THE EFFECT OF MINERAL FERTILIZATION ON HEAVY METALS CONTENT IN TOMATO FRUIT

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ABSTRACT

The goal of our study was to investigate the effect of different mineral fertilization doses on the heavy metals content (Fe, Mn, Cu, Zn, Ni, Co, Cr, Pb and Cd) in tomato fruit grown in uncontaminated area. The heavy metals bioaccumulation rates have also been investigated.

The experience was done in a cambric cernosium soil, with low acidity reaction, very good content in nitrogen, phosphorus and potassium and the high natural fertility potential favorable vegetables cultivation in Romanian Western Plain area. Also, this soil is very rich in iron, zinc, cooper and cobalt but fall below acceptable parameters under the laws of our country.

The study was performed on control soil samples (without fertilizers) and soil samples after differentiated NPK fertilization in variable dozes: $N_{30}P_{30}K_{30}$, $N_{45}P_{45}K_{45}$, $N_{60}P_{60}K_{60}$ and $N_{120}P_{60}K_{60}$.

Although the soil analyses showed the presence of cobalt, chromium and lead in certain concentrations, except for cadmium which is not detectable, in tomatoes grown in the investigated area these heavy metals not found. Other micronutrients were very low values, well below the legal maximum allowed in vegetables cultivated in Romania. These results suggest that this area is favorable to ecological vegetables crops.

Keywords: mineral fertilization, heavy metals, bioaccumulation rates, tomatoes

INTRODUCTION

Tomato (*Lycopersicum esculentum*) is the most popular and widely cultivated seasonal fruit vegetable crop; it is grown in the backyard of most people's home (SAINJU, 2003).

Heavy metals occur naturally in soils, and some of these, such as copper (Cu), zinc (Zn), and cobalt (Co), play an important role in the nutrition of plants and animals, while others, such as cadmium (Cd), lead (Pb), and arsenic (As), have deleterious effects on various components of the biosphere. Normally, these elements are present in the soil at concentrations or forms that do not pose a risk to the environment, but their levels can be altered by different anthropogenic routes (LIMA, 2009).

Depending on the physical and chemical properties of the soil (particularly pH and redox potential), heavy metals are mobilised in the soil solution and are adsorbed by the plants. Some heavy metals reach the soil directly, under the form of fertilisers used as a supplement for plant nutrition or indirectly, as a result of amendaments or other chemical substance applications (herbicides, insecticides) (GOGOASA, 2004) and industrial emissions, transportation, harvesting process, storage and sale (NORMALIZA, 2009). Heavy metals may impair plant physiology by reducing respiration and growth, interfering with photosynthetic processes and inhibiting fundamental enzymatic reactions if accumulated at high concentrations. When these toxic metals are present in soil at a low concentration, plants continue to grow uniformly despite accumulating these metals. The ability of plants to accumulate heavy metals into their organs may hence be used to monitor soil pollution, and in particular the amount of heavy metal (MALIZIA, 2012).

During the last few decades, the toxicity of heavy metals has drawn attention of many environmental scientists. Heavy metal accumulation leads to the loss of agricultural yield and hazardous health effect. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystem through contaminated water, soil and air (LOKESHWARI, 2006).

MATERIAL AND METHOD

Soil samples were taken 0-25cm depth and were collected before the establishment of tomato crop. The fertilization was applied in spring, with four weeks before tomatoes plantation. Were use dry/granulated fertilizers NPK 15:15:15 and the nitrogen high dose supply with urea application (MAIA, 1983). No herbicides were used.

Analytical method of soil samples: The soil samples were analyzed by method recomanded by SR Iso: 11047 based on the measuring of heavy metals absorbance in aqua regia extracts and were determined by atomic absorption spectrometry in air/acetylene flame using Atomic Absorption Spectrometer contrAA[®]300 by Analytik Jena, using standard work conditions and the wavelength dominate (λ) for each chemical element. The correlation coefficient for the calibration curves (r^2) its: Fe - 0.9988, Mn - 0.9959, Cu - 0.9942, Zn - 0.9873, Ni - 0.9952, Co - 0.9998, Cr - 0.9761, Pb - 0.9975 and Cd - 0.9928. For iron, manganese, cooper and zinc determination were using diluted samples of 1:10 in deionized water; nickel and lead were using work solution. Concentrations have been reported as mean values of three replicates.

Analytical method of tomato samples: Tomatoes samples were collected on June-July at thoroughly fruit maturity. 20.00 g fresh tomatoes were dried at 105° C to 3 hours, calcinated at 650° C for 3 hours; added 10.00 mL pure HNO₃ 0.5N solution and to run dry. The mineral residue were solubility in 25.00 mL pure HNO₃ 0.5N (MAIA, 1983). This solution was used for heavy metals determination under similar conditions of soil samples. All chemicals used in this study were analytical reagent grade (Merck); deionized water.

Heavy metals **bioaccumulation rate (BR)** in the tomato fruit, which represents the percentage of the element present in the tomatoes in relation to total content in the soil (VYSLOUZILOVA, 2003), was calculated according the formula:

$$BR = \frac{Me_{plant}}{Me_{soil}} \cdot 100 \ (\%)$$

where: Me $_{max}$ = concentration of metal in the tomatoes (mg/kg); Me $_{max}$ = concentration of metal in the soil (mg/kg).

RESULTS

A fertilizer is said to be complete when is contain nitrogen, phosphorus and potassium. Nitrogen (N), phosphorus (P) and potassium (K) are in quantitative terms the most important minerals for the tomato fruit as they account for more than 90% of the mineral content (SAINJU, 2003). Of these three nutrients, nitrogen and phosphorus are more important for tomato plant. Phosphorus it has low mobility and availability in soils. Phosphorus availability in the soil is generally improved by the addition of N to the K (HABY, 2011).

Tomatoes need moderate to high levels of P and K (ARSHAD, 1999). From total content of metals in soil, only a small part is available. Metal availability strongly depends on pH, which is influenced by the level of mineral fertilization (SAINJU, 2003).

The soil properties also influence the uptake of heavy metals (MEDIOUNI, 2006). The cernosium soils have normal heavy metals content. The mean concentrations of heavy metals in this soil is: Mn - 200-2000 mg/kg (GOIAN, 2000), Cu mobile forms - 5-11 mg/kg, Co - 12-29 mg/kg, Pb - < 20 mg/kg, Cd - 1.2-1.5 mg/kg, Zn - 25-70 mg/kg and Co- in trace (IANOS, 1995).

The experimental data of heavy metal contents in soil are presented in *Table 1*. The studied area presented normal levels of heavy metals. Our experimental data are in agreement with data from the literature (GOIAN, 2000; BORDEAN, 2011) for soil and regional condition. The order of accumulation of heavy metals in soil samples was: Fe > Mn > Zn > Ni > Pb > Cu > Cr > Co > Cd. The heavy metals distributions in researched soil were lowest content values that the WHO/FAO maximum permissive limits: Pb - 100, Cd - 3, Ni - 75, Cr - 400 mg/kg.

| | Heavy metals content (mg/kg dry matter) | | | | | | | | | | |
|--------------------------|---|--------|------|-------|-------|------|------|-------|----|--|--|
| | Fe | Mn | Cu | Zn | Ni | Co | Cr | Pb | Cd | | |
| Soil samples* | 4340.78 | 231.92 | 7.68 | 47.87 | 12.87 | 5.03 | 6.08 | 11.51 | | | |
| Normal values** | - | 900 | 20 | 100 | 20 | 15 | 30 | 20 | 1 | | |
| Warning threshold** | | 1500 | 100 | 300 | 75 | 30 | 100 | 50 | 3 | | |
| Intervention threshold** | - | 2500 | 200 | 600 | 150 | 50 | 300 | 100 | 5 | | |

Table 1. Heavy metals concentrations in soil

Source: *own research; **Ordinance 756/1997.

Although the soil analysis showed that is very rich in iron, zinc, copper and cobalt but fall below acceptable parameters under the laws of our country (ORDINANCE 756/1997), in tomato fruit samples these quantities are very low, well below the legal maximum allowed in vegetables. Maximum limits accept in Romanian legislation for heavy metals content in vegetables: Cu - 5.0 mg/kg fresh matter, Zn - 15.0 mg/kg, Pb - 0.5 mg/kg and Cd - 0.1 mg/kg (ORDINANCE 975/1998). The concentrations of heavy metals in vegetables were in according with the WHO/FAO maximum permissive limits: Pb - 0.3, Cd - 0.2, Ni - 10, Cr - 2.3 mg/kg. The mean values of Fe, Mn, Cu, Zn and Ni concentrations in tomato are given in *Table 2*.

| Fertilization doses | Heavy metals content (mg/kg dry matter) | | | | | | | | |
|---|---|-------|-------|-------|-------|--|--|--|--|
| | Fe | Mn | Cu | Zn | Ni | | | | |
| Control | 4.49 | 0.815 | 0.860 | 2.460 | 0.106 | | | | |
| N ₃₀ P ₃₀ K ₃₀ | 4.84 | 0.831 | 0.878 | 2.489 | 0.139 | | | | |
| N45P45K45 | 6.20 | 1.010 | 1.107 | 2.496 | 0.165 | | | | |
| N ₆₀ P ₆₀ K ₆₀ | 4.56 | 0.663 | 0.564 | 1.621 | 0.107 | | | | |
| N120P60K60 | 5.87 | 1.041 | 0.564 | 2.823 | 0.186 | | | | |

 Table 2. Micronutrients in tomato fruit

Source: own research

Iron is the abundant metal; is a link element between macro and microelements. Fe has the highest content in tomatoes by $N_{45}P_{45}K_{45}$ fertilization doses (6.20 mg/kg) and the lowest content in Fe was identified a control samples (4.49 mg/kg). Mn highest accumulation (1.041 mg/kg) is observed a $N_{120}P_{60}K_{60}$ fertilization doses. The Zn level was higher everything to the maximum fertilization doses studied. The concentration of cooper content ranged from 0.564-1.107 mg/kg. Ni is present only in trace at 0.106-0.186 mg/kg.





Fertilization doses

N30P30K30 N45P45K45 N60P60K60 N120P60K60

NOPOKO

The order of heavy metals content in tomato fruit samples was: Fe > Zn > Cu > Mn > Ni.

In general, plants do not absorb or accumulate lead. However, in soils testing high in lead, it is possible for some lead to be taken up. Higher concentrations are more likely to be found in leafy vegetables and on the surface of root (GOGOASA, 2004).

Although the soil analyses showed the presence of cobalt, chromium and lead in certain concentrations, except for cadmium which is not detectable, in tomatoes grown in the investigated area these heavy metals not found.

Heavy metals and nutritive contents of tomatoes depend on growing conditions (MITEVA, 2001). OLSEN (1972) found that phosphorus fertilisation at high rates caused an increase in Zn deficiency in plant and PATRA et al. (1982) found that an application of P increased Fe content of the plant with a decrease in Zn, Cu and Mn content. Excess level of P in the soil can decrease the solubility of Fe and its translocation in tomato, thereby increasing its deficiency. The toxicity in tomato appears when Mn concentration in the soil is >80 mg/kg and in the plant >1000 mg/kg. The toxicity can be reduced by applying water soluble P fertilizer, such as triple superphosphate, which reduces Mn availability. High P level in the soil can also reduce Zn availability to tomato and results deficiency (SAINJU, 2003). In their similar studies, ATAOGLU and SEZEN (2004) were found that N application increases the Zn content of the plant parts while Zn content goes down with P application. K fertilization has no effect on Zn content. Their results show broad agreement with our study.

Figure 1 illustrates the bioaccumulation rates values for some heavy metals in tomato fruit grown in uncontaminated soil.

BR increases to $N_{45}P_{45}K_{45}$ fertilization doses and decreases sharply a $N_{60}P_{60}K_{60}$ fertilization doses and then increases again. The higher BR value of manganese (0.44), nickel (1.44) and zinc (5.89) is observed a $N_{120}P_{60}K_{60}$ fertilization doses and a $N_{45}P_{45}K_{45}$ fertilization doses for iron (0.14) and cooper (14.41). Of all the heavy metals the iron content in soil and in tomato fruit is high but the BR value is very low.

CONCLUSIONS

The experience was done in a cambric cernosium soil very rich in iron, zinc, cooper and cobalt but fall below acceptable parameters under the laws of our country.

The order of accumulation of heavy metals in soil samples was: Fe > Mn > Zn > Ni > Pb > Cu > Cr > Co > Cd.

The order of heavy metals content in tomato fruit samples was: Fe > Zn > Cu > Mn > Ni. The other elements (Co, Cr, Pb and Cd) are not found.

Metal availability in soil is influenced by the level of mineral fertilization. Phosphorus fertilisation increased Fe and decrease Zn, Cu and Mn content of tomatoes; N application increases the Zn content of the plant, and K fertilization has no effect on Zn content.

In conclusion, different doses of N, P and K fertilizers were applied to tomato crop soil determined different bioaccumulation rate in tomato fruit. We can even say that this uncontaminated area is favorable to ecological vegetables crops, mainly tomatoes.

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