Scientific Papers. Series B, Horticulture. Vol. LXIII, No. 1, 2019
Print ISSN 2285-5653, CD-ROM ISSN 2285-5661, Online ISSN 2286-1580, ISSN-L 2285-5653

THE QUALITY OF SOILS WITH KNOWN ELECTRICAL CONDUCTIVITY

Carmen CONSTANTIN[1, 2], Mihaela ZUGRAVU[1], Mugurași CONSTANTIN[1], Maria PARASCHIV[2, 3]

[1]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd., District 1, Bucharest, Romania
[2]National Institute of Research and Development for Biological Sciences Bucharest, 296 Splaiul Independentei St., Bucharest, Romania
[3]Research Center for Advanced Materials, Products and Processes, Politehnica University of Bucharest, 313 Spl. Independenței, District 6, Romania

Corresponding author email: mariaparaschiv@gmail.com

Abstract

This paper presents the elemental content found in two saline soil samples with a certain electrical conductivity and the differences between two variants of extraction. The soil samples collected from a region in South-East of Romania affected by salinization process were investigated using a semi quantitative (SMA) inductively coupled plasma with mass spectrometry analysis (ICP–MS). Thus, the multi-elemental analysis of soil samples was preceded by one-step digestion in a high-pressure microwave system. For matrix destruction two mixtures of reagents were used: A - HNO_3, HCl and H_2O_2 in 3:1:1 (v/v), and B - HNO_3, HCl 3:1 (v/v). The electrical conductivity was realized using an adapted method, and the value was up to 10000 dS/m. Following semiquantitative analysis, the results showed that both of extraction methods showed the same elemental composition, the difference being only of the quantity of each element. Regarding the extraction efficiency, mixture A was more suitable for this type of soil.

Key words*: ecosystem services, ICP-MS, microwave digestion, salinity, trace elements.*

INTRODUCTION

Around the world salt affects the growth and development of crops, limiting nutrient availability. Salts have a negative impact on nutrient uptake, the necessary amount for plants and the activity of some enzymes by high concentrations of cations and anions (Fageria et al., 2011). Salinity is a strong factor limiting the productivity of crops because most of the crop plants are sensitive to high concentrations of salts in the soil, and the area of land affected by it is increasing (Shrivastava et al., 2015). In this sense, soil is one of the most complex biomaterials, and an important component of the terrestrial ecosystem (Young et al., 2004). Soils of natural ecosystem generates a multitude of functions, also called soil functions. These functions support the ecosystem services (Blum, 2005).

Most studies regarding the ecosystem services lack a soil component or the soil component is poorly described or too generalized. The ecosystem services depend on soil properties and components and their interactions (Adhikar et al., 2016). Some trace elements (e.g., As, B, Co, Cr, Cu, Mo, Mn, Ni, Se, Zn) are important as micronutrients to living cells, although many trace elements (Zn, As, Hg, Cd, Pb, Tl, Co, Cr, Cu, Mo, Ni, Se, Sn) can be toxic above certain levels in soils (Abbaslou et al., 2014). Overall, this phenomenon strongly affects the ecosystem services and environment. The study of salts is essential for detecting saline limits of the plants (Hannachi et al., 2018). Also, the accumulation of toxic ion or depletion may cause cell permeability, lead to lipid peroxidation, and in the end leaf necrosis (Halliwell, 1987).

With regard to trace elements in South-East soils of Romania, there is a lack of information. The content and distribution of trace elements in soil is scarce due to the fact that salinization is in the early stages, not being studied so much.

Concerning the method of analysis, this is commonly used for quick fingerprinting of the elemental composition of unknown samples (Bulska et al., 2016). The semi-quantitative analysis implies scanning the entire m/z range. The method provides fast quantitative analysis

and allows the determination of more than 70 elements with good accuracy and very low detection limits. In analyses for which very low detection limits are not required a semiquantitative ICP-MS analysis mode can be used (Krzciuk, 2016).
The semi-quantitative data can be used to estimate the content of the elements which will be further quantified.
This is a step-in to establish the concentrations of standard solutions (Chen et al., 2008).
The objective of this paper is to determine the concentration ranges of selected elements in studied soils and electrical conductivity values in order to establish what kind of plants can grow on it so that the balance of the ecosystem can be restored.

MATERIALS AND METHODS

The experimental work was carried out on soil sampled SE region of Romania, affected by salinity (Figure 1).

Fig. 1. Sample soil area

The soil samples were collected from 6 points, of which only 1 and 6 were taken into this study. The samples were collected as follows depths: 0-30 cm, 30-60 cm, 60-90 cm. The soil electrical conductivity was realized (Amezketa, 2007). Determination of specific electrical conductivity was realised according to the reference standard: - SR ISO ISO 11265 + A1: 1998 Soil quality.
The soil sample is dried in the atmosphere and sieved through a 2 mm sieve. 10 g of soil were weighed over to which 50 mL of ultrapure water was added. The samples were agitated for 1 hour at 15 rpm. After decanting, the electrical conductivity was read directly in the prepared suspension sample.

Fig. 2. Sample soil

The soils samples were mixed resulting 2 samples and subjected to microwave digestion: 0.100 g of soil sample were weighed in Teflon tubes.
The following reagents were added: HNO_3, HCl and H_2O_2. Of them two combinations were used as follows: method A - HNO_3, HCl and H_2O_2 in 3:1:1 (v/v), and method B - HNO_3, HCl 3:1 (v/v), *aqua regia* (Turek et al., 2012).
The Teflon container with sample and reagents is inserted into the shield. The bowl provided with the protective spring is placed in the propeller rotor segment.
Once the safety bolt has been secured by the torque wrench, the container segment has been inserted into the Ethos Up microwave digestion system. The same protocol described both for reference was applied without soil sample.
The specific mineralisation method for soil samples had the following parameters: t1 (ramp) 10 minutes, power (Pmax) 1800 W, temperature (Tmax) 200 ºC, cooling time 15 minutes. After the heating cycle has been completed, the containers were left to cool in the microwave cavity for about 20 minutes. The samples were brought to a final volume of 50 ml then subjected to ICP-MS analysis using Helium as carrier gas and an Agilent 7700 + ASX 500 + G3292A Spectrometer.
Using argon as a plasma gas has some limitations. The argon plasma does not generate substantial quantities of elements possessing high ionization energies. Because the ionization energy of He (24.6 eV) is higher than that of Ar (15.8 eV), the use of He-ICP as an ion source for MS has potential of enhancing the degree of

ionization for every element, in particular for non-metals (Okino et al., 1996).

RESULTS AND DISCUSSIONS

The soil samples were firstly subjected to electrical conductivity measurements, which were realized using an adapted method (Rayment et al., 1992) and the results are presented in Table 1. According to the soil classification (Canfora et al., 2014), the tested soils are saline, the registered electrical conductivity values being greater than 4 dS/m.

Table. 1. Electrical conductivity of tested soil samples

Sample	EC dS/m
P1a, 0-30 cm	87,000
P1b, 30-60 cm	45,000
P1c, 60-90 cm	30,500
P6a, 0-30 cm	106,400
P6b, 30-60 cm	48,500
P6c, 60-90 cm	32,000

The results are in accordance to the classification of soil salinization (Canfora et al., 2014; Tóth, 2017; Chhabra, 2004), the soil samples being saline. According to Amezketa, (2007), soils are non-saline (EC values of the average profile below 4 dS m^{-1}), slightly saline (EC values between 4 and 8 dS m^{-1}), moderately saline (EC values between 8 and 16 dS m^{-1}), and strongly saline (EC > 16 dS m^{-1}).
For these soil types are recommend moderate halophytes such as *Limonium* spp., *Gipsophilla* spp., *Celosia* spp., and halophytes such as *Festuca arundinacea* L., *Amaranthus* spp., *Portulaca oleracea* L., *Salicornia* spp., respectively. These species not only will help to restore soil balance (macro and microelements, microbial populations, enzymes, etc.), but also, in the long term, they are able to improve the quality of both the ecosystem services and human life, by restoring floristic and fauna diversity. The results obtained from semi-quantitative ICP-MS analysis are shown in Fig. 1a, 1b, 1c, 1d.
In figure 1a, are presented the major elements. With regard to the extraction method, the results showed that method A was relevant for Na and Mg, while method B for K and Ca. From sample point of view, sample 2 contains more Na, Mg and Ca, while sample 1 contains more K. Between the samples, significant differences were observed in the case of Na, K and Ca content. The results are similar with those found by Voica et al., (2012) in some sample soils from Cluj area.

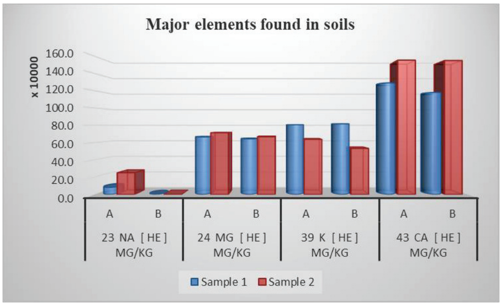

Fig. 1a. Results from ICP-MS semi – quantitative analysis

With regard to the identified microelements, they are shown in Figures 1b, 1c, 1d. Thus, in Figure 1b, large quantities of Mn were found in sample 1, and the extraction method A was the best. The presence of this element in soil is very important, being essential for plants. It is involved in metabolic processes and as an enzyme antioxidant-cofactor (Millaleo et al., 2010). Superoxide dismutase (SOD2 or MnSOD) is an endogenous antioxidant enzyme in the pathway that converts reactive oxygen species (ROS) to hydrogen peroxide (H_2O_2) (Mikhak et al., 2008).

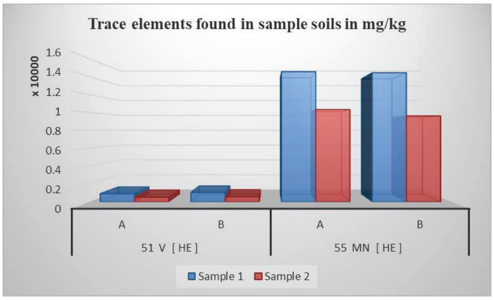

Fig. 1b. Results from ICP-MS semi – quantitative analysis

In Figure 1c, traces of elements are presented in micrograms. In this sense, Ni was revealed in quantities greater than Cu, Se and Mo. Method A has been highlighted for all elements.
Nickel is very important for some enzymes, biochemical, physiological and growth responses (Yusuf et al., 2011).

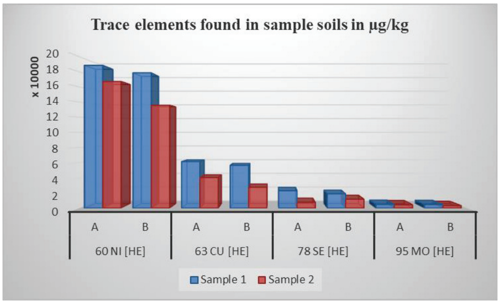

Fig. 1c. Results from ICP-MS semi – quantitative analysis

In Figure 1d, traces of Co, Zn, Ag, Cd and Pb are presented. As can be seen, the most suitable method for Zn, Ag, Cd and Pb is B. Between the two samples, Co, Zn, Ag and Cd sample 1 have high values for them, while sample 2 has high content of Pb.
According to Zurayk et al., (2001), salinity and heavy metals can occur concurrently in soil and water. However, trace elements, such as Se, Cd, Cu, and Ni, may occur in appreciable concentrations, from anthropic activity or geochemical characteristics (Deverel et al., 1990).

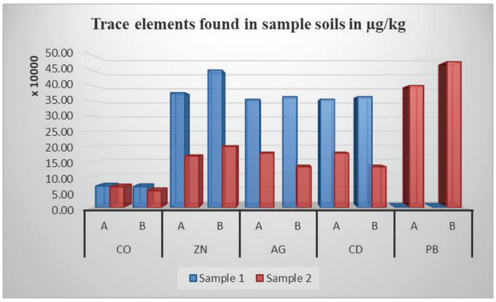

Fig. 1d. Results from ICP-MS semi – quantitative analysis

In terms of microelements like V, Cu, Mo, Se and Co, there were no significant differences between the extraction methods A and B, only between samples. Of the above-mentioned elements, only Pb was the exception, registering very high values for the second analysed sample.
Considering other microelements like Ni, Cu, Zn, Se, Mo, Ag, Cd, Pb were identified both for extraction methods and samples, in order of µg/kg.

Other elements such as Al and Fe were identified as being out of range, being under the detection limit. One possible explanation could be that the major soil elements are typically present in too high a concentration to enable their simultaneous determination with elements of low abundance (Entwistlef, 1997).
According to Wuana et al., (2011) the presence of toxic metals can inhibit the biodegradation of organic contaminants. The presence of heavy metals in soil may lead to risks and hazards to humans and the ecosystem.
According to Levy et al., (1992), in the soil, heavy metals as lead, cadmium, copper, manganese can be absorbed, being redistributed into different chemical forms, also their concentrations in the environment may be used as indices of environmental pollution (Mahimairaja, 2000).

CONCLUSIONS

The adequate protection and restoration of affected ecosystems affected by salinization require full quant characterization and remediation.
The electrical conductivity values for soils were higher than 4 dS/cm, highlighting a very high salinity content that is unsuitable for a large number of species and limits the land use to those salt-tolerant crops.
With regard to the ICP-MS analysis, the elemental content (e.g. Na, K, Mg, Ca, V, Mn, Ni, Cu, Se, Mo, Co, Zn, Ag, Cd, Pb) was the same in both case of extraction A and B.
With regard to the extraction methods, first mixture A was more efficient than B, as showed the high values of the majority of elements.
One such instance, crops of varying salt tolerance shall be grown sequentially, starting with the highly species, and ending with most sensitive tolerant salt crops.

ACKNOWLEDGEMENTS

This work has been developed and was financially supported through the Romanian National Research Program PNIII, Subprogram 3.2 International and European Cooperation - Horizon 2020, financing contract no. 44/2018, Integrated system of bioremediation –

biorefinering using halophyte species - code: ERANET-FACCE-SURPLUS-HaloSYS.

REFERENCES

Abbaslou, H. Martin F., Abtahi, A., Moore, F. (2014). Trace element concentrations and background values in the arid soils of Hormozgan Province of southern Iran. *Archives of Agronomy and Soil Science*, 60, 1125–1143.

Adhikari, K., Hartemink, A. E. (2016). Linking soils to ecosystem services — A global review, *Geoderma* 262, 101–111.

Amezketa, E. (2007). Soil salinity assessment using directed soil sampling from a geophysical survey with electromagnetic technology: a case study. *Spanish Journal of Agricultural Research*, 5(1), 91-101.

Blum, W.H., 2005. Functions of soil for society and the environment. *Reviews in Environmental Science and Bio/Technology*. 4 (3), 75–79.

Bulska E. and Wagner B. (2016). Quantitative aspects of inductively coupled plasma mass spectrometry. *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences*, 374(2079), 1-18.

Canfora L., Bacci G., Pinzari, F., Lo Papa, G., Dazzi, C., Benedetti, A. (2014). Salinity and bacterial diversity: to what extent does the concentration of salt affect the bacterial community in a saline soil? *PLoS One*. 9, 1-15.

Chen, H., Dąbek-Złotorzyńska, E., Rasmussen, P. E., Hassan, N., Lanouette, M. (2008). Evaluation of semiquantitative analysis mode in ICP-MS. *Talanta* 74, 1547–1555.

Chhabra, R, (2004). Classification of Salt-Affected Soils. *Arid Land Research and Management*, 19, 61-79.

Deverel, S. J., Fujii, R. (1990). Chemistry of trace elements in soils and groundwater. *Agricultural salinity assessment and management*, Tanji, K. K. Ed., American Society of Civil Engineers: New York.

Entwistlef, J. A., Abrahams, P. W. (1997). Multi-element analysis of soils and sediments from scottish historical sites. the potential of inductively coupled plasma-mass spectrometry for rapid site investigation, Journal of *Archaeological Science*, 24(5), 407-416.

Fageria, N. K., Hans, R. Gheyi, Moreira, A. (2011) Nutrient bioavailability in salt affected soils. *Journal of Plant Nutrition*, 34, 945-962.

Hannachi, S., and Van Labeke, M. C. (2018). Salt stress affects germination, seedling growth and physiological responses differentially in eggplant cultivars (Solanum melongena L.). *Scientia Horticulturae*, 228, 56-65.

Halliwell, B. (1987). Oxidative damage, lipid peroxidation, and antioxidant protection in chloroplasts. *Chemistry and Physics of Lipids*, 44, 327-340.

Krzciuk, K. (2016). Intelligent analysis of samples by semiquantitative Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique: a review. *Critical Reviews in Analytical Chemistry*, 46(4), 284-290.

Mahimairaja S. (2000). An overview of heavy metals: impact and remediation. *Current Science,*78(7), 34–44.

Mikhak, B., Hunter, D. J., Spiegelman D., Platz, A. E., Wu K., Erdman, Jr. W., and Giovannucci, E., Manganese superoxide dismutase (MnSOD) gene polymorphism, interactions with carotenoid levels and prostate cancer risk, *Carcinogenesis*, 29(12), 2335–2340.

Millaleo, R., Millaleo, M., Reyes-Díaz, A.G., Ivanov, M., Mora, L., and Alberdi, M. (2010). Manganese as essential and toxic element for plants: transport, accumulation and resistance mechanisms. *Journal of Soil Science and Plant Nutrition,* 10(4), 476 – 494.

Okino, A., Ishizuka, H., Hotta, E., Shimada, R. (1996). IEEE Conference Record - Abstracts. IEEE International Conference on Plasma Science, doi: 10.1109/PLASMA.1996.550934.

Rayment, G. E., Higginson, F. R. (1992). Australian laboratory handbook of soil and water chemical methods, Melbourne, Inkata Press. *Australian Soil and Land Survey Handbooks*, 3.

Shrivastava, P., and Kumar, R. (2015). Soil salinity: A serious environmental issue and plant growth promoting bacteria as one of the tools for its alleviation, *Saudi Journal of Biological Sciences*, 22(2), 123–131.

Tóth, T. (2017). Classification and mitigation of soil salinization, subject: environmental issues and problems, *Oxford Research Encyclopedia of Environmental Science,* Oxford University Press USA, 1-38.

Turek, A., Wieczorek, K., and Wojciech, M. (2019). Wolf digestion procedure and determination of heavy metals in sewage sludge—an analytical problem. *Sustainability*, 11, 1-10.

Voica, C., Dehelean, A., Iordache, A., Geana, I. (2012). Method validation for determination of metals in soils by ICP-MS, *Romanian Reports in Physics*, 64(1), 221–231.

Young, I., Crawford, J. (2004). Interactions and self-organisation in the soil-microbe complex. *Science*, 304, 1634–1637.

Yusuf, M., Fariduddin, S. Q., Ahmad H. A. (2011). Nickel: an overview of uptake, essentiality and toxicityin plants. *Bulletin of Environmental Contamination and Toxicology*, 86, 1–17.

Zurayk, R. A, Khoury, N. F., Talhouk, S. N., and R. Baalbaki Z. (2001). Salinity-heavy metal interactions in four salt-tolerant plant species. *Journal of plant nutrition*, 24(11), 1773–1786.

Wuana, R. A. and Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *International Scholarly Research Network ISRN Ecology*, 2011, 1-21.

Levy, D. B., Barbarick, K. A., Siemer E. G., and Sommers, L. E. (1992). Distribution and partitioning of trace metals in contaminated soils near Leadville, Colorado. *Journal of Environmental Quality*, 21(2), 185–195.

EX·TERRA·AVRVM