Serbian Society of Soil Science University of Belgrade, Faculty of Agriculture

BOOK OF PROCEEDINGS

3rd International and 15th National Congress

SOILS FOR FUTURE UNDER GLOBAL CHALLENGES



21–24 September 2021 Sokobanja, Serbia Serbian Society of Soil Science University of Belgrade, Faculty of Agriculture

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FOREWORD

The Serbian Society of Soil Science continues its tradition of hosting conferences, which is one of its primary activities. It organized the 3rd International and 15th National Congress – Soils for Future Under Global Challenges in the International Decade of Soils 2015–2024, collaborating with the University of Belgrade Faculty of Agriculture and under the auspices of the Ministry of Education, Science and Technological Development of the Republic of Serbia, along with sponsors and numerous contributors of papers. Namely, the International Union of Soil Sciences (IUSS) proclaimed the International Decade of Soils 2015-2024. In the Vienna Soil Declaration of 7 December 2015, IUSS recognized the key roles soils play in addressing major resource, environmental, health and social challenges currently facing humanity.

Due to the COVID-19 pandemic, the Congress was held as an online event, in combination with limited physical presence of international and domestic participants who observed the prescribed epidemiological measures and recommendations of the Serbian Government.

The topics of the Congress were grouped into the following four sessions: (i) Soil fundamentals, (ii) Soil-water-plant-atmosphere continuum, (iii) Soil degradation and soil and water conservation, and (iv) Soil and water future socio-economic pathways. The thematic areas were selected to support the distinct efforts of agriculture, and humankind in general, to deal with current resource, environmental, health and social issues.

Growing population pressures, industrialization and intensive use of soil exhaust natural resources and limit the performance of soil functions, such as biomass production, water purification, carbon sequestration, and the like. The additional impacts of climate change, land use changes and the above-mentioned global changes affect the ability of soils to regenerate and even lead to degradation. The future capacity of soils to support life on Earth is in question.

A number of conferences on soil and global changes have been held worldwide over the past several years. Continuing these efforts, we need to keep in mind that the study of soils has changed rapidly. Previously, soil science was seen as supporting agriculture and forestry, and justified by increased soil productivity. However, the focus has recently expanded considerably. Soil science is now a major component of each environmental science course, given that soil plays a key role in elementary natural cycles. Soil pollution is also extremely important, often more persistent than air or water pollution. The impacts of global changes on soils are viewed from a much broader perspective than only several decades ago. However, despite the interest in new fields, the agricultural imperative must not be forgotten. Agriculture remains the main economic purpose of the use of soils and hunger is certainly among the most serious potential disasters set off by global changes.

Ninety-eight contributions were accepted for presentation at the Congress. More than 320 authors and co-authors from 18 countries participated. Fourty contributions from the Congress and included in this Book of Proceedings. They reflect the outcomes of the most recent research of 154 authors and co-authors from 15 countries worldwide. This shows that most of the presentations were a result of teamwork, which not only guarantees a comprehensive approach, but also quality.

Seven distinguished domestic and international professors and scientists prepared the keynote speeches. The submitted papers are available on the website of the Serbian Society of Soil Science (https://congress.sdpz.rs). The contributions contained in this Book of Proceedings have been reviewed by international peers.

An excursion completed the program and content of the Congress. It included showing of four soil profiles of the dominant soil types in the Sokobanja area, including Calcomelanosol, Brownized Calcomelanosol, Calcocambisol and Vertisol, under different land uses (native meadow, devastated native pasture, native forest and intensive apple orchard).

It is our wish to see all the positive outcomes of the Congress implemented in due course, along with recommendations of scientists and professionals. This would fulfil the objective of the Congress in the best possible way. The permanent legacy of the Congress should be the inclusion of soil in the core of policies that support environmental protection and sustainable development.

In closing, I wish to express once again my sincerest gratitude to all who contributed to the publication of this Book of Proceedings.

September 2021 in Sokobanja

Tomas Tojut

Prof. Dr. Boško Gajić

President of the Serbian Society of Soil Science Editor-in-Chief of the Book of Proceedings

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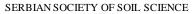
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TOXIC ELEMENTS IN SOILS FROM VLASINA REGION

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Abstract

In this research, the optimized three-step sequential extraction procedure for the fractionation of micro- and macroelements, proposed by Commission of European Communities of reference (BCR) has been applied to the soils from Vlasina region. Element concentrations in the extracts were determined using ICP OES. Magnetic susceptibility (MS) was measured using magnetic susceptibility meter. The index of geoaccumulation (I_{geo}) has been applied to assess trace elements distribution and contamination in studied soils. An assessment of toxic element levels in the studied soils is made by comparing the total contents of the extracted elements with the limit values determined by Serbian Regulation. Metal fractionation showed that easily mobile form is dominant for lead and manganese. Other elements (Zn, Ni, Cr, Co, As, Cu, Cd, and V), found dominantly in the residual fraction indicate that these elements may be an indicator for natural sources input. Obtained results indicated that the soils from Vlasina region were not contaminated with toxic elements and the origin of elements is mostly from natural processes such as soil and rock weathering.

Keywords: contamination; extraction; fractionation; magnetic susceptibility

INTRODUCTION

The widespread contamination of soil with potentially toxic elements (PTE) represents currently one of the most severe environmental problems that can seriously affect environmental quality and human health. Activities in urban areas, including emissions from transport (exhaust gases, tyre wear, particles formed by road erosion), industrial waste (from power plants, fuel combustion, metallurgy, automobile repair plants, chemical industry, etc.), household waste, and erosion of buildings or sidewalks, etc., can be a source of soil pollution (Poznanović Spahić et al. 2018).

Elements in soils may be present in several different physico-chemical forms, i.e. as simple or complex ions, as easily exchangeable ions, as organically bound, as occluded by or coprecipitated with metal oxides or carbonates or phosphates and secondary minerals, or as ions in crystal lattices of primary minerals (Žemberyová et al., 2006). For evaluation of the PTE in the environment, it is not sufficient to measure only the total element content, it is also very important to establish the proportions of elements present in various easily and sparingly soluble soil fractions (Svete et al., 2001). From an environmental standpoint, it is



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important to determine under which conditions toxic elements could be released from sediments. Sequential extraction is an important and widely applied tool that has provided considerable insights into the environmental behaviour of potentially toxic elements (Sakan et al., 2016). In these extraction procedures various extractants are applied successively to the sediment and soil for selective leaching of the particular chemical forms of elements from samples analysed (Svete et al., 2001).

However, the PTE contamination cannot just be assessed by analysing element concentration alone. Therefore, complementary approaches that combine soil quality guidelines and the geoaccumuation index are highly recommended in order to predict the ecological risk of particular areas (Haris et al. 2017).

In order to assess the general pollution of soils from Vlasina region, the PTE contamination in this region were evaluated by using: the BCR sequential extraction procedure, the sediment quality guidelines, calculation of Igeo, and determination of magnetic susceptibility.

MATERIALS AND METHODS

Study area

In the presented study, 15 soil samples were collected in Vlasina region (Figure 1).

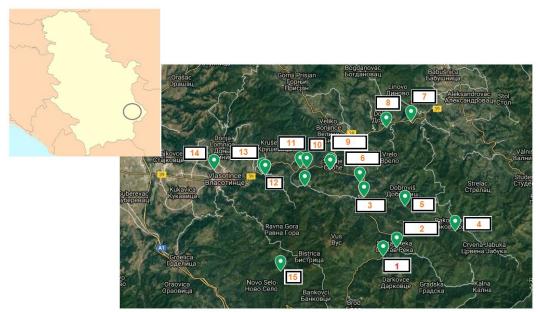


Figure 1. Sampling locations: 1- Vlasina (before all tributaries); 2 - Gradska reka (before casting in Vlasina); 3 - Vlasina (before the mouth of Tegošnica); 4 - Tegošnička reka (stone pit); 5 - Tegošnička reka (Dobroviš); 6 - Vlasina (below Tegosnica, upper walnut); 7 - Ljuberađa (medium flow); 8 - Ljuberađa (measuring profile); 9 - Ljuberađa (the mouth of Ljuberađa in Vlasina); 10 - Pusta reka; 11 - Vlasina (under Pusta river); 12 - Rastavnica; 13 - Vlasina (before the water intake); 14 - Vlasina (under Vlasotince); 15 - Zelenička reka



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Soil samples (Figure 1) were collected near the river Vlasina and its tributaries: Vlasina (6 samples), Gradska reka, Tegošnička reka (2), Ljuberađa (3), Pusta reka, Rastavnica and Zelenička reka.

Chemical analysis

Soil samples were analysed by the optimized BCR three step sequential extraction procedure (Sakan et al., 2016). The following fractions were extracted: exchangeable, reducible – bound to iron/manganese oxides, and oxidizable – bound to organic matter and sulfides. Sequential extractions were applied to 1 g of soil samples.

Element concentrations in the extracts obtained at each step of sequential extraction procedure were determined using an atomic emission spectrometer with an inductively coupled plasma iCAP-6500 Duo (Thermo Scientific, United Kingdom). The analytical data quality was controlled by using laboratory quality assurance and quality control methods. The total amounts of elements in this paper are defined as the sum of the element contents in three fractions plus aqua-regia extractable content of the residue.

Determination of magnetic susceptibility (MS)

Magnetic susceptibility (MS) was measured using magnetic susceptibility meter SM30. Each sample was measured in triplicate and the mean value was taken as final result of measurement, to assure as much precise data as possible.

Geo-accumulation index

This determination equation was introduced by Müller (1979) as a quantitative measure of the intensity of contamination in aquatic sediments. The equation used for the calculation of I_{geo} was as follows:

$$I_{geo} = \log_2 C_n / 1.5 \cdot B_n \tag{1}$$

where C_n - the measured concentration of toxic elements and B_n - the geochemical background. Background contents of elements were calculated for each element as the 75 th percentiles of the frequency distribution of the data – soil content (Dos Santos et al., 2013). The I_{geo} is typically divided into six grades: $I_{geo} = 0$: background concentration; $I_{geo} = (0-1)$: unpolluted; $I_{geo} = (1-2)$: moderately polluted to unpolluted; $I_{geo} = (2-3)$: moderately polluted; $I_{geo} = (3-4)$: moderately to highly polluted; and $I_{geo} > 5$: very highly polluted (Haris et al. 2017).

RESULTS AND DISCUSSION

Distribution of elements among fractions

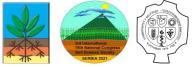
Geochemical fractionation of elements (F1-F4) is shown in Figure 1. The diagrams show that the elements Zn, Ni, Cr, Co, As, Cu, Cd, and V were mostly concentrated in the



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Figure 2. Partitioning of studied elements in soils



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"residual fraction" (F4). The exceptions are Pb and Mn with dominant presence in the "reducible fraction" (F2). It can be concluded that the most mobile elements are Pb and Mn, as they make up a significant part of elements detected in the mobile fraction F2. This result indicates that lead was primarily associated with Fe-Mn oxides and this is in accordance with earlier findings (Sakan et al., 2016). Lead may be released from the soil if there is a change in Fe and Mn oxidation state and thus may pose a long-term source of contamination. Fractionation of Zn, Ni, Cr, Co, As, Cu, Cd, and V showed that the major portion of these elements was in the residual fraction. The elements are retained within the crystal lattice of minerals and in well-crystallized oxides, and could be used as an indicator of natural sources input.

Comparison of total element content with soil standard

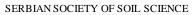
The total content of the investigated elements (Table 1), extracted from the soil sample was compared with the limit and remediation values defined by the Decree on limit values of polluting, harmful and dangerous substances in the soil ("Official Gazette of RS", No. 30/2018 and 64/2019).

	Content (Studied soils)	MAV*	RV**
Cd	0.34-0.66	0.8	12
Cr	17.6-39.8	100	380
Cu	15.4 -38.8	36	190
Ni	8.97-24.5	35	210
Pb	6.41-48.2	85	530
Zn	30.5-84.3	140	720
As	5.52-15.5	29	55
Со	5.12 -22.2	9	240
V	16.1- 45.1	42	250

Table 1. Comparison of element content with soil standard $[mg kg^{-1}]$

* Maximum allowed values;** remediation value

An increased content of the following elements was observed: Cu in the soil sample near the Tegošnička river (Dobroviš), V in the soil sample near Vlasina (in front of the water intake, below the Pusta river), as well as Co in several locations. The values of copper and vanadium content are slightly higher than the maximum limits defined by the Serbian Regulation. These elements are predominantly bound in the residual, immobile, fourth fraction (about 50% of extracted Cu, 70% V and 50% Co), which indicates that the aforementioned elements do not represent a danger to the environment. Taking into account the rock composition characteristic for this region, the binding site of microelements such as Co, Ni, Cr, and Cu could be shales, as well as ultrabasites-basites and serpentinites. Considering that, due to the influence of complex geological substrate, it is possible to expect increased cobalt contents in the soil and its origin is natural. Given that the highest percentage of Co is bounded to immobile fractions, there is no risk of environmental contamination.





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Magnetic susceptibility (MS)

In this research, Boxplot analysis of the studied elements and magnetic susceptibility were performed and the obtained results are shown in Table 2. Most of the studied elements does not show any statistical anomaly: Zn, Ni, Mn, and V. Their distribution is completely regular and it is assumed that their origin is natural, without any anthropogenic influence.

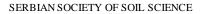
Sample	Outlier
1	Cd, As
2	As
3	-
4	MS
5	MS
6	Cr, Co
7	-
8	-
9	-
10	Cu, Cr
11	-
12	-
13	-
14	Pb, Cd
15	Pb

Table 2. Anomalies of studied elements and magnetic susceptibility (MS)

Also, it is important to mention that all other elements, which show some anomaly, mostly show weaker anomalies (outliers). Majority of these anomalies are most probably of natural origin and anthropogenic influence is obviously not significant in the studied area.

Index of geoaccumulation

The calculated I_{geo} values for Zn, Ni, Cu, Cr, Pb, Cd and As are shown on Figure 3. The majority of investigated soils were in class 0 (background concentration) with the exception of samples 5 and 6 for Cr and 10 and 15 for Pb, which were in class 1 (unpolluted). This indicates that the soils in Vlasina region were practically uncontaminated regarding quoted elements. Negative Igeo values for most soils indicated that there was no contamination and that the origin of elements is mostly from natural processes such as soil and rock weathering.





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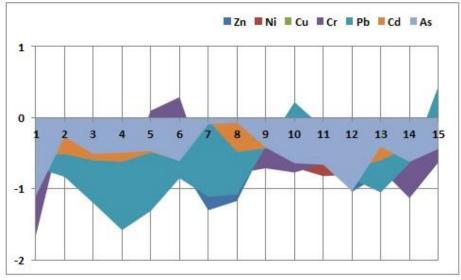


Figure 3. Index of geoaccumulation

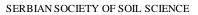
CONCLUSION

In this manuscript are studied the contents of micro- and macroelements in the soils from Vlasina region. Fractionation of Zn, Ni, Cr, Co, As, Cu, Cd, and V showed that the major portion of these elements was in the residual fraction, implying that these elements were strongly bound to the soils. Lead showed a different partitioning pattern than other studied metals, with a large percentage in Fe-Mn oxide fraction, indicating that slight redox potential changes may make significant influence on the removability of Pb.

The results of magnetic susceptibility measurements confirm the hypothesis of the dominant natural (geogenic) origin of the elements from the metamorphic rocks that predominate in this area. The calculated Igeo values indicated that the origin of elements are predominantly natural processes such as soil and rock weathering. Results of our research indicated that studied region is not under significant anthropogenic influence and that Vlasina is a clean area.

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