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CONTENTS OF CADMIUM (Cd), CHROMIUM (Cr) AND LEAD (Pb) IN THE AGRICULTURAL LAND IN THE DRY MASS ALFALFA FROM VARIOUS LOCALITIES

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This paper presents the results of the chemical analysis of the content of heavy metals (cadmium, chromium and lead) in the soils from the agricultural plots in four sites of the individual sector sown with the variety alfalfa Banat ZMS II. The test sites v. Jegunovce – Tetovo, v. Radusha – Skopje, and v. Kochilari – Veles are in the vicinity of certain pollutants (factory Jugochrom – Jegunovce, an abandoned mine for chromium and iron in Radusha, the smeltery of lead and zinc – Veles), while the v. Saraj – Skopje site is located in the middle of the noncontaminated environment and is taken for results comparation. The content of heavy metals (Cd, Cr and Pb) in the dry vegetation mass of the experimental alfalfa from the same sites was also researched in two phases of development where the following values were found such as <50 (Cd), <2.00 (Cr) and <2.00 (Pb) mg / kg dry mass, namely alfalfa selective capability to the analyzed heavy metals, besides their presence in soils, primarily chromium whose values were higher than the maximum permissible amount (>100 mg/kg soil).

Key words: heavy metals; Cd; Cr; Pb; agricultural land; soil; alfalfa; dry mass; phase development; noncontaminated; selectivity

СОДРЖИНА НА КАДМИУМ (Cd), ХРОМ (Cr) И ОЛОВО (Pb) ВО ЗЕМЈОДЕЛСКО ЗЕМЈИШТЕ И ВО СУВА МАСА НА ЛУЦЕРКА ОД РАЗЛИЧНИ ЛОКАЛИТЕТИ

Во овој труд се презентирани резултати од хемиската анализа за содржина на тешките метали (кадмиум, хром и олово) во почвите од земјоделски парцели во индивидуална сопственост на четири локалитети засеани со луцерка од сортата банат ЗМС II. Опитните локалитети беа во с. Јегуновце – Тетово, с. Радуша – Скопје и с. Коџилари – Велес, сите во близина на одреден загадувач (фабрика Југохром во с. Јегуновце, напуштениот рудник за хром и железо во с. Радуша, Топилница за олово и цинк во Велес), додека локалитетот во с. Сарај кај Скопје, кој се наоѓа во неконтаминирана средина, служеше за компарирање на добиените податоци. Испитувана беше и содржината на наведените тешки метали (Cd, Cr и Pb) во сувата растителна маса на луцерка од опитните локалитети, и тоа во две фази на развиток, при што констатираните вредности беа: <0,50 (Cd), <2,00 (Cr) и <2,00 (Pb) mg/kg сува маса, т.е се докажа селективната способност на луцерката спрема испитуваните тешки метали и покрај нивната присутност во почвата, пред сè спрема хромот чии вредности беа повисоли од МДК (>100 mg/kg почва).

Клучни зборови: тешки метали; Cd; Cr; Pb; земјоделско земјиште; почва; луцерка; сува маса; фази на развиток; неконтаминираност; селективност

INTRODUCTION

Most common content of Cd in soil ranges from 0.1-1.0 mg/kg, while the maximum allowab-

le amounts of Cd amounted 3.0 mg/kg (Stavreva, 2002).

Chromium in soil is found as Cr^{3+} and Cr^{6+} , that being uptake foster than plants in comparison

with Cr^{3+} . The sixvalency chrome (Cr^{6+}) in the presence of chromium organic matter is reduced in such from it's found in soil (Zlatareva et al., 1999). Most common content of chromium in soil ranges from 20–50 mg/kg, while the maximum amount allowable (MAA) is 100 mg/kg soil (Kloke, 1980; quote Ubavić et al.1995).

The content of lead in pedosphere is about 0.001%. As an integral part of the lead dust comes in the soil and this accumulation in plants affected toxicly (Jordanov et al. 1997). There are different interpretations permissible amounts of lead in soil. For example on the allowed amount of lead in the soil pH of 4–7 is considered 200.0 mg/kg, or 50 mg/kg soil by Minev, 1985, a quote from Trpeski et al. 1997.

By determining the content of heavy metals (Cd, Cr and Pb) and the dry weight of alfalfa leaves and stems the objective was determined by their presence and extent of uptake of soil solution. In case of exceeding the allowable limits they may have adverse effect not only on growth and development of the plant (Cvetanovska & Kratovalieva, 2002; Baszynski et al. 1986; Ernst, 1980), but also on home ruminant animals (ARC, 1980; Grace, 1989) and finally their poisoning, especially in terms of content of cadmium, lead and mercury (Adamović et al., 2002).

MATERIALS AND METHODS

The approach of taking soil samples is based on sampling of individual trials by zig-zag methods of adequate depth and then forming the average test which presents the state of chemical parameters in the proving plot.

The laboratory soil is brought in the air condition at room temperature then through a sieve of 1 mm stored in paper bags.

The content of cadmium, chromium and lead in the soil is determined by the wet combustion procedure (HNO₃:HCl = 1:3) and reading A.A.C.

For the determination of heavy metals in the dry mass of alfalfa grown in field conditions, samples are taken over two phenophases (before flowering and during flowering). The quadratic method takes the plant mass of alfalfa measured, then air dried weight again and grounds. The samples are kept in dry place in paper bags.

The content of cadmium, chromium and lead in plant dry mass was performed by wet combustion with HNO₃, HClO₄, H₂SO₄ (10.0 : 1.0 : 0.25) and reading of A.A.C.

RESULTS AND DISCUSSION

The contents of heavy metals in soil (Cd, Cr, Pb)

Cadmium (Cd)

Most common content of cadmium in soil ranges from 0.1–1.0 mg/kg, while the maximum permissible amount of Cd amounted 3.0 mg/kg (Stavreva, 2002).

The research showed that the content cadmium in soils of the surveyed sites with alfalfa was lower than 1.0 mg/kg (Table 1) and as such they do not belong to the soils contaminated with this element.

Chromium (Cr)

The most common content of chromium in the soil ranges from 2–50 mg/kg, while the maximum amount allowed (MAA) amounted to 100 mg/kg soil (Kloke, 1980).

Measuring the amounts of chromium in soils on sites with experienced ones own alfalfa higher content of MAA (282.5 mg/kg soil) has been found in the village Radusha, while the localities of v. Jegunovce 47.37 mg/kg, v. Saraj 17.87 mg/kg soil and under the limit of MAA, i.e. v. Kochilary are in limits of MAA (93.25 mg/kg).

Lead (Pb)

As an integral part of lead dust comes in soil and its accumulation in plants affected toxically.

There are different interpretations for the allowed amount of lead in soil. For example, allowed amount of lead in soil pH in the 4–7 is 200 mg/kg soil. Other authors the amount of 50.0 mg/kg soil, a quote from Trpeski, 1997, consider permissible.

The obtained values for the content of lead in soil in localites of v. Saraj (22.50 mg/kg), v. Jegunovce (20.25 mg/kg) and v. Radusha (21.87 mg/kg) do not show significant differences, whereas in v. Kochilari (28.25 mg/kg) soil the values are significantly higher. The measured lead content in v. Saraj (22.50 mg/kg soil) is not in favor of the assumption of an ecologically clean environment, while in v. Kochilari higher values are expected.

Table 1

| Location | | mg/kg soil | |
|--------------|--------|------------|-------|
| | Cd | Cr | Pb |
| v. Saraj | < 1.00 | 18.87 | 22.50 |
| v. Jegunovce | < 1.00 | 47.37 | 20.25 |
| v. Radusha | < 1.00 | 282.5 | 21.87 |
| v. Kochilari | < 1.00 | 93.25 | 28.25 |

The content of heavy metals (Cd, Cr, Pb) in soil

Recently the accumulation of lead in soil and its impact on vegetation is being investigated by several authors: Sovent (1992), Haygarth & Jones (1995), Kahle (1993) a quote from Mededović, 1999.

CONTENT OF HEAVY METALS (Cd, Cr AND Pb) IN DRY MASS OF ALFALFA

The results from a three years research showed that the content of cadmium in the leaves and stems of alfalfa are lower than 0,50 mg/kg dry mass.

The observed values go in favor of the results obtained from the chemical analysis of soils given in Table 1, which indicating low presence of Cd (lower than 1,00 mg/kg soil) are considered not contaminated.

The average values for the content of chromium in leaves and stems of alfalfa are added in Table 2. Despite the different amounts of chromium measured in soils experienced ones (Table 1), which in v. Radusha are higher then the maximum permissible amounts (282.5 mg/kg).

However in the dry mass of the experience alfalfa the amount of Cr was lower than 2.00 mg/kg. The obtined data indicate claims of selective ability of alfalfa to some heavy metals (Davis & Smith, 1980).These results do not conform the finding of its increased uptake depending on the amount of chromium in soil (Zlatareva, 1999).

Shill higher contents of chromium makes its most suitable environment for the growth of alfalfa because his depressing effect on the uptake of important microbiogen elements (Jusufi E., 2009) and other authors for uptake of chromium, iron, molybdenum and toxicity (Athar, 2002).

Table 2

| The content of heavy | metals (Cd, | Cr, Pb) in dry |
|----------------------|-------------|----------------|
| | mass | |

| | mg/kg dry mass | | | | | | | |
|--------------|----------------|--------|--------|------|--------|--------|--|--|
| | Leaves | | Stems | | | | | |
| Location | Cd | Cr | Pb | Cd | Cr | Pb | | |
| | b. flower | | | | | | | |
| v. Saraj | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Jegunovce | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Radusha | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Kochilari | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| | flowering | | | | | | | |
| v. Saraj | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Jegunovce | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Radusha | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |
| v. Kochilari | 0.50 | < 2.00 | < 2.00 | 0.50 | < 2.00 | < 2.00 | | |

Lead (Pb)

Despite differences in the content of lead found in soil, i.e. under optimate 30 mg/kg soil (Table 1) in dry mass in leaves and stems of all experimental variations, measured contents of lead were lower than 2.0 mg/kg (Table 2). Lower values of dry mass before correlation with lower contents in lead soil solution but also a result of selective capacity of alfalfa against lead (Haygarth & Jones, 1995; Kahle, 1993) its low mobility (Kratovalieva et al., 2001) also the ability of Pb for binding in the cell wall of roots with only a small amount which reaches to the protoplasm ((Ernst, 1972).

CONCLUSIONS

- The obtained values for the content of heavy metals (Cd, Cr, Pb) in soil plots of the experienced plots indicate that some in terms of cadmium (lower than 1.0 mg/kg) and lead (sub 50 mg/kg) are not contaminated, i.e. are within the maximum allowed amount.

- The soil in v. Radusha has chromium that exceeds maximal allowed content (282.5 mg/kg), in v. Kochilari (93.25 mg/kg) which is in board of MAA (100 mg/kg) while significantly lower are in v. Jegunovce and v. Saraj (47.37 mg/kg and 18.87 mg/kg).

- The location of v. Radusha proved to be the most favorable environment for the development of alfalfa primarily because of higher amount of chromium depressing effect in the uptake and other significant microbiogen elements.

– Dispite different amounts of lead and especially of chromium in soil their amount in dry mass alfalfa is lower than 2.0 mg/kg, i.e. cadmium its lower than 0.50 mg/kg. Data favor the claims of the existence of protective mechanisms of plant to certain microbiogen elements which in certain amount are toxic.

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