

MACRO AND MICRONUTRIENTS DISTRIBUTION IN CALCARIC ALUVIOSOIL

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Abstract

In times when healthy diets and personalized nutrition is one of the EU top-priority, sustainable production systems that both preserve and improve soil qualities and grant the agricultural products nutritional value, must be used at most. In this context, the content of macro and micro-elements both in soil and crop plants plays high importance and should be continuously monitored and used for the benefit of food production chains. Microbial inoculants are one of the many ways to enhance the plant's nutrient uptake capacity and increase crop yield and quality. They participate in the geochemical cycling of micronutrients and increase the available form of primary/major nutrients near plants rhizosphere. Soil organic matter also contributes to the nutrients cycle and maintains soil structure. The present study presents the soil nutrients content (N, K, Ca, Mg, Na, F, Cu, Zn, Mo, Se) in 2019, for an experimental field cultivated with organic tomatoes in Buzău county, Romania and attempts to establish some correlation between these elements. The high throughput ICP-MS analysis gives the total content of those elements, of which a part became available throughout the year and the presence and activity of soil microorganisms may accelerate this availability, which can be further exploited inside the organic or sustainable production systems by farmers.

Key words: ICP-MS, macronutrients, micronutrients, total content, soil fertility.

INTRODUCTION

Macro and micronutrients are very important for physiological and metabolic processes in plants. Nitrogen, phosphorus, and potassium are the primary nutrients for plants and are often deficient in cropped soils. Reduced concentrations of nutrients are found in sandy soils, as alluvial soils, (prone to leaching, micronutrient deficiencies of iron, manganese, copper, zinc, and boron), soils with high pH (affect the availability of iron and manganese) or soils intensively cropped. Crop rotation, the addition of bio-products, as organic amendments, organic fertilizers or microbial inoculants, environment protection and good agricultural practices etc are used to balance the nutrients soil content and availability (Mikula et al., 2020; Dhaliwal et al., 2019; Ionescu et al., 2016; Rashid et al., 2016; Madjar et al., 2014; Vlahova et al., 2014; Nagacevschi, 2013). Nitrogen (N) is a vital element needed for the survival of all livings. For plants is essential

both for growth and development and for crops, it significantly increases and enhances yields and their quality. N has a vital role in biochemical and physiological functions in plants. Potassium (K) is considered the second most important nutrient for plants, often termed as "the quality nutrient", a key parameter of soil fertility and plant growth (Rashid et al., 2016). K is essential for photosynthesis, photosynthates translocation, maintenance of turgescence, activation of enzymes, and reducing excess uptake of ions such as Na and Fe in saline and flooded soils (Cakmak, 2005). High-yielding crops can remove a large amount of potassium from the soil. Phosphorus (P) is essential for proper development of plants roots and hastening plants maturity. It plays an important role in photosynthesis, storage and transfer of energy, respiration etc. Without enough supply of phosphorus, plants are unable to complete their production cycle as expected (Wakeel, 2013).

In addition to NPK, calcium (Ca), magnesium (Mg) and sodium (Na) are considered the secondary nutrients, with essential role in plants growth, development and health. Ca is the predominant nutrient in the soil clay and organic matter particles. Parent material with higher content in calcium or magnesium enrich soils content in these nutrients, depending on the soil evolution pathways (Kowalska et al., 2019; Kelling et al., 2013). Ca is involved in the mechanism of controlling P bioavailability in soils and ensuring a good aeration and improving soil structure by displacing sodium (Norton, 2013). It can also influence the abundance of genes in soil microbial communities (Neal et al., 2019), a very important factor for microbial inoculants use in crop technologies. Magnesium (Mg) is a key element of the chlorophyll molecule, so important for photosynthesis and for activation of most plant enzymes that are needed for growth while contributing to protein synthesis. The uptake of K, Ca, and Mg by the plants from the soil depends by the concentration and the ratios of these nutrients (Bonomelli et al., 2019). The micronutrients presence and availability to plants, even in trace amounts, is essential to plants growth.

Micronutrients, such as iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), selenium (Se) are essential elements that plants need in smaller quantities. Are involved in activity of various enzymes responsible for the carbohydrate's metabolism, nucleic acids, proteins and lipids. Their deficiency can severely affects crop yield. Iron (Fe) is essential for plant growth, because it influence gene regulation, metabolic activity and elements distribution within cells and within plants. Limited iron availability in soils is one of the main limiting factors of yield and quality of agricultural productions worldwide, particularly in alkaline and calcareous soils (Mimmo et al., 2020; Chen et al., 2019).

Micronutrient deficiency can occur in intensively cropped soils fertilized only with macronutrients. Alluvial soil requires more frequent organo-mineral fertilisers applications (Stănilă et al., 2015).

The soil health and its structure is influenced by physical, biological and chemical processes (Cojocaru, 2019; Ku et al., 2019; Singh et al., 2016) and the availability of macro and

micronutrients in soil for plants is the result of a perpetual translocation of mineral nutrients from inaccessible forms in easy absorbable forms (Abanda et al., 2011; Pallardy, 2008).

In this study we used ICP-MS technique to quantify few of the macro and micronutrients in a calcareic aluviosoil soil profile in 2019, as this method has higher sensitivity, selectivity and detection limits than other elemental analysis techniques. The results will be used in the further years to identify correlations between the dynamic of these total contents at different soil depths and the soil microbiota, including the added microbial inoculants used in tomato crop technology.

MATERIALS AND METHODS

The experiment was conducted in the organic research plot from Vegetable Research and Development Station Buzău, Romania, in 2019. The macro and microelements content analysis were made in the Research Centre for Study of Food and Agricultural Products Quality, University of Agronomic Sciences and Veterinary Medicine of Bucharest. The soil samples were taken at six depth intervals (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm, 80-100 cm and 100-120 cm).

Soil samples collected in plastic zip bags were than air-dried in the laboratory and milled. Subsamples were homogenized and sieved with 250 µm sieve. All used reagents were analytical grade and suprapure (nitric acid 65% and hydrochloric acid 37%, Merck). The water used for samples preparation and calibration curve was purified by the Milli-Q system. The microwave extraction method was used after EPA Method 200.2 and Method 3050B using both solvents nitric acid and hydrochloric acid. Microwave-assisted digestion procedure was used for soil samples preparation and quantification of macro and microelements at Agilent ICP-MS (with MassHunter Workstation software). The multi-element ICP-MS calibration standard was used for the calibration curve.

The total N content was determined with Kjeldahl method, using 0.1 N hydrochloric acid indicator for titration.

Statistical analyses were performed using Microsoft Excel 2016 from Windows 10.

RESULTS AND DISCUSSIONS

Among the primary nutrients, nitrogen and potassium were analysed.

The total nitrogen content (Figure 1) decreases with depths, from 1700 mg/kg in the arable layer till 500 mg/kg at 1.2 m depth. According to Madjar, 2008, a supply of total N between 0.141 and 0.22 % in soils indicate a medium content of this macronutrient and due to high requirements of vegetables in N, as tomatoes, supplementary fertilization is needed. This recommendation is enforced by the sandy soil structure, which makes N easily leachable.

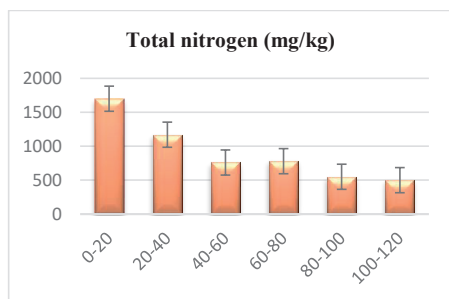


Figure 1. The total nitrogen content of the soil profiles

The concentration for K varied between 7,308 mg/kg to 4,221 mg/kg in soil profiles. The results are in concordance with Voica et al., 2012 who also find K concentration between 1,317.3 mg/kg to 7,767.4 mg/kg in Sălaj and Cluj soils. We also find a very high positive correlation ($r = 0.966$), $R^2 = 0.9337$ between K and Na content in soil profiles (Table 1). According to Madjar, 2008, a supply of total K below 0.8% in soils indicate a low content of this macronutrient.

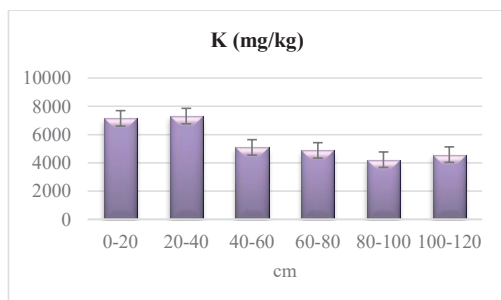


Figure 2. The total potassium content of the soil profiles

Considering the three forms of K - unavailable, slowly available and exchangeable, our analysis indicates the need of potassium based fertilisers.

Among the secondary nutrients, calcium, magnesium, and sodium were analysed.

The highest content of calcium (24,568 mg/kg) was found in 20-40 cm soil profile (Figure 3). Jodral-Segado et al. (2006) also found the results of calcium content of 18,790-49,470 mg/kg. We also find a high positive correlation with potassium ($r = 0.732$) and iron ($r = 0.796$). According to Madjar (2008) a Ca content of 2% indicate a medium content, a surprising result for a calcaric aluviosoil.

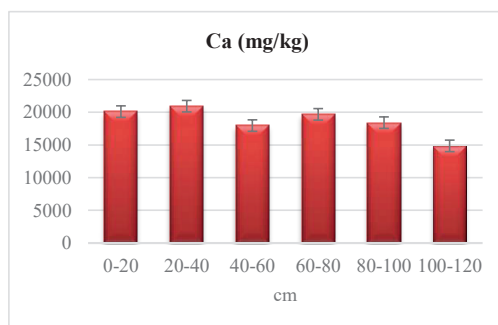


Figure 3. The total calcium content of the soil profiles

In the case of magnesium (Mg), it was observed a high positive correlation with potassium ($r = 0.865$) and calcium ($r = 0.746$) (Table 1). According to Madjar, 2008, a Mg content around 0.6% is more specific for a clay soil, than a sandy soil, which indicate high reserves for this element.

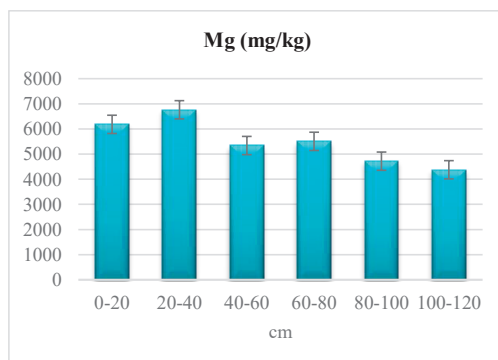


Figure 4. The total magnesium content of the soil profiles

Of the total exchangeable bases, Mg represents 18%, a confirmation of high content of this macronutrient in our soil.

Na content varied between 403 mg/kg in 0-20 cm soil profile to 235 mg/kg in 80-100 cm soil profile (Figure 5).

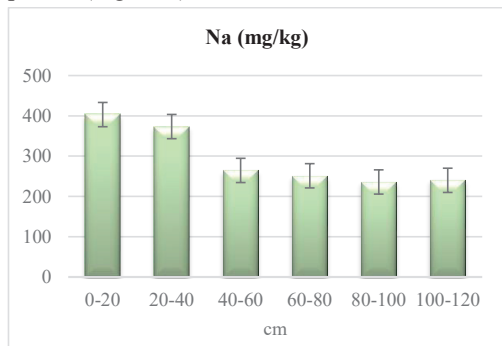


Figure 5. The total sodium content of the soil profiles

Although ICP-MS gives the total content of certain elements in soils, we could still analyse the results as a potential resource for the “total exchangeable bases”, which refers to the sum of the bases (calcium, magnesium, potassium, and sodium) from the soil, in exchangeable form (Table 1).

Table 1. Correlation between Ca, K, Mg and Na content in soil profiles in 2019

	Ca	K	Mg	Na
Ca	1			
K	0.732	1		
Mg	0.746	0.865	1	
Na	0.643	0.966	0.742	1

Of the total exchangeable bases, Ca represents 59.5%, K 21.1%, Mg 18.3% and Na 1.2%.

Among the micronutrients, iron, copper, zinc, molybdenum and selenium were analysed.

The total iron content, between 14.4 and 22.9% (Figure 6) is medium for Romanian soils, according to Madjar (2008), with highest values in the first 40 cm of depth, with a maximum of 2.29% in the second horizon. Still, if the total content may look somehow high, it must be remembered that only a very small amount of this content is soluble and available for plants.

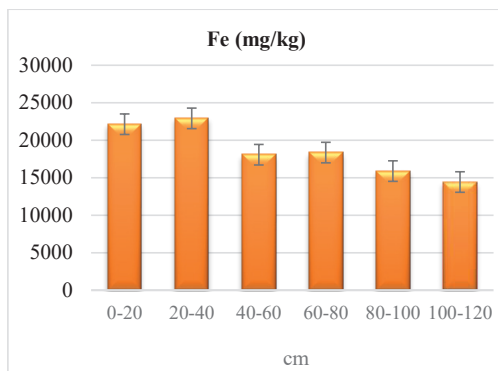


Figure 6. The total iron content of the soil profiles

The total copper content, between 15.74 and 36.4 mg/kg (Figure 7) is low for the deeper layers and high for the arable layer (Madjar, 2008). Usually, only 20-30% of this total content may be soluble and available for plants.

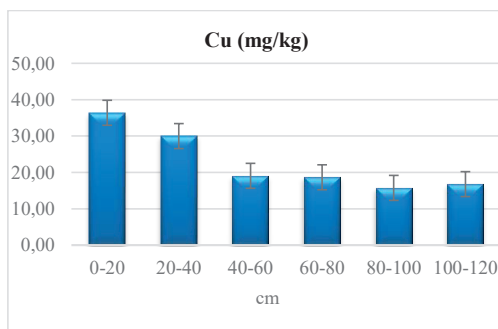


Figure 7. The total copper content of the soil profiles

The total zinc content, between 28.59 and 66.51 mg/kg (Figure 8) is under the know limits for Romanian soils (Madjar, 2008). Usually, only 10-30% of this total content may be soluble and available for plants.

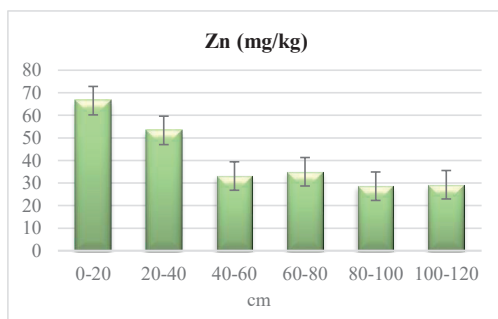


Figure 8. The total zinc content of the soil profiles

The total molybdenum content, between 0.75 and 1.29 mg/kg (Figure 9) falls under the known limits for Romanian soils, of 0.6-3.5 mg/kg (Madjar, 2008). Usually, only 0.05-0.15 mg/kg represents the accessible forms for plants.

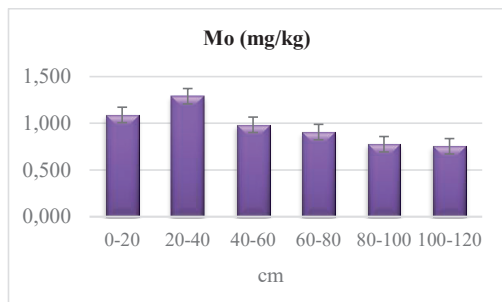


Figure 9. The total molybdenum content of the soil profiles

According to El-Ramady, 2015, non-seleniferous soils contain less than 1 mg/kg, whereas seleniferous soils can range between 2 and 100 mg/kg Se. Our analysis indicates a relatively low content of selenium in our soils, but a special attention should be given to the content from the arable layer.

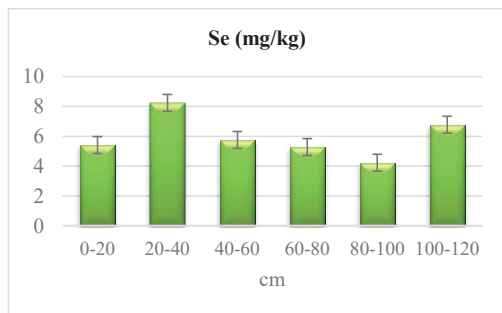


Figure 10. The total selenium content of the soil profiles

As a general remark, the soil total content in micronutrients reflects a good supply for the calcareous soil from Buzau county (Table 2).

Table 2. Correlation between analysed microelements content in soil profiles in 2019

	Zn	Cu	Fe	Se	Mo
Zn	1				
Cu	0.998	1			
Fe	0.895	0.896	1		
Se	0.296	0.340	0.407	1	
Mo	0.781	0.799	0.954	0.614	1

CONCLUSIONS

Soil fertility is one of the most important issues for modern agriculture today and the way we use the technological resources to maintain its health and prevent environmental pollution will deeply impact the generations of tomorrow. The fertilizations must be realized only considering the existing content of nutrients in soil, the physical and chemical processes that may lead to variations of available and unavailable forms and the requirements of the cultivated crops. Our analysis revealed that ICP-MS is a high throughput and reliable technique that allows fast analysis of the total content of nutrients in soils, providing results comparable with those obtained by other laborious techniques and may provide fast answers to farmers and valuable information about the nutrients dynamic in the plants rhizosphere through the cropping season.

ACKNOWLEDGEMENTS

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0301/ 28PCCDI, within PNCDI III.

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