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ASSESSMENT OF HEAVY METALS CONTENT IN CALCARIC ALLUVIAL SOIL FROM BUZAU COUNTY UNDER RESTRICTION OF ORGANIC FARMING

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Abstract

One of the most important aspects regarding food safety is the heavy metal content of food and agricultural products. Due to the rapid development of different industries and other anthropogenic activities, the environmental contamination suffered an exponential increase. The assessment of the soils and crops heavy metal content is unavoidable nowadays, even mandatory for specific products. Also, it provides important information regarding the characterization of a specific area, of the soils properties variations and allows correlations between different elements and agricultural practices. Our study aims to evaluate some of the most common heavy metals (Pb, Cd, Ni, Co, Zn, Cu, Mo, As and Cr) found in one calcaric alluvial soil from Buzau county used for tomato cultivation in organic farming system. We aimed both to establish the compliance with national and European legislation and determine a correlation between these elements, in the context of using microbial inoculants for crop protections. The soil samples were taken only from the surface layers (0-20 cm depth), from plots planted with Florina 44 tomato variety, microwave digested and the elements were quantified using ICP-MS method. The obtained values showed that the soil content is within the legislation limits and allowed us to illustrate some correlations between different heavy metals.

***Key words**: heavy metals, organic farming, Buzau county, tomato.*

INTRODUCTION

Over the past decades, heavy metal pollution has grown steadily, exposing both human health and the environment to increasing risks (Tchounwou et al., 2012). Heavy metals form a separate group of pollutants, especially due to properties such as long residual and half-life, soil residence time (> 1000 years), as well as bioaccumulation and bioamplification in food chains. However, some of these metals, such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential micronutrients for organisms, being necessary for different physiological and biochemical mechanisms (WHO, 1996). However, excessive amounts of these metals can cause adverse reactions in plant and animal organisms. Other metals such as lead (Pb) and cadmium (Cd) have no established biological functions and are considered non-essential (Hazrat et al., 2019). These are considered by EPA (The Environmental Protection Agency) as hazardous contaminants.

Although heavy metals are naturally part of the earth's crust, anthropogenic activities play the biggest role in environmental contamination, the most notable being waste disposal & treatment, mining, chemical industries, agricultural and pharmaceutical activities, transportation (Raja Rajeswari et al., 2014). Soil is one of the most affected components of the environment. EEA (European Environmental Agency) estimates that in 2019, in Europe exists 2.5 million potentially contaminated sites, but only 45% of them have been identified. The existence of a significant number of unidentified sites demands that for the correct characterization of an area, a series of analyses must be carried out to determine heavy metal abundance. Since most heavy metal inputs act on the surface layer (0-20 cm), an analysis of this layer is sufficient for soil characterization (Hou et al., 2014). Also, mineral uptake is prevalent in this range for most crop plants (Kismányoky et al., 2010). Heavy metals are found in soils in different forms, and they are influenced by several physical and chemical properties of the soil. Thereby, pH, conductivity or amount and type of other metals can influence solubility, mobility, bioavailability and biotoxicity of heavy metals (Shahid, 2017). Although the dissolved form fraction of heavy metals is the most important regarding availability for plants, the international and national authorities use the total content of heavy metal as reference values. (European Commission, 2001). As the European Union has not established general heavy metal limits for soils, each country has its own legislation. However, FOMA (Organic and Organo-mineral Fertiliser Manufacturers´ Spanish Association) presents in a report published in 2014 (Revision of the Fertilisers Regulation) some limits of the European legislation, which appear in Directive 86/278/EEC (Table 1). In Romania, heavy metal limits are established in Order 756/1997 (Table 1). Because there is no specific legislation for organic farming, the same values are applied, as long as the Inspection and Certification Bodies for organic farming do not impose other restrictions.

Table 1. Maximum permissible levels of studied heavy metals in current legislation (mg/kg)

	Directive 86/278/EEC (EU)	**Order 756/1997 (Romania)**		
Metal	**Limit values**	**Reference value in soils**	**Alert threshold *sensitive soils**	**Intervention threshold *sensitive soils**
Cadmium	1-3	1	3	5
Copper	50-140	20	100	200
Nickel	30-75	20	75	150
Lead	50-300	20	50	100
Zinc	150-300	100	300	600
Mercury	1-1.5	0.1	1	2
Total Chromium	-	30	100	300
Cobalt	-	15	30	50
Molybdenum	-	2	5	10
Arsenic	-	5	15	25

*soils used for residential and recreational areas, for agricultural purposes, as protected areas or restrained sanitary areas, as well as the areas provided for such future uses

The present study evaluates the content of mineral elements on a field under conversion to organic farming, treated with microbial inoculants. Soil microorganisms can have different effect on each element. Certain elements can be solubilized, in this way becoming bioavailable, while others can be immobilized in the soil. These bio-transformations have been studied for different heavy metals such as As (Khalid et al., 2017; Rahman et al., 2014), Hg (Leveque et al., 2014), Pb (Ahmad et al., 2016; Leveque et al., 2014) or Zn (Cavagnaro et al., 2010).

As the applied microbial treatment can change the soil composition, the analysis of the heavy metals was made as a safety measure, decreasing or increasing the concentration of them being a possible side effect. For this reason, we must ensure that the site remains within the limits required by law.

MATERIALS AND METHODS

The present study follows the evolution of the heavy metal content in a calcaric alluvial soil from Buzau county - Romania, which was treated with microbial inoculants. The field is in conversion to organic farming, and it was planted with Florina 44 tomato variety in 2019. Other studies were carried out in 2018 for the characterisation of the same soil, and the results confirmed that the soil composition respects the legislation limits (Dobrin et al., 2018).

Soil samples were taken from topsoil (0-20 cm), from several points of tomato field, in two stages: in summer (July - month 7) and in late autumn (November - month 11) - denoted as Exp3 and Exp4. We used as control samples from corn and pea crops (V_{mp} and V_{mm}) and two replicates from soils treated with microbial inoculants (V_1 and V_2). Samples preparation and physicochemical analyses have been done in the Research Center for Studies of Food and Agricultural Products Quality, USAMV Bucharest. The samples were dried at room temperature, ground with a laboratory soil grinder and sifted through a 250-micron sieve, in order to prepare for elemental analysis. Heavy metal analysis was performed using ICP-MS technique (Agilent 7700 system). To perform this analysis, the samples were subjected to acid digestion with aqua regia (65% HNO_3 and 37% HCl in 3 to 1 proportion). An amount of 0,1000 g of each sample was placed in Teflon tubes, adding 6 ml of HNO_3 and 2 ml HCl. The digestion was accomplished using a microwave system (Ethos Up), at 180°C for 15 minutes. The following heavy metals were included in this study: Pb, Cd, Ni, Co, Zn, Cu, Mo, As and Cr.

RESULTS AND DISCUSSIONS

This study aims to determine if the microbial treatment applied to the soil produces significant changes on heavy metals content, and if these changes break the law in force. Furthermore, depending on the determined values, some correlations between these values are shown. The results are presented in figures below (Figures 1-9). Each value represents the mean of three replicates. It was preferred to represent each element on different figure because every metal concentration has a different range of values, that cannot be represented clearly together.

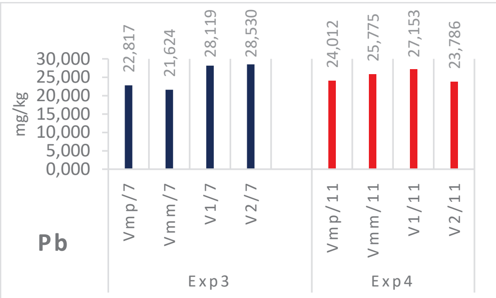

Figure 1. Pb content for the two stages

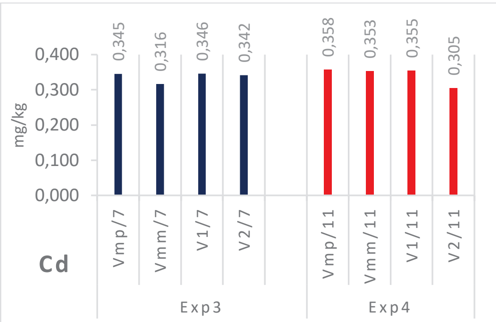

Figure 2. Cd content for the two stages

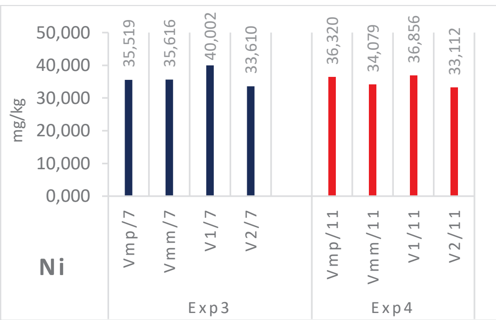

Figure 3. Ni content for the two stages

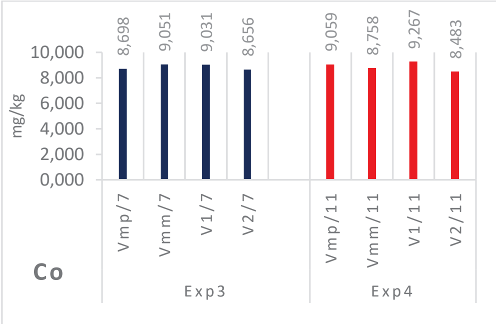

Figure 4. Co content for the two stages

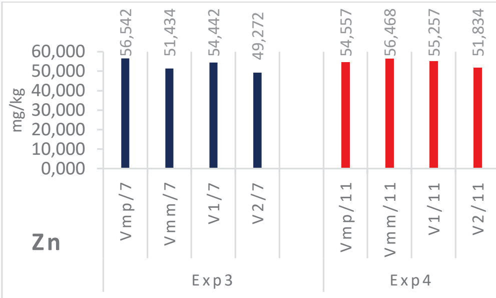

Figure 5. Zn content for the two stages

Figure 6. Cu content for the two stages

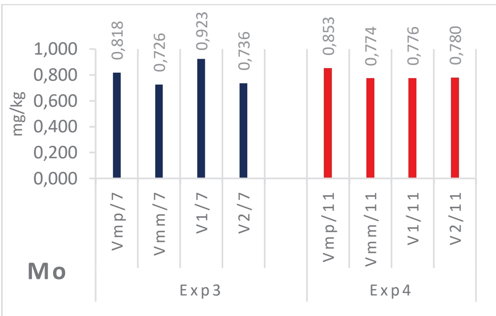

Figure 7. Mo content for the two stages

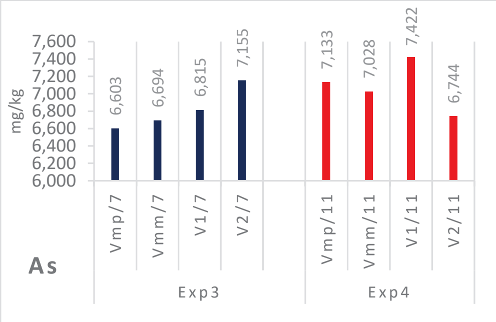

Figure 8. As content for the two stages

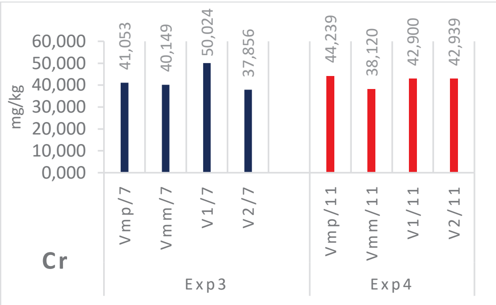

Figure 9. Cr content for the two stages

Applying T-test for the two groups of data (Exp3 and Exp4) ($\alpha = 0.05$) for each metal separately, it can be observed that there are no significant differences between the two sets of samples (Table 2).

Table 2. T-test value comparing the set of samples taken in summer with the set of samples taken in late autumn

Metal	p-value	Significance
Pb	0.9643	No significant diff
Cd	0.7272	No significant diff
Ni	0.5244	No significant diff
Co	0.8769	No significant diff
Zn	0.4261	No significant diff
Cu	0.3393	No significant diff
Mo	0.9190	No significant diff
As	0.2015	No significant diff
Cr	0.9435	No significant diff

Although the table looks flat, it is important to note that the heavy metal concentrations varied insignificantly. This result was rather expected, beside the fact that none of the values exceeded the maximum limit according to law. Considering the values of all 12 determinations (three replicates of four samples), some correlations can be found. Regarding the content of Zn and Cr in summer, it can be determined a weak positive correlation between them (Pearson correlation coefficient $\rho = 0.4805$). On the same elements, in autumn there was a weak negative correlation ($\rho = -0.4178$) (Figure 10). That may be due to microbial treatment that can influence the solubility of one element over another.

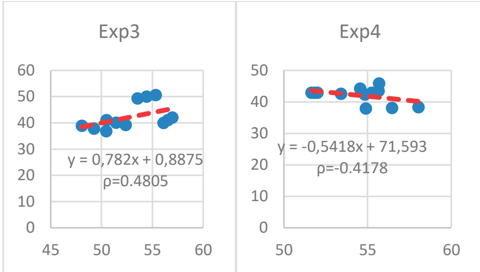

Figure 10. Change of direction between Exp3 and Exp4 on Zn and Cr correlation

Regarding the correlation between Co and As, can be observed that on first stage, there was no correlation ($\rho = -0.0469$) between them and at the second stage this relation was replaced by a strong positive correlation ($\rho = 0.9000$) (Figure 11).

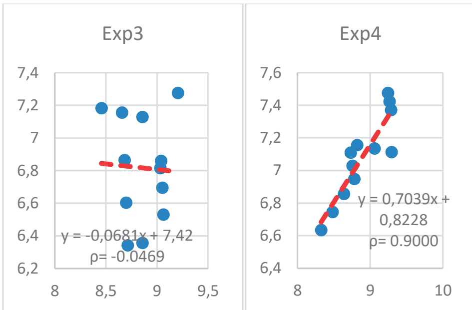

Figure 11. Occurrence of new correlation between Co and As on the second stage

On the other hand, some of the correlations were maintained in the same direction. It's the case of Cu and Ni whose values were in strong positive correlation ($\rho = 0.7283$) and kept a moderate to strong positive correlation ($\rho = 0.6270$) (Figure 12).

The same way, Pb and Cu were in weak positive correlation on the first stage (ρ=0.3182) and become a strong positive correlation on the second stage (ρ=0.7898) (Figure 13).

Since these groups of values followed the same trend, the microbial inoculants treatment didn't influence the behaviour of these metals in the soil enough to be observed.

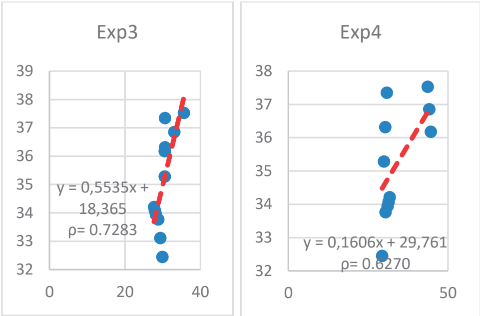

Figure 12. Maintenance of the same direction between Exp3 and Exp4 on Cu and Ni correlation

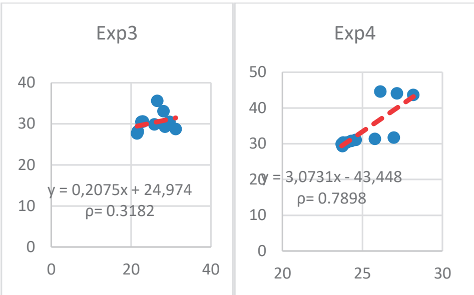

Figure 13. Maintenance of the same direction between Exp3 and Exp4 on Pb and Cu correlation

CONCLUSIONS

Regarding the heavy metal content of the soil, between the two sampling periods, no significant difference was observed in any of the elements analysed in this study. Also, none of the elements exceeds the maximum legal limit after the microbial treatment.

There was observed some changes, meaning that after the treatment, the positive correlation between Zn and Cr content has been reversed to negative correlation. Also, a new strong positive correlation emerged between Co and As after the microbial treatment.

The Cu and Ni content kept the same positive correlation for both stages of sampling, but at a lower level for the second stage.

The values for Pb and Cu kept also a positive correlation for both stages of sampling, but much stronger for the last taken samples.

Could not be established any relation for the rest of the heavy metals.

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