McKelvey et al., 2011; Streetsetal, 2011)**. Mercury and its compounds are toxic to humans and the environment. Mercury is found in various chemical forms and is able to cause a wide variety of clinical effects **(Bernhoft, 2012)**.

The toxicity of mercury and its compounds to humans, such as a taxy, narrow vision, hearing loss and death were firstly described in 1865 **(Grandjean et al., 2010)**. Man receives the highest concentrations of mercury through the food chain and the largest sourceof food consists of animal origin **(Tóth et al., 2012)**.

The high doses of mercury can be fatal to humans, but even relatively low doses can have a serious effect on the nervous system and the development. Nowadays it has been disscused a lot about the harmful effectson the cardiovascular, immune and reproductive systems. Mercury also slow down microbiological activity in soil and under the regulation of classification of ground and surface water is one of the most hazardous substances to health. Mercury is persistent and can change the environment into methylmercury, the most toxic form. The phytotoxicity of mercury depends on its form and sorption. Elemental mercury is a potential source of highly toxic gases. Plants possess different degrees of tolerance of mercury **(Samešová, 2012)**. The plants may be exposed to either direct effect of mercury as antifungal agents, particularly through the crop seed treatment or foliar spray or by an accident. The exposure to mercury may occur through soil, water and air pollution.The concentration of mercury in above – ground parts of plants depends largely on foliar uptake Hg^0 volatilisation from the soil. Wilde dible fungiare characterized by high bioaccumulative ability – they are able to take from substrate and then aggregated up to several tens of its concentrationin soil **(Árvay et al., 2014; Árvay et al., 2015)**.

The factors that are affecting the accumulation of mercury by plants are organic matter contentin the soil or sediments, organic carbon content, redox potential and total metal content. Generally, mercury up takein plants could be related to the degree of soil pollution **(Patra and Sharma, 2000, Tomáš et al., 2012, Árvay et al., 2013; Tomáš et al., 2014)**.

MATERIAL AND METHODOLOGY

The aim of our work was the evaluation of transfer of mercury from sludge to edible part of chosen cereals. The objectives were achieved in simulated conditions of growing pot experiment. We used agricultural soil from the location of Výčapy – Opatovce for the realization of the experiment. The sludge, which was added at various doses, was taken from Central Spiš area from locality of Rudňany near the village where was mined iron ore that contains mainly copperand mercury during last few decades. We used three types ofcereals: barley (*Hordeum sativum L.*) variety PRESTIGE, spring wheat (*Triticum aestivum L.*), variety ISJARISSA and oat (*Avena sativa L.*) variety TATRAN. The length of growing season was 90 days.

Before the establishment growing pot experiment we performed all necessary analyses in soil and sludge. We determined soil reaction, content of nitrogen by Kjeldahl method, phosphorus content, potassium and magnesium contentby Mehlich II solution. Subsequently, we determined the content of heavy metals in the acid mixture HNO_3 and HCl (decomposition by aqua regia) by AA Swith Varian AA240FS (Australia). For analysis of each elelment, we used the multi-element standard SigmaAldrich (Germany).

To every one of all tested pots was weighed 5 kg of soil with 1 kg of silica sand, while the bottom of the container was filled with a small drainage layer of gravel. In each pot was applied the calculated dose of sludge.

Crop shave been harvested at full maturity time and after drying were assessed by mercury by AAS for AMA254 (Czech Republic). Seed samples are analyzed directly without modification.

For statistical evaluation of obtained results was used a statistical program STATISTICA 6.0 Cz. Wetested the resultson the level of descriptive statistical evaluation, and overall visual indication of the level factor, variability and the deviation was expressed in text. For statistical evaluation we used T-test at the level $p \leq 0.05$.

RESULTS AND DISCUSSION

Soil from the locality of Výčapy – Opatovce has analcalic soil reaction with medium level of humidity. It is characterized by good content of phosphorus and potassium and a high content of magnesium.The contents of heavy metals do not exceed the limit values **(Act No. 220/2004 Coll.)**.

Sludge from the locality of Rudňany has a strongly alkaline soil reaction. It is characterized by a very low content of phosphorus and potassium. Mercury content (57.81 mg.kg^{-1}) exceeds the maximum permissible amount by 5.78 times **(Act No. 188/2003 Coll.)**.

Mercury content in barley seeds in D variant has increased by 7.9 times in 2013 and 14.2 times in 2014 compared to variant A (soil without addition of sludge). Escalating amount of sludge added to the soilis proportionally reflected in mercury content in the seeds of barley. In 2013 the mercury content in the seeds of barley was almost a half lower than in 2014.

Mercury contentin barley seeds in all variants exceeded the maximum permissible amount specified by The Codex Alimentarius of Slovak republic (CA SR).

Statically significant difference between 2013 and 2014 in mercury content in the seeds of barley was obtained in the variant D. In other variants was not statistically significant difference.

The highest mercury content of seeds of wheat was obtained in the variant D in 2014 where the Hg content in the seeds was higher by 5.7 times than in variant A. The differences between the mercury content of variants C and D was not as significant as in the case of barley. The difference between the highest mercury content of seeds of wheat in variant D in the year 2013 and 2014 had not a

Table 1 Variants of the experiments.

variants	
A	soil 100%
B	soil 90%, sludge 10%
C	soil 80%, sludge 20%
D	soil 70%, sludge 30%

Table 2 The content of microelements in the soil.

MEHLICH II (mg.kg^{-1})			
K	**Ca**	**Mg**	**P**
287.5	6948.0	392.0	587.5

Table 3 The contents of heavy metals in the soil (decomposition by aqua regia) and comparison of **Act No. 220/2004 Coll. of Slovak Republic** (mg.kg^{-1}).

	Cd	**Pb**	**Cu**	**Zn**	**Cr**	**Ni**
soil	0.70	18.2	18.4	55.6	17.2	30.6
Act No. 220/2004	0.70	70	60	150	70	50

Figure 1 Simulated conditions of growing pot experiment.

Table 5 Mercury content in the seeds of wheat variety Jarissa in 2013 and 2014 (mg.kg^{-1}) and the comparison of mercury content with Codex Alimentarius of Slovak republic (CA SR).

	WHEAT	
variants	**2013**	**2014**
A	0.001821	0.001395
B	0.003241	0.001866
C	0.006582	0.004729
D	0.006809	0.007966
CA SR	0.05	0.05

Table 6 Mercury contentin the seeds of oat variety Tatran in 2013 and 2014 (mg.kg^{-1}) and the comparison of mercury content with Codex Alimentarius of SR (CA SR) .

	OAT	
variants	**2013**	**2014**
A	0.002971	0.002288
B	0.007252	0.003753
C	0.009468	0.010078
D	0.019722	0.040756
CA SR	0.05	0.05

high level of significance.

Mercury content in wheat seeds in all variants was not exceeded the maximum permissible amount specified by Codex Alimentarius of SR (CA SR) .

Regarding the differences in mercury content in wheat seeds was not obtained statistically significant difference beetween different years.

The largest in take of mercury was obtained in oat seeds. Mercury contentin variant D (maximum addition of sludge) was higher by 17.8 times than in variant A in 2014. In 2013 the mercury content in the seeds of oat was almost a half lower than in 2014. The most significant increase in mercury conten tin the seeds of the oat option C and D was recorded in 2014.

Although oat is characterized by the highest accumulation of mercury in the seeds, the content was not exceeded the maximum permissible amounts specified by Codex Alimentarius of SR (CA SR).

Statically significant difference between 2013 and 2014 in mercury contentin the seeds of oat was obtained in the variants B and D.

Bajčan et al., (2010) measured mercury concentrations in the samples taken agricultural crops grown on all uvial soils in the region of Hont. Hg content in the grains wer in a range of less than 0.0001 mg.kg-1 to 0.0198 1 mg.kg^{-1}, what is significantly less mercury as maximum allowable limit for Food (0.05 mg.kg^{-1}).

Hg content corresponds to the content in the soil, the greater Hg content in thes oil, the higher the Hg content in the grain cereals. The highest Hg content in the grain weset in the grain of the barley from area Markušovce and 0.2006 mg.kg^{-1}, what It represents four times the limit value **(Šabo, 2013).**

In general, the acceptability of the soil for the plants Hg low, tending accumulation in the roots, but the aerial parts of the plants absorbed from the atmosphere directly Hg. To of total Hg in plants has, according to some authors direct deposition up to 90% share. The natural average concentration of Hg in the plants are moved between 0.005 - 0.17 mg of Hg. kg^{-1}, with values of 1 - 3 mg Hg.kg^{-1} are considered phytotoxic **(Toman et al., 2000).**

The following figures show the comparison of the mercury contentin the seeds of commodities in different variants.

Figure 2 shows that the mercury content of the seeds of each cereal in variants B, C and D increases with increasing addition of sludge intot he soil. The smallest storage capacity of mercury was recorded in spring wheat variety ISJARISSA. In a variant D was 0.006809 mg.kg^{-1} of mercury content, which represents almost a half of the amount that has been accumulated by seeds of barley and by 3 times smaller than accumulated amount in the case of seeds of oat in the same variant.

Figure 3 shows a similar situation as Figure 2, thus increasing doses of sludge into the soil affected also by increased mercury content in the seeds of varieties of all crops.The results obtained from the two years can therefore say that in terms of accumulation of mercury seeds equence is as follows wheat < barley < oat.

Increased mercury content in soil in each variant due to the addition of sludge had a statistically significant effect on mercury content in the seeds of all variants ata significance level of $p<0.05$.

For all crops the additions of sludge into the soil have a statistically significant effect on mercury content in different variants ata significance level of $p <0.05$.

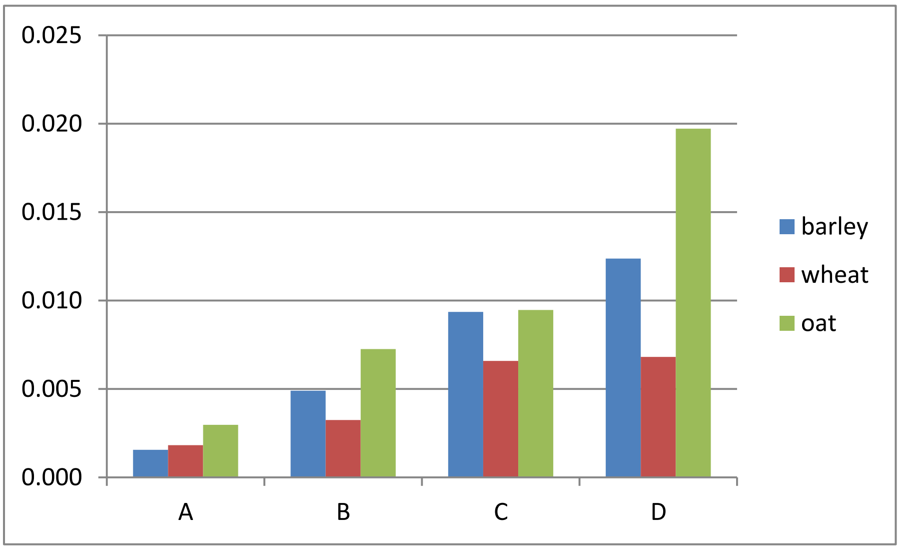

Figure 2 Mercury content in the seeds of various cereals in all variants ($mg.kg^{-1}$) that were grown in the year 2013.

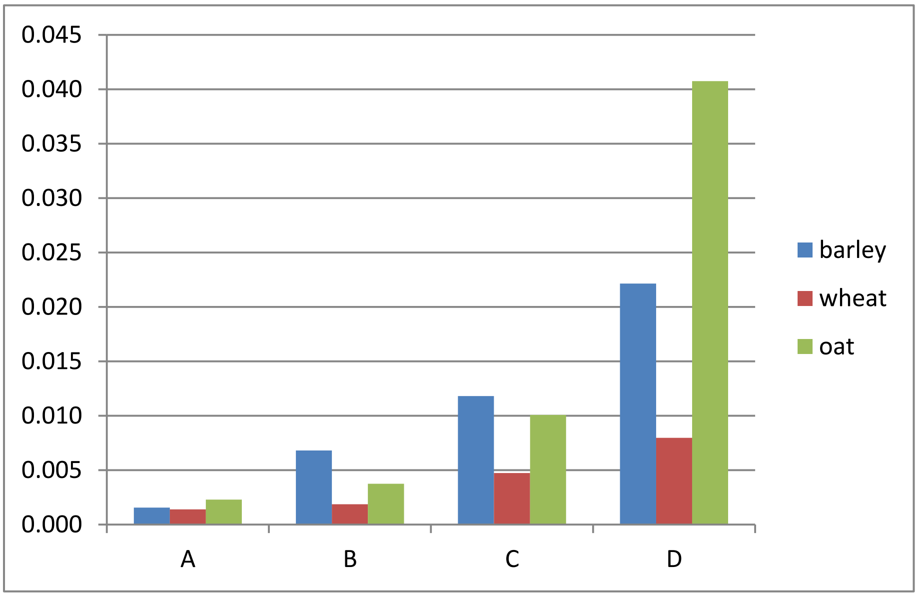

Figure 3 Mercury content in the seeds of various cereals in all variants ($mg.kg^{-1}$) that were grown in the year 2014.

CONCLUSION

The results showed that the amount of sludge added in specified amounts into the soil increases mercury content in seeds of crops.

Although oat was characterized by the highest accumulation of mercury in the seeds, the content was not exceeded the maximum permissible amount specified by Codex Alimentarius of SR.

From the obtained results of two years can be concluded that the accumulation of mercury by seed follows wheat < barley < oat.

The results showed that the suitable cultivation of the cereals in localities, which are contaminated with heavy metals, especially by mercury, that the high content of mercury in soil do not pose a risk of accumulation of the metal into the cereal grain.

Increasing number of toxic metals in soil leads to an increased content of the emetals in crops and subsequently in animal products. This may have adverse effects on people who consume these products.

There are two main reasons why the contamination of the environment with heavy metals causes concern. First, it can reduce the productivity of plants used as human food and animal feed. Second, it affects the quality of agricultural products.

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