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MULTIELEMENT ANALYSIS IN SOILS UNDER DIFFERENT MANAGEMENT SYSTEMS BY ICP-MS TECHNIQUE

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Abstract

*Soil is a major source of both macronutrients and micronutrients which are needed for plants to grow. The macronutrients are required in large quantities due to their importance in cellular components like proteins and nucleic acids. The micronutrients have essential and specific roles in molecules involved with energy transfer process and enzymes. On the other hand, in soils can be found toxic elements as well which have been added to soils due to the usage of fertilizers, pesticides and from atmospheric deposition. The purpose of the present paper is to determine the content of macronutrients (C, N, K, Mg, Ca), micronutrients (Fe, Na, Mn, Co, Mo, Zn, Cu and Ti) and heavy metals (*Pb, Cd, Ni, Cr, As*) from soil samples using ICP-MS (inductively coupled plasma- mass spectrometry) technique. In this study where used three types of soil: conventional soil, ecological soil and soil in the second year of conversion. Different quantities of nutrients were observed between the three soil samples during the conversion from conventional to ecological.*

Key words*: ICP-MS, macronutrients, micronutrients, soils, toxic elements.*

INTRODUCTION

For a better understanding of nutrients contribution in food quality it is very important to determine the mineral content of soil because soil is a major source of both macronutrients and micronutrients that plants need to grow.

Some micronutrients like Iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) play critical role in the biological processes of organisms, being essential in small quantities to microorganisms, plants and animal organisms, including humans (Shahid et al., 2015). Excessive amounts of these elements can become harmful to organisms. Their availability in appropriate levels in soil is very important not only for plant growth and development, but also for preventing any potential build-up of certain nutrients in order to sustain agricultural production (Shahid et al., 2015). The source of micronutrients in soil is the addition of chemical fertilizers, organic fertilizers such as livestock manure and sewage sludge, irrigation water, and atmospheric deposition (Li et al., 2010). On the other hand, macronutrients as Calcium (Ca), Magnesium (Mg), Potassium (K) are required in large amounts in soil due to their significant role during the entire plant life by performing various beneficial activities in plant metabolism as well as protecting plants from various abiotic and biotic stresses (Shanker & Venkateswarlu 2011; Rowley et al. 2012; Morgan & Connolly 2013).

Heavy metals such as Pb, Cd, Ni, Cr, and As (a metalloid) have a negative effect on organisms and are known as the “main threats” since they are very harmful to both plants and animals (Chibuike & Obiora, 2014). Although heavy metals are naturally present in the soil, there are some activities like mining and smelting of metals, burning of fossil fuels, use of fertilizers, and pesticides in agriculture that lead to increased concentration of these elements to amounts that are harmful to plants, animals and humans (Raskin et al., 1994).

The purpose of this study is to asses the elemental characterization of three type of soils under different management systems using the inductively coupled plasma- mass spectrometry (ICP-MS) technique.

MATERIALS AND METHODS

Sample Materials

For this study, three types of soil (calcaric alluvial soil) under different management systems with pH= 7.8 were taken from the same area at a depth of 0-20 cm: conventional soil (S_1), soil in second year of conversion (S_2) and ecological soil (S_3). In the first year of conversion were cultivated: autumn cabbage and zucchini. The ecological soil is certified, being cultivated with basil and beans in 2016 and okra in 2017. These cultures were bio-treated with milk and garlic. Conventional soil was used for the cultivation of beans (2018), celery and flowers and was treated with chemical fertilizers and pesticides. Sampling was performed in autumn 2018. Soil samples were dried, disaggregated using a porcelain pestle, sieved at 2 mm, the volume was reduced by quartering and riffling and at the end samples were sieved through 200 μm to obtain the test samples.

Microwave-Assisted Digestion Procedure

Microwave digestion was performed in a close microwave oven system (Milestone Ethos Up). This microwave system is equipped with two magnetrons, temperature and pressure sensor for homogeneous temperature distribution and easy CONTROL software that monitors control parameters throughout digestion (temperature, pressure and power). The digestor was prepared according to the manual instructions and the parameters of the digestion procedure were programmed as follows: t_{max} = 210°C, P_{max} =1800 W; t (ramp) = 20 min, t (heating at maximum temperature) = 20 min, t (vent)= 15 min (Roje, 2010).

Before and after digestion all the Teflon vessels of the microwave system were cleaned by applying 5 mL of the acid reagent and 5 ml MQ-water (in each Teflon vessel) and introduced into digestor following the cleaning procedure. Then the vessels were rinsed with MQ-water and dried under laminated air at the ambient temperature. For the digestion method, a test portion of about 0.1 g was weighed into a 120-mL Teflon-PFA microwave digestion vessel. The digestion was performed by adding to the soil sample a mixture of $HCl:HNO_3:H_2O_2$ (3:1:1). The control was prepared in the same conditions and with no soil addition. This digestion method is a modified aqua regia digestion suggested by the Italian legislation (Ministerial Decree, 1999). Hydrogen peroxide was used to enhance the destruction of organic matter (Gaudino et al., 2007). For each soil sample the digestion was performed in triplicate. After digestion, each aliquot was quantitatively transferred to a volumetric flask and diluted with Milli-Q water (18.2 MΩ• cm, 25 °C) to 50 ml. The solutions were allowed to stand for 24 h without removing the undissolved residue, filtered through PTFE filters (pore size 0.45 μm, 25 mm diameter) and then analyzed by ICP-MS. For the measurements of the elements, the digested solutions were diluted to 0.8/10 with MQ-water.

For digestion purposes were used nitric acid (HNO_3 Suprapure 65%, Merck), hydrochloric acid (37%, Merk) and hydrogen peroxide (H_2O_2 30%, Honeywell, Fluka).

The soil digested samples were analysed by ICP-MS 7700 Agilent (inductively coupled plasma- mass spectrometry). Measurements were made using the Agilent MassHunter Workstation software that automates the analysis process and accurately interprets the results.

The calibration curve was performed with the standard multi-element calibration solution: 1000 mg/L of Fe, K, Ca, Na, Mg; 100 mg/L of Sr; 10 mg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, U in 5% HNO_3 and 1% HCl.

The estimation of soil organic carbon was determined using the Walkley-Black chromic acid wet oxidation method (De Vos et al., 2007). For the total nitrogen (total concentration of organic nitrogen and ammonia) estimation was used Kjeldahl method (Marty et al., 2017).

RESULTS AND DISCUSSIONS

The results obtained after the samples were analysed at ICP-MS are noted in Table 1. In the table are quantified macronutrients, micronutrients, and heavy metals for the three types of soil: conventional, soil in conversion and ecological soil. At the same time can be observed that the relative standard deviation of isotopes signals was less than 5%.

Table 1. ICP-MS results on three agricultural soil samples expressed in mg/kg

Element	Soil samples		
	S1	S2	S3
K	10547.67 ± 0.18	8947.64 ± 0.05	7873 ± 0.03
Ca	21895.08 ± 0.46	17953.57 ± 0.17	18283.36 ± 0.24
Mg	7730.22 ± 0.12	6108.34 ± 0.01	5867.68 ± 0.03
Na	577.9 ± 4.4	451.1 ± 2.3	453.27 ± 2.4
As	7.5 ± 0.1	6.54 ± 0.2	4.12 ± 0.09
Be	1.44 ± 0.11	1.10 ± 0.09	1.06 ± 0.048
Cd	0,45 ± 0.02	0.42 ± 0.006	0.16 ± 0.004
Co	9.6 ± 0.5	7.75 ± 0.4	7.39 ± 0.2
Cr	10.52 ± 0.15	7.52 ± 0.17	7.343 ± 0.12
Cu	35.86 ± 1.1	31.33 ± 0.4	20.96 ± 0.5
Mo	1.62 ± 0.09	1.01 ± 0.19	1.13 ± 0.02
Sb	0.85 ± 0.04	0.59 ± 0.03	0.54 ± 0.01
V	22.05 ± 0.47	18.15 ± 0.14	18.08 ± 0.25
Zn	13.00 ± 0.5	13.96 ± 0.5	12.23 ± 0.5
U	1.23 ± 0.03	1.18 ± 0.004	0.68 ± 0.02
Fe	98989.90 ± 1.4	83421.94 ± 1	79948.68 ± 1
Al	15886.22 ± 0.4	12951.20 ± 0.04	12006.3 ± 0.08
Mn	675.3 ± 0.008	634.65 ± 0.01	614.82 ± 0.002
Ba	215.73 ± 2.3	231.9 ± 1.9	171.5 ± 1.7
Sr	101.57 ± 1.8	89.30 ± 0.7	82.81 ± 0.8
Ni	46.93 ± 0.6	34.26 ±0.3	13.08 ± 0.6
Pb	24.6 ± 0.3	18.17 ± 0.4	15.5 ± 0.3

Macroelements

The macronutrients are those elements from soil that are demanded in relatively high levels. From the Figure 1. can be observed that the macronutrients ^{39}K, ^{44}Ca, ^{24}Mg were found in higher concentrations in conventional soil compared to ecological and soil in conversion. These results can be associated with the application of chemical fertilizers rich in macronutrients. According to Lacatusu (2016) soil analysed being a calcaric alluvial soil founded on fluvial deposits has total potassium content 0.6-1.2%, calcium content between 4-5 % and magnesium content 1.2 %.

Regarding the other major macroelements (C and N) that were determined using chemical methods can be noticed that their presence is higher in S3 compared with S1 (Figure 2).

Total nitrogen from soil samples can be interpreted in accordance with the following content ranges: 0.271 – 0.600 % (high content) and > 0.600 % (very high content) (Lacatusu et al., 2000).

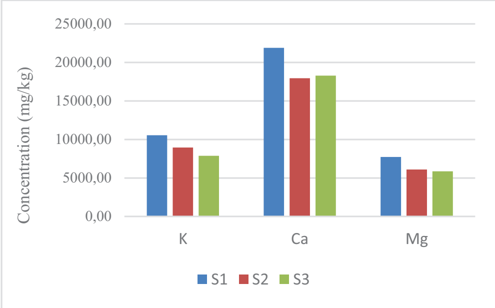

Figure 1. Macronutrients from soil samples (mg/kg)

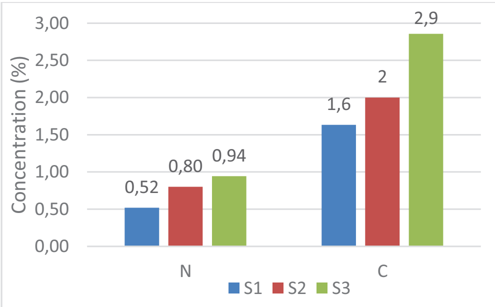

Figure 2. Major macronutrients from soil samples (%) obtained using analytical methods

Microelements

Microelements (also called trace elements) are chemical elements found in very small amounts in soils, rocks, waters and organisms that are needed to increase yield, improve the quality of plant products, and protect plants and animals against diseases and pathogens. According to Order 756/97 "Regulations on environmental pollution assessment" the normal value in soil of ^{55}Mn is 900 mg/kg and for ^{137}Ba is 200 mg/kg (Table 2).

Table 2. Normal values of trace elements according to Order 756/97 "Regulations on environmental pollution assessment"

Trace element	Normal values (mg/kg)
Arsenic	5
Barium	200
Cadmium	1
Cobalt	15
Chromium	30
Copper	20
Manganese	900
Molybdenum	2
Nickel	20
Plumb	20
Vanadium	50
Zinc	100

From figure 3 can be observed that this micronutrients accomplish the normal values and are higher in soil S1 compared to S3 due to the application of fertilizers rich in micronutrients.
Most fertilizers used on the soil are soluble because they are salts. Once they are dissolved in the soil, they increase the salt concentration of the soil solution, which in turn increases the solution's osmotic potential. The greater the osmotic potential, the more difficult it is for the seeds or plants to extract the soil water they need for growth (Graebing et al., 2002). The results show that the repeated usage of the fertilizers increase in the sodium quantity conventional soil (Figure 3) compared with ecological soil.

Figure 3. Micronutrients from soil samples (mg/kg)

In terms of abundance in soil, iron is part of the macroelement category. However, considering the amount of iron solubilized in soil solution (mg/kg) and especially the amount iron that plants absorb and the functions it performs in the nutritional process, iron belongs to the group of microelements (Lacatusu, 2016). Iron is an essential mineral which has an important role in the fundamental biological processes (photosynthesis, respiration, nitrogen fixation and assimilation, and DNA synthesis) being also a co-factor of many enzymes involved in the synthesis of plant hormones (Briat, 2005).
From the figure 4 is noticed the higher availability of iron in the three types of soil with a higher concentration in S1.
Regarding the ^{27}Al presence in soil, its toxicity occurs under acidic conditions below a pH of 4.7 (Kochian et al., 2004).

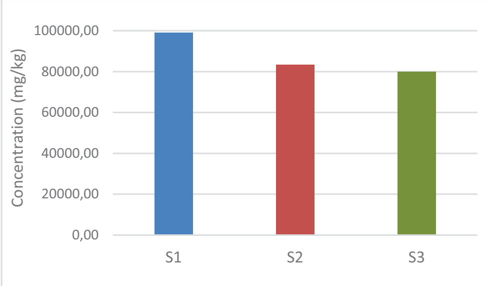

Figure 4. Iron presence in soil samples (mg/kg)

Magistad (1925) conclude that soils whose reaction values lie within the range pH 4.7 and pH 8.5 do not contain aluminium in soluble form, and therefore, are not toxic to plants. Therefore, the quantity of aluminium determined from soil samples is highlighted in figure 5, where were noticed small amounts of aluminium which are not toxic due to the soil samples pH (7.8).

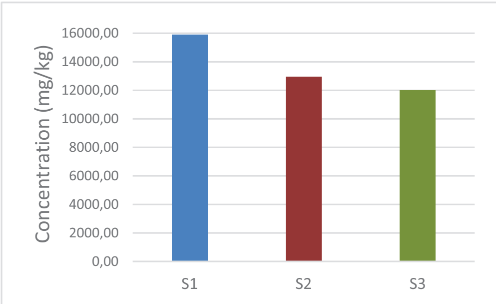

Figure 5. Aluminium presence in soil samples (mg/kg)

Some heavy metals are essential or important for both plants and animals (Cu, Zn, Co), others only for animals (Cr, Ni) and some are not important for animals or plants (Pb, Cd, Ag, Se) (Adriano, 1986).
In our country the total ^{63}Cu content of soils varies from 2 to 60 mg/kg (Davidescu et al., 1988), but most sites are characterized by Cu content in the range 20-30 mg/kg. At the same time the total Zn content in the upper horizon of the main agricultural soil types in Romania varies between 11 and 97 mg/kg (Bajescu & Chiriac, 1984). The availability of ^{63}Cu and ^{64}Zn in the three soil samples is highlighted in figure 6.
The results obtained for the soil samples are in concordance with research mentioned above.

The Cu content varies from 20.96 mg/kg in ecological soil to 35.86 mg/kg in conventional soil and Zn content doesn't show significant differences between the three types of soil analysed (12.23 mg/kg in ecological soil, 13 mg/kg in conventional soil and 13.96 in the conversion soil).

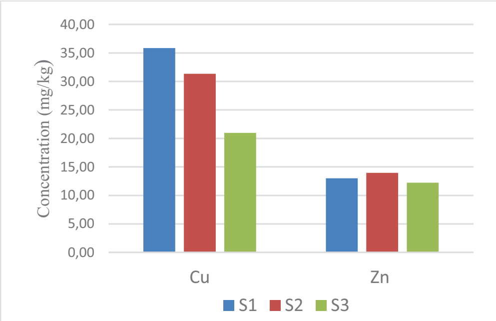

Figure 6. Availability of Cu and Zn in soil samples (mg/kg)

The regulation presented previously in the article, Order 756/97, established for ^{75}As and ^{59}Co the following accepted limits: 5 mg/kg for ^{75}As and 15 mg/kg for ^{59}Co. Results presented in figure 7 show that ^{75}As exceeds normal limits in S1 compared with S3. This increase is due to the use of chemical fertilizers and pesticides that contain trace amounts of heavy metals and metalloids (Chandrajith et al. 2009).

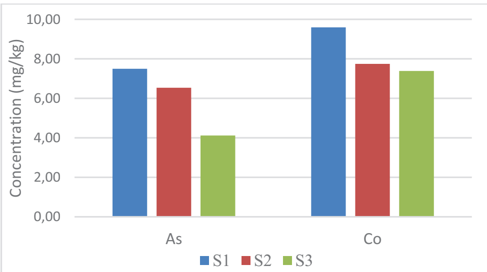

Figure 7. Heavy metals (As, Co) from soil samples (mg/kg)

In figure 8 are pointed out results of the presence of three heavy metals (Ni, Pb, Cr) in the soils taken into analysis. They show higher concentration of the heavy metals in conventional soil (Ni 46.93 mg/kg, Pb 24.6 mg/kg, Cr 10.52 mg/kg) compared with the ecological soil (Ni 13.08 mg/kg, Pb 15.5 mg/kg, Cr 7.34 mg/kg). According to the Order 756/97 the concentration of Ni from the conventional soil is higher (46.93 mg/kg) than normal values found in soil (20 mg/kg). The results are concordance with the average value reported by Kabata – Pendias and Pendias (2001), that is 25 mg/kg.

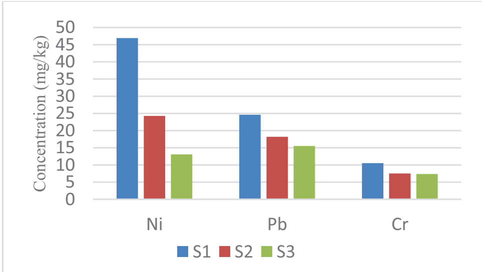

Figure 8. Heavy metals (Ni, Pb, Cr) from soil samples (mg/kg)

CONCLUSIONS

The three soil samples analysed in this study throught ICP-MS technique highlight the presence of 22 elements (Fe, K, Ca, Na, Mg, Sr, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn, U), which were divided in macroelements, microelements and heavy metals. Each of the elements analysed plays an important role in soil functions and plant health and protection. The concentrations obtained for each element analysed were in concordance with studies of other researchers. Exception makes Ni which was found in higher concentrations that the normal limits allowed. Activities like applying fertilizers and pesticides in agriculture lead to an increase of concentration of heavy metals to amounts that can be harmful to plants, animals and humans.
The application of chemical fertilizers showed an increase of micro and macro nutrients concentration in conventional soil compared with ecological soil. On the other hand, the repeated addition in soil of chemical fertilizers and pesticides lead to a decrease of total nitrogen and soil organic matter (N and C) in conventional soil.

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