

INFLUENCE OF FERTILIZATION AND THE KIND OF FERTILIZER UPON THE CONTENT OF MANGANESE AND ANTIOXIDANTS IN TOMATOES

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ABSTRACT

An experiment in two levels of potassium fertilization with two sources - potassium sulphate and potassium nitrate, was carried out. The experimental data showed that after fertilization the manganese content in tomatoes increased, which confirmed that a large amount of manganese was extracted from soil. When the fertilizer also contained manganese, its content in tomatoes increased 4-5 times.

It has been determined that the change of the manganese content in the leaves and the stem depends on the amount of the applied fertilizer. With the increase of the amount of the fertilizer the manganese content in the leaves increased, while in the stems it decreased. That type of changes in the content of manganese in the tomato fruit, stem and leaves can be explained by the mechanism of the element uptake from soil.

***Keywords:** manganese determination, crystal violet, plants, fertilization.*

INTRODUCTION

In agricultural production it is very important to have sound knowledge about the content of heavy metals in the vegetables and fruits for consumption, with the aim of assessing their suitability to be used for human and animal food. Heavy metals can come from three different sources: from soil, from fertilization when they are contained in the applied fertilizer and from the leaves at spraying. Vegetables are sources of a line of powerful antioxidants: lycopene, as well as vitamins A, C, E. It has been proved that tomatoes are a main source of many nutritious carotenoids, as well as lycopene. According to some authors [1-5] the content of antioxidants and the microelement manganese in tomatoes is genetically predestined and it is affected by agrotechnical practices and by the climatic factors. The climatic factors have a significant effect on the synthesis of vitamin C and the pigments, including lycopene and carotenoids. According to Lecatus [6] the effect of fertilization, as

an element of the agrotechnical practices, on the synthesis of antioxidants is complex and still it has not been thoroughly studied. Manganese takes part in a number of important physiological and biological processes - in the nitrogen metabolism, photosynthesis, breathing and maintaining the needed oxidation-reduction conditions in the cell. Manganese insufficiency leads to a considerable accumulation of nitrates, disturbance in the protein synthesis in plants and illness to some plants [7]. The manganese content in vegetables and foods varies in a wide range [8-12].

That is why the aim of the present research is to study the influence of the amount of fertilizer and its kind upon the content of manganese and antioxidants in the production of tomatoes.

EXPERIMENTAL

Plants were cultivated in seedlings in a steel-glass hot-house. The sowing was carried out at the rate

of 3 g m⁻². The experiment was set according to the block-method in four replications. The experimental work was carried out on a too leached meadow-maroon soil with tomatoes. The experiment was performed in seven variants at two levels of potassium fertilization, as two sources have been tested - potassium sulphate and potassium nitrate (industrial fertilizers). Mineral nitrogen (NH₄⁺-N+NO₃⁻-N) – 2.1 mg/100g soil, movable forms of P₂O₅ and K₂O - respectively 20.5 mg and 17.7 mg/100 g soil, content of humus – 2.1 % had been determined. The active acidity of soil pN_(H₂O) – 6.9-7.0 was established by a standard method. According to the adopted classification [18] by pH, the soil used was neutral or slightly acid.

The basic fertilization was carried out on the basis of the agrochemical analysis of the soil, as it comprised 30 kg dka⁻¹ triple superphosphate and potassium fertilizer (K₂SO₄ and KNO₃), according to variants from 2 to 7. The feeding up with nitrogen is carried out in three stages: before planting, first earthing up, and after 20 days. NH₄NO₃ has been used. Potassium is brought twice: before planting and sprout of first raceme as large as peanut, respectively. Variants of the experiment:

1. basic fertilization with 30 kg dka⁻¹ triple superphosphate – N:P:K= 1.5:1.3:0 a norm for consumption of K₀.
2. Fertilization with 30 kg dka⁻¹ triple superphosphate and K₂SO₄ - N:P:K= 1.5:1.3:1.0 a norm for consumption of K₈
3. Fertilization with 30 kg dka⁻¹ triple superphosphate and K₂SO₄ - N:P:K= 1.5:1.3:1.3, a norm for consumption of K₁₆
4. Fertilization with 30 kg dka⁻¹ triple superphosphate and K₂SO₄ - N:P:K= 1.2:1.0:1.5, a norm for consumption of K₂₄
5. Fertilization with 30 kg dka⁻¹ triple superphosphate and KNO₃ - N:P:K= 1.5:1.3:1.0, a norm for consumption of K₈
6. Fertilization with 30 kg dka⁻¹ triple superphosphate and KNO₃ - N:P:K= 1.5:1.3:1.3, a norm for consumption of K₁₆
7. Fertilization with 30 kg dka⁻¹ triple superphosphate and KNO₃ - N:P:K= 1.2:1.0:1.5, a norm for consumption of K₂₄

Indices:

K₈ = 16 kg dka⁻¹ K₂SO₄, respectively KNO₃;
 K₁₆ = 32 kg dka⁻¹ K₂SO₄, respectively KNO₃;
 K₂₄ = 48 kg dka⁻¹ K₂SO₄, respectively KNO₃.

Determination of manganese in soil: A portion of 1 g of air-dry soil (previously grinded and passed through a sieve); is extracted with nitric acid (dilution of 32 ml of nitric acid, 15.8 mol l⁻¹, ρ ≈ 1.42 g ml⁻¹, and filling up with water to 1 litre) by standing for 16 h at room temperature, followed by boiling under reflux for 2 h [13]. The extract is then clarified and made up to volume of 50 ml with nitric acid. In this solution manganese is determined by flame atomic absorption spectrometry.

Determination of manganese in fertilizers: Potassium sulphate (consists of K₂O – 50 %; Cl – 1.5 %; MgSO₄ and CaSO₄ – 5.2 %) and potassium nitrate (consists of nitrogen –13.5 %; K₂O – 46 %) have been used. 1 g K₂SO₄ and respectively 8 g KNO₃ are dissolved in distilled water and then filled up with water to the volume of 50 ml. In these solutions manganese is determined by flame atomic absorption spectrometry.

Determination of manganese in plant material: A portion of 2 g of air-dry plant material (stems, leaves, fruit of tomatoes) was placed into a Kjeldal flask and moistened with 4 ml distilled water. 5 ml conc. H₂SO₄ and 10 ml conc. HNO₃ were added. When all the organic material was oxidized, the solution was heated at a higher temperature for 10 min [14]. After cooling the solution was diluted with water and filtered. Portions of 3 ml conc. H₂SO₄, 2 ml conc. H₃PO₄ and 0.1 g potassium periodate were added for oxidation of Mn(II) to Mn(VII). The mixture was heated up to boiling and the temperature was maintained for 10 min [15]. After cooling, the solution was diluted with water and filtered. Aliquot parts of this solution were taken for analysis.

In plant material manganese is determined by means of a new extraction spectrophotometric method with Crystal Violet, developed by us [16].

Determination of vitamin C: 10 g of cut up plant material is transferred into a mortar and 20 ml of 1 % HCl are added. This plant material is then swiftly grinded to the formation of a homogeneous mass, and after that is transferred into a 100 ml graduated flask. The graduated flask is filled up to the mark with 1 % solution of H₂C₂O₄, shaken up, and left to stay for 10 min. After that the sample is filtered through a folded filter and is collected into a 100 ml flask. 10 ml are taken from this filtrate and are titrated from a microburette with 0.001 N solution of 2,6-dichlorophenole-indophenole sodium to the appearance of pink colour [17].

Determination of carotene: 10 g of cut up plant material is ground into a mortar with sand. Na_2CO_3 is added for neutralization and 10 ml CH_3COCH_3 . The probe is centrifuged and is treated again with CH_3COCH_3 for the appearance of a colourless extract. The last material is transferred into a graduated funnel, 15 ml of benzine are added, and extracted again. Acetone can be removed by portions of distilled water. The purged and dewatered benzine solution is passed through a chromatographic column for separation of carotene from the other pigments. The benzine solution of carotene is transferred into a 50 ml graduated flask and is filled up to the mark with water. It is photometered in 460 nm [17].

Apparatus. Spectrophotometer UV-VIS with 1-cm light path quartz cells and Atomic Absorption Spectrophotometer "Perkin Elmer" (Germany) were used for the measurements.

RESULTS AND DISCUSSION

The content of manganese in the used soil and fertilizers, as well as the basic elements in soil, is presented on Table 1. As it can be seen, the manganese content in soil was comparatively high and the contents of the rest of the elements like calcium, magnesium and iron were typical for the soil type. In respect of the fertilizers, the potassium nitrate fertilizer contains manganese (1.75 mg kg^{-1}) whereas the potassium sulphate fertilizer has no manganese. The content of manganese in tomatoes depending on the amount of fertilizer and its kind, is shown on Fig. 1. It can be seen that in fertilization with potassium nitrate the content of manganese in tomatoes increases sharply, whereas for the fertilizer potassium sulphate a slight increase can be seen only in the first fertilization, but after that the content stays constant. Obviously, the presence of manganese in fertilizers like in potassium nitrate, leads to an increase of its content in the fruit. Nevertheless, it can be supposed that the potassium nitrate fertilizer makes easier an extraction of larger amount of manganese from soil. That is why, the concentration of manganese in tomatoes is 4-5 times higher (Fig. 1). It can be suggested also that the highest content of Mn in the tomatoes can be related to the ratio of the basic nutritious elements $\text{N:P:K} = 1.5:1.3:1.0$ in fertilization with K_2SO_4 and KNO_3 .

The content of manganese in the leaves and stems is significantly higher than that in the fruit, and is high-

est in leaves, which determines the essential role of this element in the physiological processes in the plant, as can be seen on Fig. 2 and Fig. 3. In stems and leaves for the two potassium fertilizers, the highest content of Mn is found for a ratio of the nutritious elements $\text{N:P:K} = 1.5:1.3:1.3$.

An interesting tendency is observed in the change of the manganese content in the leaves and the stem depending on the amount of applied fertilizer. With the increase of the amount of the fertilizer, the manganese content in the leaves increased, while in the stems it decreased or stayed constant, when fertilizer contains Mn like in KNO_3 (Figs. 2 and 3). Since the processes of manganese accumulation in the fruits, leaves and stem are interrelated, obviously when increasing the amount of the fertilizer applied, the manganese accumulates in the leaves at the expense of the fruit and stem, thus leading to its decrease in the latter with the increase of the amount of the fertilizer.

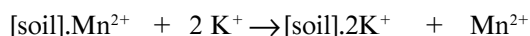
That type of changes in the content of manganese in the tomato fruit, stem and leaves can be explained by the mechanism of the element uptake from soil. For slightly acid soils, the following order has been established [18]: $\text{H}^+ \gg \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Al}^{3+} > \text{Fe}^{3+}$

Manganese was not included in the order as it has a significantly lower ion-exchange activity. Consequently, we suggest that after fertilization the potassium

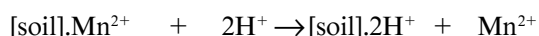
Table 1. Content of manganese in soil and fertilizer.

Sample		Mn, mg kg ⁻¹			
Soil		1095			
Potassium sulphate		-			
Potassium nitrate		1.75			
Content of other elements in soil, mg kg ⁻¹					
Ca	Mg	Fe	Zn	Mo	Cu
3171	3834	149.6	110.6	1.0	40.6

contained in the fertilizer enters into an ion-exchange reaction with the manganese contained in soil:



The manganese released is absorbed by the roots and enters the plant. Even without fertilization manganese could be extracted during the reaction and it could enter the plant:



The hydrogen ions also have a higher ion-exchange potential. That mechanism explains the reason for the increase of manganese in tomato fruit after fertilization. When there was manganese available in the fertilizer, the element entered the plant directly and due to that the ion content in tomatoes increased 4-5 times (Fig. 1).

An interesting fact is that the accumulation of manganese in fruits reached a maximum with the increase of the fertilization rate (Fig. 1). That maximum was reached at lower fertilization rates when the fertilizer did not contain manganese. It should be taken into account that the content of manganese in the soil is limited. The leaves are the active component and the manganese content in them increased until reaching a certain fertilization level after which it began to decrease with the further increase of fertilization. Even when applying a fertilizer that did not contain Mn, the content of the element in the fruit and the stems began to decrease or did not change significantly (Figs. 2 and 3). It has to be taken into account that when increasing the fertilizer the yield is also increasing, that can also influence the manganese content.

An important problem is the content of vitamin C, lycopene and carotene antioxidants in tomatoes. The content of vitamin C, lycopene and carotene depending on fertilization is presented in Figs. 4 and 5 with the aim of establishing eventual correlation between them. It is known that lycopene is a pigment, which is very susceptible to potassium deficiency. The figures show that the content of vitamin C, as well as that of lycopene and carotene, does not depend on the amount of the fertilizer applied. Obviously the content of those ingredients in fruits is limited to a certain degree. Especially the content of vitamin C in tomatoes is lower, as compared to a large number of the fruits used for food [4].

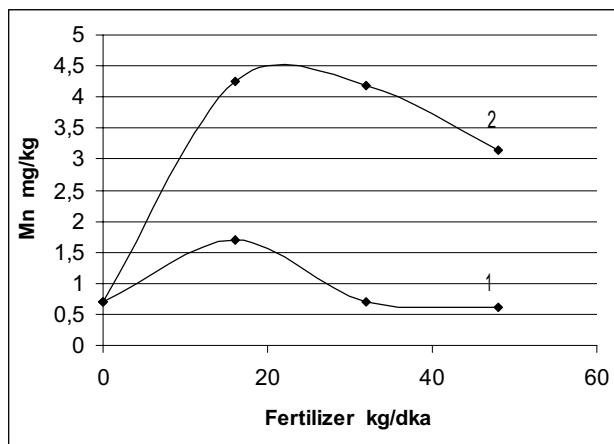


Fig. 1. Content of Mn in fruit of tomatoes with different potassium fertilization: 1 - K₂SO₄, 2 - KNO₃.

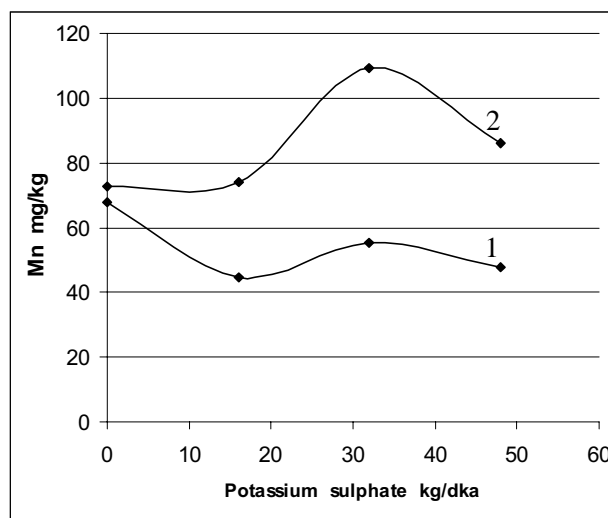


Fig. 2. Content of Mn in stems (1) and leaves (2) of tomatoes for fertilization with K₂SO₄.

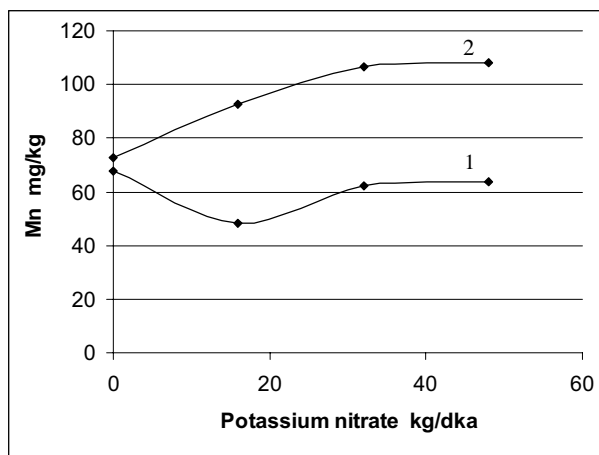


Fig. 3. Content of Mn in stems (1) and leaves (2) of tomatoes for fertilization with KNO₃.

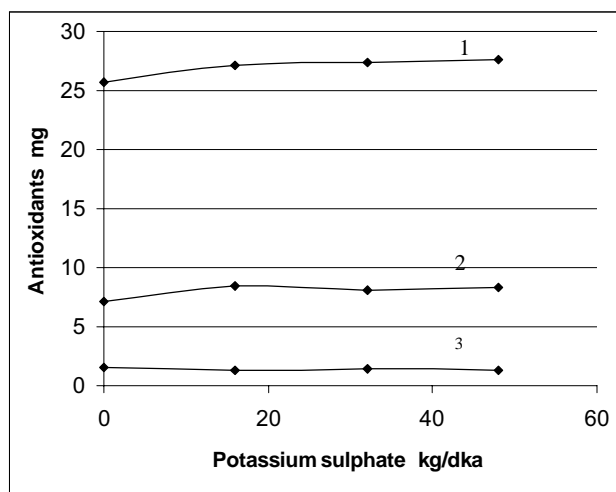


Fig. 4. Content of the antioxidants Vitamin C (1), Lycopene (2) and β -Carotene (3) in fruit of tomatoes for fertilization with K_2SO_4 .

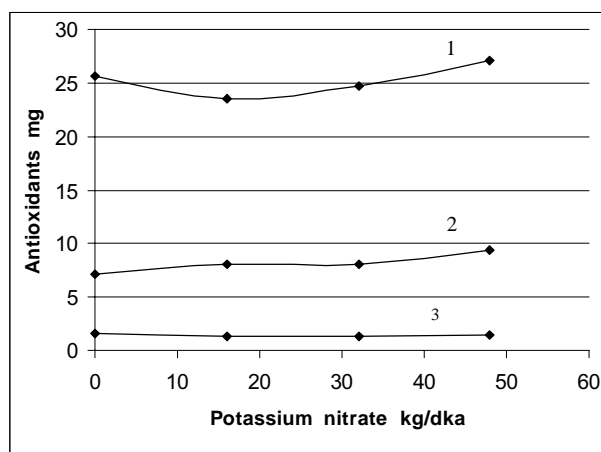


Fig. 5. Content of the antioxidants Vitamin C (1), Lycopene (2) and β -Carotene (3) in fruit of tomatoes in fertilization with KNO_3 .

The most important characteristic in tomato production related to fertilization is the yield obtained. As yield and quality not always change in parallel, a higher significance attains the effect of manures upon the nutritious value of the production which is very important for the health of consumers. Fig. 6 presents the tomato yield as a function of the amount of fertilizers. As it might be expected, the increase of the amount of the fertilizer applied per decare, increased the yield. Fertilization with potassium nitrate did not cause any significant change in the yield compared to fertilization with the sulphate of potash fertilizer. Such an effect was established only at lower fertilization levels. If these observations are compared to data about the manga-

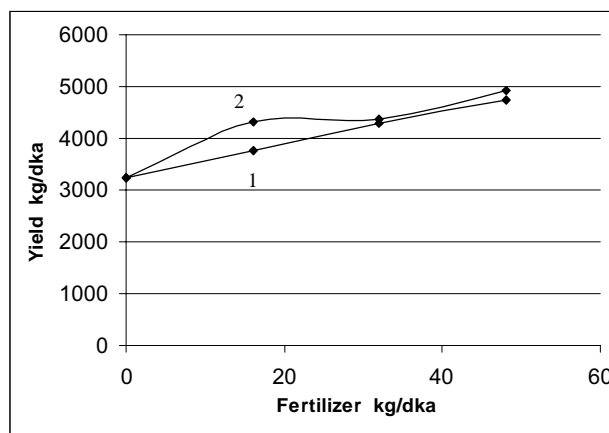


Fig. 6. Relationship between yield and potassium fertilization with K_2SO_4 (1) and KNO_3 (2).

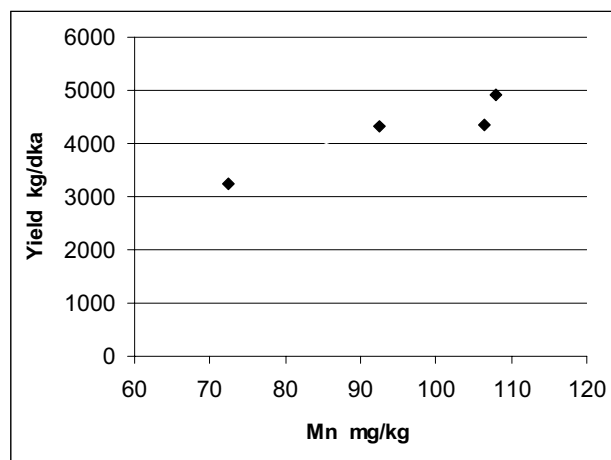


Fig. 7. Relationship between yield and the content of Mn in leaves.

nese content in fruits, it might be concluded that only at the beginning the yield and the content of manganese in tomatoes increases with the increase of the amount of the fertilizer. It can be supposed that the major role is played by the cation content of the fertilizer and the anion content has lower effect. The latter was exerted only at lower fertilization levels.

If there is a certain correlation, it is between the yield and the manganese content in the leaves. That relation is presented in Fig. 7. With the increase of the manganese content in leaves, the yield also increased. It is very important to note that such a correlation has not been established between the yield and the content of manganese in tomatoes.

CONCLUSIONS

- The availability of manganese in soil leads to its accumulation in the fruit of tomatoes.
- In fertilization with potassium nitrate and potassium sulphate the extraction of manganese from soil can be facilitated, and its content in tomatoes can be increased.
- The availability of manganese in fertilizer leads to the increase of its content in the fruit up to four - five times.
- The highest concentration of manganese can be accumulated in the leaves of tomatoes.
- The content of Vitamin C, lycopene and β -carotene is not influenced by the amount of fertilizer and the content of manganese.
- A certain interrelation can be found between the content of manganese in leaves, the yield and the amount of fertilizer.

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