

Multi-elemental Analysis of Topsoil from Medvednica Mt. (Croatia) by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) after Microwave-assisted Digestion with *Aqua Regia*

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Abstract: The paper deals with multi-elemental analysis of the topsoil (0–10 cm) samples taken on the Medvednica Mountain, which is situated near Zagreb (the capital of Croatia) and some of its parts are ordinarily visited by the citizens and other hikers. During the past years, Medvednica Mt. has attracted the attention of several researchers from various scientific branches, e.g. geologists, biologists, silviculture scientists, etc. The list of the elements that were determined in this research consists of 25 selected metal(loid)s and (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V, and Zn) as well as C(org). The soil samples, which were tested in this study, were grouped according to their acidity. The samples were digested by *aqua regia* employing microwave digestion system. The selected metal(loid)s then were quantified employing ICP-OES technique. Organic carbon was determined by dry ashing method. Measurement quality control was carried out by multi-elemental analysis of the certified reference material for soil GBW07425. The results of the tested soil samples show that the mass fractions of most of the tested elements lie in their usual ranges, but in the samples that were collected in the areas which are anthropogenically influenced the concentrations of some of the elements (e.g. Cr, Ni, Pb, Zn) were elevated.

Keywords: *Aqua regia*, Soil, Metals, Metalloids, ICP-AES, Microwave digestion.

INTRODUCTION

S OIL, especially topsoil, being a part of a forest ecosystem, is the most exposed to the input of harmful substances. Among such substances are trace metal(loid)s. These elements are naturally present in the environment (water, air, rocks and soil), but they also can be introduced to the environment (and subsequently enter soil) due to various human activities, such as industry,^[1,2] traffic,^[3,4] or fertilisers usage.^[5] Some of them are essential nutrients (both for plants and animals), but at elevated levels can become toxic.^[6] Therefore, quantitative analysis of trace elements is usually carried out to determine if the soil is contaminated (or if there is a deficiency of trace elements)

and in order to assess bioavailable fraction of such chemical elements in soil.^[7] It has to be mentioned that there are various definitions of the term “trace elements”; in this context of soil, “trace elements” are considered elements that are present there in concentrations of less than 100 mg/kg or 1000 mg/kg.^[8]

Interactions of a chemical element with soil particles – and its subsequent mobility – depend on the characteristics of the soil as well as on the chemical properties of the chemical element. The main parameters that affect soil sorption and desorption of metal(loid)s are pH and Eh values, the nature of sorbents, a fine granulometric fraction (< 0.02 mm), organic matter content, oxides, and hydroxides (dominantly those of Fe, Mn, and Al), and microorganisms.^[9,10]

In their study, Dinić and co-workers^[11] concluded that the bioavailability of trace elements is mostly related to their content in the so-called pseudo-total fraction.

In the context of a multi-elemental characterization of soil it is worth mentioning that there is a large number of various analytical methods of quantitative analysis of metal(loid)s in such type of samples that has been described in the scientific literature.^[12–14] Most of those methods consist of quantification of the analytes in solutions that are prepared by wet digestion of soil samples, while for the quantification some of the spectrometric techniques (e.g. AES, AAS, ICP-MS) are usually employed. So, the first step of such a research is a selection of a digestion reagent, and this selection is in a connection to scopes of the research. Thus, if one wants to know a total content of an element in soil, he/she should carry out a procedure for total digestion of soil samples, i.e. a digestion reagent should contain hydrofluoric acid (HF).^[15] On the other hand, when a goal of a research is quantification of (toxic) chemical elements in soil that can be taken up by plants (and subsequently enter the food chain), researcher should employ less strong extraction media.^[13] Even though *aqua regia* is a quite strong reagent, it is set as a referent digestion reagent for quantification (and comparison with maximum allowable mass fractions) of hazardous chemical elements in soils in many countries^[16,17] and it was used in this research, too.

This paper describes the research of topsoil at Medvednica Mt. which is situated in the north-western part of the Republic of Croatia, and its southern slopes coincide with the northern parts of Zagreb (Figure 1) with ca. 22 000 ha of forests. The forests are extended from 150 m above sea level to the top (Sljeme – 1 035 m) which is situated in the central part of the massif.^[18] Geologically, Medvednica Mt. is characterised by a complex structure with lot of various lithological units that were formed in a relatively small area. According to Halamić et al.,^[19] under the forest parts, the following lithological units can be found: parametamorphic rocks, orthometamorphic rocks, igneous rocks, Mesozoic clastic rocks, Tertiary clastic rocks, Mesozoic carbonate rocks and Tertiary carbonate rocks. Above such a diverse parent material diverse soils have been identified: Dystric Cambisol, Eutric Cambisol, Luvic planosol, Mollic, Haplic and Leptic Cambisol, Haplic luvisol and Rendzic Leptosol.^[20,21] Complex geological structures with a variety of lithological units and diverse soils together with the relief, are reflected in the diverse forest vegetation.^[18] Such a complex and heterogeneous geological-lithological structure, which interacts with other pedogenetic factors, results in even greater soil heterogeneity. Therefore the processing and interpretation of results can be complicated. To simplify the approach, we decided to use the pH values as a discriminant variable.

Mt. Medvednica draws attention of researchers of various scientific interests: from geographers^[22] to geologists, from agronomy or forestry scientist to (geo)chemists. In the context of research that included various soil (or rock material) testings, there were carried out several investigations during the past decades on Mt. Medvednica. Thus, Jelaska and Nikolić wanted to know if there is a relation between forest plant diversity and chemical characteristics of soil.^[23] Halamić et al. have researched relationship between stream sediment geochemistry and adjacent drainage basin lithology.^[19] Various geological and mineralogical investigations of soils and sediments on Mt. Medvednica were carried out by Gverić and co-workers.^[24,25] Also, Galović and Peh performed a geological research with aim of finding a relation between chemical characteristics of soil and bedrock material; the authors took the samples in six points that are situated in the areas of Mt. Medvednica that were assumed isolated from anthropogenic influence.^[26] Pernar et al. carried out chemical characterization of soil on Mt. Medvednica wanting to know if there is a connection between the distribution of beech-fir forests and basic chemical characteristics of soil (e.g. pH, carbonate content, and the content of biogenic elements C_{org} , N_{total} , P, K, Ca, and Mg).^[18] It is worth mentioning the paper published by Šerić Jelaska and co-workers where they described a bio-geochemical research of the presence of six selected toxic (or potentially toxic) elements in soil as well as in litter and ground beetles on Mt. Medvednica.^[27]

In the context of publications that deal with geochemical characterization of topsoil on Mt. Medvednica, there are a few papers which deserve attention, because they treat determination of toxic elements in soil in the areas around historical mining sites. Jug and co-workers have analyzed presence of mercury (Hg) in soil in the area of “Zrinski mines” and have found that Hg is present in soil in higher concentrations around the mine entrance than in the peripheral areas of the mine.^[28] Perković and co-workers carried out multi-elemental (Pb, Zn, Cd, and Cu) characterization and pollution assessment in the area of “French Mines” and have found that these toxic metals are present in elevated concentrations there. Such testings are important, because – as it has already been mentioned in the text – Mt. Medvednica is an important leisure time destination.^[22] where excursionists practice various activities such as mushroom picking.^[29,30] That implies an importance of carrying out various environmental chemistry testings in order to know the “health status” of the area, especially because some parts of this mountain were being (and still are) anthropogenically influenced.

In this research, the determination of 25 selected chemical elements (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn) and

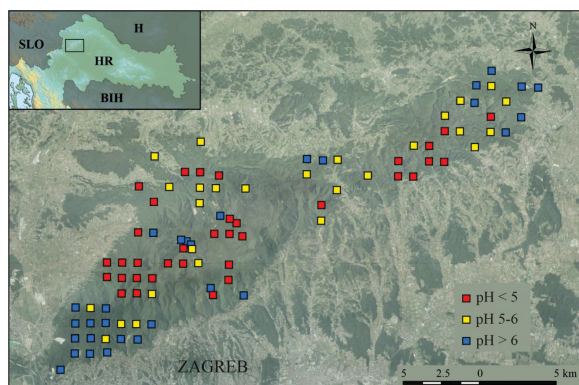


Figure 1. The map indicating sampling points ($N = 93$).

organic carbon (C) in the topsoil samples taken from 93 sample points on the Medvednica Mt. has been carried out. The soil samples were grouped according to their acidities. Quantification of the analytes was done by means of inductively coupled plasma–optical emission spectrometry (ICP-OES) in the digestates that were prepared by microwave-assisted digestion procedure using *aqua regia*. Also, organic carbon content in the tested samples was measured by dry ashing method.

EXPERIMENTAL

Sample Collection and Preparation

The 93 composite topsoil (0–10 cm) samples have been collected in the area of the Medvednica Mt. as it is demonstrated in Figure 1. The procedure of collection of the samples has been previously described by Pernar and co-workers.^[18] For purpose of this research the collected samples were divided into three groups, according to the ranges of their pH values: $\text{pH} < 5$; $5 < \text{pH} < 6$; $\text{pH} > 6$. Such acidity ranges were selected according to the classification which is given by Croatian Directives on the Protection of Agricultural Land from Pollution.^[31]

The preparation (i.e. drying at ambient temperature, grounding, sieving through 0.2 mm \times 0.2 mm sieve, and storing in 60 mL-polypropylene vessels) of the collected soil samples was carried out as it is recommended by ISO 11464:2006.^[32]

Chemicals

High-purity nitric acid (HNO_3 , 65 %, *supra pur*, Fluka) was employed for acidification ($\psi = 1\%$) of all the solutions that were employed in this work.

External calibration of the ICP-spectrometer have been carried out by measurement of a series of the solutions that were prepared by appropriate dilution of the commercially purchased standard multi-elemental solution produced by Carl Roth, Germany, which contains Al, As, Ba,

Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn ($100 \pm 0.2 \text{ mg L}^{-1}$, 5 % v/v HNO_3). For the preparation of a solution for calibration of the major elements, *Multielement standard solution III for ICP* (Ca, Mg, K, Na; 5 % v/v HNO_3), Fluka, Switzerland, has been used too.

Ultrapure water ($0.055 \mu\text{S/cm}$) was employed throughout this work and was being prepared by means of Siemens Water Technologies Ultra Clear™ TWF UV instrument, which is based on reverse osmosis technology and equipped with UV-lamps.

All solutions were stored in polypropylene vessels. All the vessels were pre-washed in nitric acid, 10 % (v/v), (HNO_3 , 65 %, *p.a.*, Carlo Erba Reagenti, Italy) and subsequently, prior to use, were rinsed with ultrapure water.

Nitric acid (HNO_3 , 65 %, *p.a.*, Carlo Erba Reagenti, Italy) and hydrochloric acid (HCl, 37 %, *p.a.*, Carlo Erba Reagenti, Italy) for digestion of the soil sample were used.

Certified reference material (CRM) for soil GBW07425 (also denoted as GSS-11), produced by Institute for Geophysical and Geochemical Exploration, Langfang, China was used for measurement quality control.

Instruments

Microwave digestion system Anton Paar Multiwave 3000, equipped with high-pressure Teflon vessels and the rotor XFS-100 was employed for performing wet digestion of the soil samples ($\sim 0.1000 \text{ g}$ each) with *aqua regia*, which was prepared *in situ* by mixing concentrated HNO_3 (2.5 mL) and concentrated HCl (7.5 mL). 200 °C was selected as the maximum temperature for the digestion process, while maximum power of the microwave radiation was set at 1200 W. The total duration of a digestion cycle was 60 min. Other details of the digestion procedure can be found elsewhere.^[33] After a digestion cycle is completed, each obtained digestate was transferred to polypropylene volumetric flasks (Nalgene, Rochester, NY, USA) and diluted to 100 mL, then subject to centrifugation (Tehtnica centric 322A, 3000 rpm, 20 min) and final 10-fold dilution (1 mL of each sample to 10 mL of the final solution) that was carried out in 20 mL-scintillation vials (Kartell, Italy). The described digestion procedure was adapted from US EPA Method 3051A.^[34] According to the microwave oven producer's instructions as well as adopted practice,^[35] between each two cycles of the samples digestions a cleaning procedure of the Teflon vessels was carried out.^[33]

Quantification of the analytes was carried out by means of the optical emission spectrometer with inductively coupled plasma, ICP-OES (Thermo Fisher iCAP6300 Duo). Recommendations given in US EPA Method 6010D^[36] were adopted. Table 1 reports the most important analytical parameters of the instrumental measurement, while the main characteristics of the instrument used can be found elsewhere.^[33]

Organic carbon content (C_{org}) was determined by dry ashing method using Flash 2000® Combustion NC Soil Analyzer (Thermo Fisher Scientific, Waltham, MA, USA).^[37]

Soil acidity was determined in suspensions that were prepared in a 1:5 (w/v) ratio, were being shaken for 5 minutes and measured with pH-meter Schott, pH-meter CG842 equipped with a glass electrode.

Statistical Analysis

Descriptive statistics: number of samples, mean and standard deviation, minimum and maximum were generated for all analysed variables (elements). Differences between the selected metal(loid)s among three pH-value classes: $pH < 5$; $5 < pH < 6$ and $pH > 6$ were assessed using one-way ANOVA. Individual differences were tested using Tukey's multiple post-hoc test. If the Levene's test for homogeneity of variance appeared to be statistically significant, the non-parametric Kruskal-Wallis H-test was applied and individual differences were tested with the multiple (post-hoc) comparison of average ranks.

Pearson correlation coefficients were determined by correlating pH values, organic carbon content (OC), and metal(loid)s concentrations.

The statistical analyses were carried out using the programs Statistica 14.0.1.25^[38] and Excel.

For all statistical tests, a level of 1 % was considered significant.

RESULTS AND DISCUSSION

Detection Limit of the Method and Control of the Quality of the Measurement

In the scientific literature, there are a lot of methods for calculation of limit-of-detection values described.^[39] The detection limit of the method (MDL) was calculated as a 3-fold standard deviation of the measurements of the blank solutions of the procedure with the dilution factor included as it is a usual practice in soil analysis.^[33] In this work $N = 21$ procedural blanks solutions were measured. Also, the

Table 1. Important analytical parameters used with the ICP-OES spectrometer Thermo Fisher iCAP6300 Duo

Parameters	ICP-AES operating conditions
Instrument	Thermo Fisher iCAP6300 Duo
RF power	1150 W
Auxiliary Ar flow	0.5 L min ⁻¹
Sample Ar flow	0.65 L min ⁻¹
Coolant Ar flow	12 L min ⁻¹
Sample introduction system	<ul style="list-style-type: none"> • auto-sampler CETAC ASX-260 connected by peristaltic pumps • concentric nebulizer with cyclonic spray-chamber
Peristaltic pumps rate	45 rpm
Peristaltic pumps tubes	<ul style="list-style-type: none"> • sample: orange/white • rinsing: white/white
Flush (take-up) time	45 s
Washing time between samples	60 s
Plasma view	Auto view
Maximum measuring time	<ul style="list-style-type: none"> • low wavelengths (160-230 nm): 15 s • high wavelengths (230-847): 5 s
Lines measured (nm)	Al-167.079, As-189.042, Ba-455.403, Be-234.861, Ca-393.366, Cd-214.438, Co-228.616, Cr-205.552, Cu-324.754, Fe-238.204, K-766.490, Li-670.784, Mg-279.553, Mn-257.610, Mo-202.030, Na-589.592, Ni-231.604, Pb-220.353, Sb-217.581, Se-196.090, Sr-407.771, Ti-334.941, Tl-190.856, V-310.230, Zn-213.856
External calibration points	<ul style="list-style-type: none"> • 0 µg/L (all elements) • 1 µg/L (all elements, except Ca, K, Mg, and Na) • 10 µg/L (all elements, except Ca, K, Mg, and Na) • 100 µg/L (all elements, except Ca, K, Mg, and Na) • 2000 µg/L Ca, 200 µg/L K, 400 µg/L Mg, 1000 µg/L Na
Linearity ranges	<ul style="list-style-type: none"> • 0–1000 µg/L (Al, Co, Cu, Li, Pb, Tl) • 0–5000 µg/L (As, Cd, Cr, Mn, Mo, Ni, Se, Ti, V, Zn) • 0–10000 µg/L (B, Be, Fe, Mg, Sb, Sr) • 0–20000 µg/L (Ca, K, Na)
Number of parallel measurements	3
System rinsing solution	Nitric acid, HNO ₃ , <i>supra pur</i> , $\psi = 1\%$

aliquotes of the selected soil certified reference material, were subject to analysis ($N = 16$). Table 2 presents the results of the determination of the MDLs as well as the results obtained for the soil CRM (GBW07425, i.e. GSS-11).

Generally, the results given in Table 2 shows that recovery values are consistent with the fact that *aqua regia* does not completely destroy soil particles (that is why mass fraction values of the elements in soil that are measured in the digestates prepared with *aqua regia* are often called “pseudo-total”). It is known that *aqua regia* provides partial recovery of Al, Ba, Cr, and K due to their binding in silicate core of soil particles or in other insoluble fractions of soil.^[40]

In the literature there are several papers that contain results of analyses of the certified reference material GBW07425, and some of them had been obtained after its digestion with *aqua regia* and subsequent quantification (of a limited number of analytes) by means of ICP-OES. Our results obtained for Co, Cr, Mn, and Ni are in a good agreement with previously published ones.^[41–43] It is worth mentioning that – even though ICP-OES technique is less sensitive and precise than ICP-MS – the recovery values (Table 2) are consistent with the recovery values (%) that had been previously obtained (and published) after the testings by means of ICP-MS of a similar certified reference material for soil.^[44]

Table 2. Method detection limit (MDL) and the results of the soil CRM (GBW07425) analysis

	MDL (mg/kg)	Certified reference material			
		Certified (mg/kg)	Determined ^(a) (mg/kg)	RSD (%)	Recovery (%)
Al	43.9	69300	38550 ± 5170	13	56
As	18.2	7.4	< MDL	n.d.	n.d.
Ba	4.58	634	268 ± 20	8	42
Be	2.53	2.25	< MDL	n.d.	n.d.
Ca	810	9510	7290 ± 602	8	77
Cd	0.925	0.125	< MDL	n.d.	n.d.
Co	2.95	11.6	11.3 ± 1.3	12	97
Cr	1.88	59	52.7 ± 7.5	14	89
Cu	13.9	21.4	17.0 ± 2.3	13	79
Fe	45.3	29450	31400 ± 2260	7	> 100
K	508	22410	9390 ± 1070	11	42
Li	33.8	30	< MDL	n.d.	n.d.
Mg	68.2	7240	6590 ± 484	7	91
Mn	4.15	572	613 ± 42	7	> 100
Mo	2.65	0.6	< MDL	n.d.	n.d.
Na	152	14700	1030 ± 90	9	7
Ni	4.80	25.4	23.5 ± 2.8	12	99
Pb	19.0	24.7	< MDL	n.d.	n.d.
Sb	4.90	1.17	< MDL	n.d.	n.d.
Se	4.30	0.16	< MDL	n.d.	n.d.
Sr	1.66	240	74.1 ± 5.6	8	31
Ti	17.2	3920	2280 ± 230	10	58
Tl	6.85	0.51	< MDL	n.d.	n.d.
V	42.9	86	78.8 ± 5.2	7	92
Zn	22.3	78	52.2 ± 5.0	10	67

^(a) Average ± standard deviation, $N = 16$.

Multi-elemental Characterization of Topsoil Samples from Mt. Medvednica

The topsoil samples tested in this work were divided into three groups, upon their pH values (determined in water suspension). Thus, the ranges of pH values that were chosen for the grouping of the soil samples were as follows: $\text{pH} < 5$; $5 < \text{pH} < 6$; $\text{pH} > 6$, and it correspond to the pH ranges prescribed in the Directives on the Protection of Agricultural Land from Pollution.^[31] Table 3 presents Maximum allowed concentrations (MAC in mg/kg) of toxic elements in agricultural soils according to the cited Directives.^[31] Since in the Republic of Croatia (just as it is a world-wide present phenomenon) there are no directives for allowable mass fraction levels of toxic elements in forest soils, such directive(s) dealing with MACs in agricultural soils are a useful reference for comparing the obtained results with them. The results of the quantification of the selected 25 metal(lloid)s are summarized in Table 4.

The results will be discussed and compared to similar data known from the relevant literature and/or to the values of maximum allowable concentration (MAC) values that are prescribed in the Republic of Croatia by Directives on the Protection of Agricultural Land from Pollution.^[31] As it is read from the title of the cited document, those MACs refer only to soils used in agricultural production, but it gives MAC values only for a limited number of chemical elements that are usually considered toxic or potentially toxic elements when entering a food chain.

During the last ca. 30 years, in the Republic of Croatia, there have consecutively been in use four versions of the Directives on the Protection of Agricultural Land from Pollution (NN 15/1992; NN 32/2010; NN 9/2014; NN 71/2019).^[31,45-47] The first three cited documents dealt with toxic elements MAC values that depend on soil texture, while the recent one distinguishes soils by their acidity. It is worth mentioning that the first document^[45] and the newest one^[31] reports the MAC values for the largest list of the elements (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, and Zn), while the 'middle' two documents^[46,47] referred to a shorter list of potentially toxic metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn); basically, MAC values were not subject to strong variations through the time (the most notable change was that of the highest value for Zn which has been diminished from 300 to a notably lower 200 mg/kg).

Aluminium (Al) was found (Table 4) in the ranges ca. 28800 – 102000 mg/kg (in the soils with $\text{pH} < 5$), 25060 – 71100 mg/kg (in the soils whose pH lies in the range 5 – 6), and 38040 – 71050 mg kg⁻¹ (in the soil samples whose pH is > 6). Such results are in good agreement with the mass fractions that were previously found in soil samples from Medvednica Mt.^[26]

It is well known that *arsenic* (As) is a chemical element that is distributed throughout the environment,

Table 3. Maximum allowed concentrations (MAC in mg/kg) of toxic elements in agricultural soils according to the Directives on the Protection of Agricultural Land from Pollution^[31]

soil pH ranges:	< 5	5 ... 6	> 6
Cd	1	1.5	2
Cr	40	80	120
Cu	60	90	120
Hg	0.5	1	1.5
Ni	30	50	75
Pb	50	100	150
Zn	60	150	200
Mo	15	15	15
As	15	25	30
Co	30	50	60

both in inorganic and organic forms, and pose a serious health risk to humans.^[48] According to Kabata-Pendias and Mukherjee,^[49] in clean soil this element is usually present in mass fractions of ca. 5.0 mg/kg, while Croatian Directives on the Protection of Agricultural Land from Pollution^[31] prescribe MACs for this element in the range 15 – 30 mg/kg, depending on soil acidity. In most of the samples that were tested in this work, it was found that As is present in the mass fractions that are lower than its MDL, i.e. <18.2 mg/kg (Table 4). However, in a certain number of the samples, this element was found in larger mass fractions. Namely, maximum mass fraction values of As were 26.0 mg/kg (in the soil samples with $\text{pH} < 5$), 62.7 mg/kg (in the samples with pH values from 5 to 6), and 137 mg/kg (in the soil samples with $\text{pH} > 6$). Such results correspond to the results obtained by Galović and co-workers.^[50]

In the case of *barium* (Ba), Kabata-Pendias and Mukherjee^[49] report that its mass fraction range in soils is 84 mg/kg – 960 mg/kg, while the lowest mass fraction values are characteristic of organic soils and the highest values are found in loam and clay soils.^[49] In the samples tested herein (Table 4) whose pH values were < 5 , the mean value of the mass fraction was 244 mg/kg (with the maximum value 1897 mg/kg). In the soil samples whose pH values lie in the range 5 – 6, the mean mass fraction value of Ba was 280 mg/kg (while the maximum value was 437 mg/kg). Finally, in the soil samples tested in this work that are characterized with pH values > 6 , the mean mass fraction values of this element was found as 320 mg/kg (and its highest value found in the samples of this group was 885 mg/kg). Such results reveal that in all samples tested in this research, Ba is present in the mass fractions

Table 4. Organic carbon (g/kg) and pseudo-total mass fractions (mg/kg) of the analysed elements found in the topsoil samples taken from Medvednica Mt.

Element	Topsoil samples pH < 5 (pH = 3.82...4.98) N = 35				Topsoil samples pH 5-6 (pH = 5.01...5.98) N = 28				Topsoil samples pH > 6 (pH = 6.05...7.97) N = 30				Statistic test**	Intergroup comparison
	Mean ± Std. dev	Min	Max	Mean ± Std. dev	Min	Max	Mean ± Std. dev	Min	Max	Mean ± Std. dev	Min	Max	p < 0.01	
OC ^(a)	87.2 ± 36.4	37.0	191	71.2 ± 35.0	25.0	167	69.7 ± 27.6	22.3	139	53.70 ± 21.6	22.3	139	n.s. ^(b)	–
Al	56140 ± 15170	28800	101200	46520 ± 8639	25060	71100	53370 ± 8106	38040	71050	53370 ± 8106	38040	71050	K-W ^(c)	(<5; >6) (5-6)
As	–	< 18.2	26.0	–	< 18.2	62.7	–	< 18.2	137	–	< 18.2	137	–	–
Ba	244 ± 303	23.1	1897	280 ± 99	74.5	437	320 ± 132	183	885	320 ± 132	183	885	n.s.	–
Be	< 2.53			< 2.53			< 2.53			< 2.53			–	–
Ca	4145 ± 5820	346	23120	8902 ± 7835	796	35000	24380	5330	90480	24380	5330	90480	K-W	(<5) (5-6) (>6)
Cd	< 0.925			< 0.925			< 0.925			< 0.925			–	–
Co	10.1 ± 9.0	< 2.95	42.9	17.1 ± 7.9	< 2.95	34.5	15.7 ± 9.0	6.55	38.8	15.7 ± 9.0	6.55	38.8	K-W	(<5) (5-6; >6)
Cr	65.4 ± 25.9	24.4	123	70.7 ± 22.5	26.6	116	83.3 ± 16.9	57.7	129	83.3 ± 16.9	57.7	129	K-W	(<5; 5-6) (5-6; >6)
Cu	19.8 ± 14.2	< 13.9	54.7	25.4 ± 14.6	< 13.9	58.7	30.4 ± 27.0	< 13.9	111	30.4 ± 27.0	< 13.9	111	n.s.	–
Fe	37330 ± 18610	13010	81210	40710 ± 12440	24470	69350	41540 ± 10160	24410	62640	41540 ± 10160	24410	62640	n.s.	–
K	9926 ± 5305	1800	20650	11060 ± 5497	2210	21710	14200 ± 4690	6900	28480	14200 ± 4690	6900	28480	ANOVA	(<5; 5-6) (5-6; >6)
Li	36.9 ± 18.4	< 33.8	81.9	34.3 ± 19.1	< 33.8	85.8	36.0 ± 25.3	< 33.8	128	36.0 ± 25.3	< 33.8	128	n.s.	–
Mg	6535 ± 3912	1560	20690	7339 ± 2487	1830	12880	11300 ± 8360	4400	39700	11300 ± 8360	4400	39700	K-W	(<5; 5-6) (5-6; >6)
Mn	557 ± 410	63.6	1700	1509 ± 1025	495	5630	1775 ± 1546	451	7970	1775 ± 1546	451	7970	K-W	(<5) (5-6; >6)
Mo	< 2.65			< 2.65			< 2.65			< 2.65			–	–
Na	678 ± 461	174	2750	893 ± 576	285	3150	821 ± 226	416	1270	821 ± 226	416	1270	n.s.	–
Ni	24.7 ± 11.5	6.34	54.6	34.9 ± 18.1	11.6	94.5	88.9 ± 139	26.6	649	88.9 ± 139	26.6	649	K-W	(<5; 5-6) (>6)
Pb	27.6 ± 17.2	< 19.0	74.9	42.2 ± 18.5	19.8	98.6	50.1 ± 30.7	22.7	182	50.1 ± 30.7	22.7	182	ANOVA	(<5) (5-6; >6)
Sb	< 4.90			< 4.90			< 4.90			< 4.90			–	–
Se	< 4.30	< 4.30	11.2	< 4.30	< 4.30	6.36	< 4.30			< 4.30			–	–
Sr	62.5 ± 39.8	14.3	162	76.7 ± 42.3	28.2	240	85.3 ± 41.0	35.3	196	85.3 ± 41.0	35.3	196	n.s.	–
Ti	2373 ± 1979	474	10650	2936 ± 1608	662	7340	2332 ± 886	786	5272	2332 ± 886	786	5272	n.s.	–
Tl	< 6.85	< 6.85	9.48	< 6.85	< 6.85	11.0	< 6.85			< 6.85			n.s.	–
V	122 ± 48	40.6	259	115 ± 57	36.4	268	104 ± 34.9	51.6	201	104 ± 34.9	51.6	201	n.s.	–
Zn	82.9 ± 33.5	32.0	181	147 ± 113	61.0	660	158 ± 89.6	68.2	425	158 ± 89.6	68.2	425	K-W	(<5) (5-6; >6)

^(a) OC – organic carbon^(b) n.s. – non suitable^(c) K-W – Kruskal-Wallis

that are within the range for the region of central Croatia (where Medvednica Mt. is located) previously given by Halamić and Miko.^[51]

Toxicity of *beryllium* (Be) is a known fact for almost a century,^[52] and its presence in the environment should be monitored. In all soil samples that were tested in this work Be is present in the mass fractions that are lower than its MDL, namely < 2.53 mg/kg (Table 4). Be is in worldwide soils present in the range from 0.48 mg/kg to 3.52 mg/kg,^[49] while the highest mass fractions are found in clay soils.

In the soil samples taken from Medvednica Mt. and tested in this work, *calcium* (Ca) is present in a quite broad range of the mass fractions (Table 4). In the soils whose pH is < 5 Ca is present in the range 346 – 23120 mg/kg (mean: 4145 mg/kg); in the soil samples whose pH values lie in the range from 5 to 6 Ca is present in the range 796 – 35000 mg/kg (mean: 8902 mg/kg); soil samples characterized with pH > 6 contain Ca in the range 5330 – 90480 mg/kg (mean: 24380 mg/kg). Found mass fraction values of Ca in the samples analysed in this work are in accordance with previous research on the soils from Medvednica Mt.^[49]

Cadmium (Cd) is a toxic metal whose toxicity is a very well-known fact and it continuously occupies interest of researchers.^[53] Since in unpolluted soils, Cd is present in very low mass fractions, and therefore its mass concentration in a digestate is quite low, it is usually impossible to quantify it exactly. Because of that, for almost all of the samples tested herein, it was only possible to conclude that Cd is present in the mass fractions that are fewer than its MDL, i.e. < 0.925 mg/kg (Table 4). Cd is one of the trace elements whose maximum allowable concentration (MAC) has been prescribed by various versions of Croatian Directives on the Protection of Agricultural Land from Pollution, both when soils were classified based on their granulometric characteristics^[42] or upon acidity as it is currently the case;^[31] namely 0.5 – 1.0 mg/kg (for powder-loamy soil) and 1.0 – 2.0 mg/kg (for clay soil) according former and 1 – 2 mg/kg according the latter one. The results obtained in this work reveal that the soil samples from Medvednica Mt. were not overloaded with Cd.

Cobalt (Co) is a first-row (3 d) transition element and is less abundant in the Earth's crust and seawater. Also, it takes a part in a coenzyme and in usual conditions of the human environment, it is considered essential trace element for humans and other mammals, but also can become toxic for human health if enter organism in high doses.^[54] According to Kabata-Pendias and Mukherjee,^[49] mass fractions of Co in worldwide un-polluted soils are in the range 4.5 – 12 mg/kg, where the largest values are found in hard loam soils. In this study, it was found that its mass fractions were: from <2.95 mg/kg to 42.9 (with an average of 10.1 mg/kg) in the soils with pH < 5, from < 2.95 mg/kg to 34.5 (with an average of 17.1 mg/kg) in the

soils with pH values in the range of 5 – 6, and from 6.55 to 38.8 mg/kg (with an average of 15.7 mg/kg) in the soils with pH > 6 (Table 4). Such a slight increase of the mass fractions of Co with a decrease in soil acidity is in accordance with the already known chemistry of this element in soils.^[49] The above results are consistent with the results published by Galović et al. (2012).^[50] Finally, current Croatian Directives on the Protection of Agricultural Land from Pollution^[31] set MAC values for Co at 30, 50, and 60 mg/kg depending on soil acidity (pH < 5, pH = 5...6, and pH > 6, respectively). The results obtained in this work suggest that, with the only exception in the group of the samples with pH < 5, forest soil on the Medvednica Mt. is not overloaded with Co.

Chromium (Cr) is one of toxic metals that pose a risk for human health as well as for the environment in general.^[55] According to Directives on the Protection of Agricultural Land from Pollution,^[31] MAC values for Cr, depending on soil acidity, are set in the range of 40 mg/kg to 120 mg/kg. In the samples tested in this work (Table 4) and whose acidity was characterized by pH < 5 the mean value of the mass fraction of Cr was found to be 65.4 mg/kg, but in some samples there were found values that were higher – even up to 123 mg/kg. Then, in the less acidic soil samples (i.e. 5 < pH < 6) the mean mass fraction of this metal was found as 70.7 mg/kg, but in several samples its mass fractions notably exceeded this value and amount as high as 116 mg/kg. Finally, in the samples with pH > 6, the average Cr mass fraction was 83.3 mg/kg, but the highest value found in the samples of this group was 129 mg/kg. The above results are consistent with the results from Halamić and Miko.^[51]

In the Croatian Directives on the Protection of Agricultural Land from Pollution,^[31] the MAC values for *copper* (Cu) in soil, depending on soil acidity, are set in the range from 60 mg/kg to 120 mg/kg. In the samples that were tested in this work (Table 4), which belongs to the group characterized by pH < 5, the maximum value was 54.7 mg/kg (the average one was 19.8 mg/kg). A similar thing is found for the less acidic group of samples (5 < pH < 6): the maximum mass fraction of Cu was 58.7 mg/kg (the mean value was 25.4 mg/kg). On the other hand, the samples whose pH is > 6 showed a larger pseudo-total content of Cu. Thus, the average mass fraction value was 30.4 mg/kg, and the largest one was 111 mg/kg. This trend can be explained by the dependence of Cu solubility with the acidity of soil, where solubility of this element decreases with an increase of the pH value of soil^[49] and a conclusion that the soils whose samples were tested in this research are not overloaded with Cu can be drawn.

Iron (Fe) is one of the highly present elements in the lithosphere, and its average content in the Earth's crust amounts to 5 %, ^[49] while in the soil it is in a range from 0.1 % to 10 %.^[56] In all the samples tested in this work, the

mass fraction values found for this element lie in this range, namely it was between 1.3 and 8.1 % (Table 4), similar to in research of Halamić and Miko (2009).^[51]

Potassium (K) is one of the elements whose presence in the soils is not considered a critical one. Generally, in the samples that were tested in this work, the pseudo-total content of K was found in the range between 0.2 % and 2.9 % (Table 4). Mass fraction values of K that were found in the samples analysed herein are in accordance with previous research on the soils from Medvednica Mt.^[26]

Lithium (Li) is one of the less abundant metals in the Earth's crust. It is possible to find it in relatively large quantities in volcanic and sedimentary rocks. Generally, the mass fraction range of Li in soil is 4.2 mg/kg – 14.8 mg/kg.^[49] In the soil samples taken from Medvednica Mt. and tested in this work (Table 4) Li was found in the ranges of mass fractions as follows: < 33.8 – 81.9 mg/kg with the mean value of 36.9 mg/kg (in the samples with pH < 5), < 33.8 – 85.8 mg/kg with the mean value of 34.3 mg/kg (in the samples with pH from 5 to 6), and < 33.8 – 128 mg/kg with the mean value of 36.0 mg/kg (in the samples with pH > 6).

One of the major elements is also *magnesium* (Mg) and its presence, generally, is not critical in terms of soil overburden.^[57] In the soil samples tested in this work (Table 4) Mg was found in the ranges of mass fractions as follows: 1560 – 20690 mg/kg with the mean value of 6535 mg/kg (in the samples with pH < 5), 1830 – 12880 mg/kg with the mean value of 7339 mg/kg (in the samples with pH from 5 to 6), and 4400 – 39700 mg/kg with the mean value of 11300 mg/kg (in the samples with pH > 6). Found mass fraction values of Mg in the samples analysed in this work are in accordance with previous research on the soils from Medvednica Mt.^[26]

Manganese (Mn) is an element that is straight connected to Fe in the context of geochemical processes. In soils, Mn is present in a broad range of mass fractions: from 10 mg/kg to a value of even 9000 mg/kg.^[49] The average mass fraction value of Mn determined in the soil samples with pH < 5 that were analysed in this work was 557 mg/kg (with a maximum value of 1700 mg/kg). Furthermore, in the samples whose pH values are in the range 5 – 6 an average pseudo-total content of Mn was 1509 mg/kg (and a relative maximum value was 5630 mg/kg), while in the samples with pH > 6, the average pseudo-total content of Mn was 1775 mg/kg (with a maximum of 7970 mg/kg). These results (Table 4) are in good agreement with the results of previous testing of this metal in clean forest soils from Medvednica Mt.^[27]

In the context of quantification of *molybdenum* (Mo) in the soil samples that were investigated in this work (Table 4), it is only possible to conclude that this element is present in mass fractions that are fewer than its MDL, hence < 2.65 mg/kg. It is known that Mo in the soils

worldwide is present in the range of 0.1 – 7 mg/kg.^[49] Moreover, Croatian Directives on the Protection of Agricultural Land from Pollution^[31] set MAC for Mo at 15 mg/kg with no dependence on soil acidity. So, it can be concluded that the soil samples tested in this work are not overloaded with this metal.

Major element *sodium* (Na) in the soil samples from Medvednica Mt. and tested in this research (Table 4) was found in the ranges of mass fractions as follows: 174 – 2750 mg/kg with the mean value of 678 mg/kg (in the samples with pH < 5), 285 – 3150 mg/kg with the mean value of 893 mg/kg (in the samples with pH from 5 to 6), and 416 – 1270 mg/kg with the mean value of 821 mg/kg (in the samples with pH > 6). Found mass fraction values of Na in the samples analysed in this work are in accordance with previous research on the soils from Medvednica Mt.^[26]

Nickel (Ni) is a toxic metal which is considered to pose a health risk.^[53] In Croatia, its MAC is regulated by Directives on the Protection of Agricultural Land from Pollution^[31] depending on soil acidity it amounts from 30 to 75 mg/kg. In the samples of soils from Medvednica Mt. (Table 4) whose acidity was characterized by pH < 5 the pseudo-total quantity of Ni was determined in the range 6.34 – 54.6 mg/kg, with a mean of 24.7 mg/kg. In the samples whose pH values were from 5 to 6, the average pseudo-total mass fraction of this element was 34.9 mg/kg while the range was 11.6 – 94.5 mg/kg. Finally, in the soil samples with pH > 6, the mean value was 88.9 mg/kg, but the range of the mass fraction values of the samples from this group were from 26.6 mg/kg to even 649 mg/kg.

Lead (Pb) is an element that is dispersed into the environment by various human activities.^[33] Therefore, its allowable presence in the Environment is regulated by various regulations worldwide. Thus, according to Croatian Directives on the Protection of Agricultural Land from Pollution,^[31] MAC of Pb in soils, depending on soil acidity, ranges from 50 mg/kg to 150 mg/kg. In almost all of the soils that were analysed in this work (Table 4), Pb was found in concentrations that were lower than the above-cited MAC. More precisely speaking, in the samples which were characterized by the acidity of pH < 5 an average pseudo-total content of this element was 27.6 mg/kg (the range was < 19.0 – 74.9 mg/kg), soil samples with pH from 5 to 6 averagely contained Pb 42.2 mg/kg (the range was 19.8 – 98.6 mg/kg). Finally, in the soil samples with pH > 6, the mean value was 50.1 mg/kg, but the mass fraction values of the samples from this group were from 22.7 mg/kg to 182 mg/kg. The results obtained for clean forest soils are from previous research made on Medvednica Mt.^[27] Still, a possible relation of some higher values of Pb, which were found in some of the sampling points, to an influence of Pb-Ag-Zn abandoned mines^[28,58] should not be neglected.

Taking into consideration that *antimony* (Sb) is in soil usually present in the range 0.05 mg/kg – 4.0 mg/kg,^[49] it is obvious that the MDL that was obtained in this research (4.9 mg/kg) was too high to quantify it exactly in the clean soil samples. Therefore, for almost all samples that were tested in this work (Table 4), it was only possible to conclude that contain Sb in mass fractions that are <4.9 mg/kg. Still, there were a few samples that showed an overload with this element, namely the pseudo-total concentration of Sb which reached a value of 28.0 mg/kg.

Selenium (Se) is also one of the chemical elements for whose quantification in clean soils ICP-OES technique is not a favourable one. In this work, the MDL for Se was 4.3 mg/kg. In almost all the samples analysed in this work, Se was present in mass fractions that are lower than MDL (Table 4), while only in two samples, this element was quantified in slightly higher mass fractions, namely 6.36 mg/kg and 11.2 mg/kg.

Worldwide soil content of *strontium* (Sr) is from 250 mg/kg to 1000 mg/kg. Its content in soils depends on soil texture, climate zone, and anthropogenic influence.^[49] In the soil samples taken on Medvednica Mt. and analysed in this work (Table 4), pseudo-total mass fractions of this element do not exceed the lower edge of the above-mentioned range. In the context of the three groups of the soil samples that were constituted upon their acidity, it is to be mentioned that the average mass fraction of Sr was found as follows: 62.5 mg/kg (pH < 5), 76.7 mg/kg (pH 5...6), and 85.3 mg/kg (pH > 6).

According to the literature data, *titanium* (Ti) is one of the most abundant elements in soils. Its content lies in a range from 0.02 % to 2.4 %. In the samples tested in this work (Table 4) Ti is present in the range of ca. 0.05 % – 1.1 % similar to those published by Galović et al.^[50] Regarding acidity of the samples tested in this work, in the samples with pH < 5 Ti is present in the range 0.047 – 1.07 % (with an average of 0.24 %); samples with pH 5...6 contain Ti in the range 0.066 – 0.73 % (with an average of 0.29 %); finally, less acidic samples whose pH is > 6 this element contain in the range 0.079 – 0.53 % (with an average value of 0.23 %).

Thallium (Tl) was determined with a relatively high MDL (6.9 mg/kg) in this research. For that reason, in the majority of the samples (Table 4) it was not possible to quantify exactly this element. Still, in some of the samples, it was found that the mass fraction of Tl reached values of even 9.48 mg/kg (in the samples with pH < 5), 11.0 mg/kg (in the samples with pH from 5 to 6), and 14.3 mg/kg (in the soil samples with pH > 6). It is known that in uncontaminated soils Tl is present in the range of 0.01 – 2.8 mg/kg.^[49] In the context of these data, it should be concluded that some of the samples tested in this work are overloaded with this element.

According to literature data, in worldwide soils *vanadium* (V) is present in the range from 10 mg/kg to 500 mg/kg.^[49] In the soil samples taken from Medvednica Mt. in the context of this research, average mass fraction values of this element were found as follows: 122 mg/kg (with a range of 40.6 – 259.1 mg/kg) in the samples with pH < 5; 115 mg/kg (with a range of 36.4 – 268 mg/kg) in the samples with pH from 5 to 6; 104 mg/kg (with a range of 51.6 – 201 mg/kg) in the samples with pH > 6 (Table 4).

Zinc (Zn) is one of elements whose MACs are regulated by Croatian Directives on the Protection of Agricultural Land from Pollution: depending on soil acidity, MAC for this element lies in the range 60 – 200 mg/kg.^[31] In the soil samples taken from Medvednica Mt. and analysed in this work (Table 4) whose pH is < 5, there was found an average mass fraction value of Zn 82.9 mg/kg, and the range was 32.0 – 181 mg/kg. Then, in less acidic samples (pH 5...6) Zn was averagely present 147 mg/kg, while the range was 61.0 – 660 mg/kg (in several samples from this group, a Zn content notably exceeded the MAC). Finally, in the group of the least acidic samples (pH > 6) that were tested in this research, it was found that the Zn average mass fraction was 158 mg/kg, and the respective range was 68.2 – 425 mg/kg and it reveals that also in several samples from this group, the mass fraction of this metal exceeded the above-mentioned MAC value. Finally, it is to be mentioned that there is a possible relation of some higher values of Zn, found in some of the sampling points, to an influence of Pb-Ag-Zn abandoned mines.^[28,58]

Relation Between pH Values, OC, and Major and Trace Element Concentrations

In this study, Pearson's correlation was applied to determine the correlation between pH values, OC, and the selected elements' concentrations. The correlation matrix for the pH value, OC concentration, and metal(loid)s concentrations from the topsoil samples from Medvednica Mt. are presented in Table 5.

Soils with a pH < 5 are predominantly associated with parametamorphic and orthometamorphic rocks, with Dystric Cambisol being the predominant soil type. Soils with a pH in a range 5...6 have a more even distribution across different lithologic units and include a variety of soil types, while soils with a pH > 6 are mainly developed on Mesozoic and Tertiary carbonate rocks, where the predominant soil types are Luvic Planosol and Leptic Cambisol.

The pH value moderately positively correlates with Ca and Mg concentrations, but it weakly positively correlates with Co, Cr, Mn, Pb, Sr, and Zn concentrations. This is consistent with the results of one-way ANOVA and the Kruskal-Wallis test (Table 4) in which three groups of elements are separated according to the categories of pH values: Group 1 in which all 3 pH value categories are

Table 5. Correlation matrix for pH values, OC concentrations and metal(loid)s in topsoil samples ($N = 93$). Bold indicate numbers that are significantly correlated ($p < 0.01$)

	pH	OC	Al	Ba	Ca	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Ti	Tl	V
pH																				
OC	-0.28																			
Al	-0.08	0.05																		
Ba	0.13	-0.17	0.12																	
Ca	0.67	0.03	-0.10	-0.11																
Co	0.34	-0.09	0.06	-0.10	0.33															
Cr	0.36	-0.05	0.43	0.05	0.28	0.54														
Cu	0.25	0.03	0.23	0.19	0.33	0.42	0.39													
Fe	0.16	0.07	0.30	-0.09	0.25	0.75	0.51	0.44												
K	0.29	-0.32	0.51	0.33	-0.07	-0.11	0.29	0.15	-0.06											
Li	0.02	0.01	0.48	0.15	-0.04	0.21	0.27	0.22	0.26	0.36										
Mg	0.51	-0.17	0.09	-0.08	0.73	0.51	0.39	0.38	0.48	0.05	0.14									
Mn	0.37	-0.06	0.06	0.31	0.10	0.47	0.22	0.53	0.34	0.21	0.28	0.16								
Na	0.11	-0.18	0.51	0.25	-0.08	0.01	0.26	0.16	-0.02	0.67	0.26	0.05	0.16							
Ni	0.29	-0.07	0.15	0.12	0.06	0.16	0.22	0.19	0.16	0.21	0.17	0.01	0.23	0.08						
Pb	0.34	0.15	0.20	0.08	0.31	0.47	0.39	0.60	0.38	0.26	0.26	0.37	0.46	0.17	0.22					
Sr	0.32	-0.05	0.04	-0.11	0.58	0.57	0.53	0.31	0.43	-0.07	-0.03	0.49	0.09	-0.02	0.07	0.35				
Ti	0.04	0.19	-0.06	-0.28	0.34	0.73	0.40	0.15	0.63	-0.42	0.04	0.45	0.07	-0.20	0.03	0.31	0.65			
Tl	0.08	0.20	-0.05	-0.03	0.01	-0.08	0.09	0.03	-0.10	-0.01	-0.14	-0.03	-0.04	-0.01	-0.02	-0.04	-0.09	-0.08		
V	-0.11	0.12	0.26	-0.01	0.09	0.60	0.33	0.38	0.71	-0.27	0.24	0.29	0.29	-0.16	0.00	0.15	0.33	0.56	-0.10	
Zn	0.32	0.00	0.11	0.16	0.16	0.35	0.35	0.30	0.33	0.18	0.23	0.27	0.33	0.11	0.22	0.40	0.23	0.22	-0.01	0.14

significantly different: Ca; Group 2 in which category $pH < 5$ is significantly lower than the categories $5 < pH < 6$ and $pH > 6$: Co, Mn, Pb, Zn, and Group 3 in which categories of $pH < 5$ and $pH > 6$ differ significantly: Cr, K ($r < 0.3$), Mg.

The concentrations of Ca as well as Mg, which are primarily related to the carbonate substrate (and the high positive correlation with each other, $r = 0.73$) are logically positively related to the pH value, similar to in study published by Bakšić et al.^[59]

Although ANOVA did not show a significant difference between Sr concentrations of the different soil pH values categories, Pearson's correlation showed that there was a weak positive correlation between Sr and pH values. Ca and Sr^[19] noted as a factor of Tertiary carbonate rocks.

Generally, correlation between pH and an element concentration reflects chemical properties of the element in a way that ions of metals that are known to form coordinative bonds in less acidic (or neutral to basic) media show more positive correlation to pH.

In general, OC content in the topsoil of Medvednica

decreases with increasing pH value (negative correlation – Table 5). Given the fact that there are no expected (positive) significant correlations between the concentration of OC and elements (except for K, which is negative), it can be assumed that the trend of increasing concentrations of elements is dominantly influenced by the composition of the parent material. In an earlier study^[60] it was found that soils over metamorphic, igneous, and clastic rocks have a quite similar particle size distribution; therefore, the most represented textural class is “silty to clay loam”.^[60] Soils over carbonate rocks differ in a significantly higher proportion of clay fraction with textural class ranges from silty clay to clay. It is well known that fine granulometric fraction – clay fraction positively affects the concentration of elements.^[9,10]

Element pairs such as Ca-Mg ($r = 0.73$), Fe-Co ($r = 0.75$), Fe-V ($r = 0.71$) and Co-Ti ($r = 0.73$) (Table 5) showed a high positive correlation. Moderate positive correlation was recorded between some Lithophile elements such as Al-K, Al-Na, Ca-Sr, Cr-Sr, K-Na, Sr-Ti, Ti-V and between Lithophile-Siderophile elements such as Cr-Co, Mg-Co, Sr-Co, V-Co, Cr-Fe and Ti-Fe (Table 5).

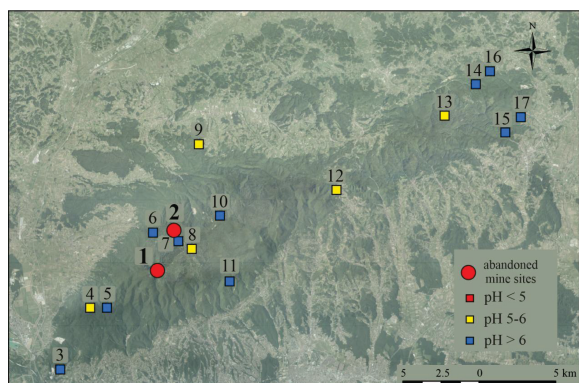


Figure 2. The sampling points on the Mt. Medvednica area with contamination factors $CF > 3$. Locations 1 and 2 correspond to the abandoned mine sites (the CF values for these two sites were calculated according to the previously published results.^[60,62]

Contamination Factors (CFs) – Assessment of Contamination of the Topsoil

In order to make further quantification of the degree of contamination of the tested topsoil with toxic elements, values of the contamination factor (CF) – as one of the commonly used indicator – have been calculated. Figure 2 displays the locations which are characterized with $CF > 3$, putting into focus the two highest categories according Papadimou et al.^[61] These two categories are: 'considerable contamination degree' ($3 \leq CF < 6$) and 'very high contamination degree' ($CF \geq 6$) (Table 6). The CF values for toxic elements in the topsoil layer was calculated using the following formula: $CF = C_s / C_{RefS}$, where C_s represents the total concentration of toxic elements in the topsoil, while C_{RefS} refers to the reference background concentration values that are published at Galović et al. as "Medvednica Mt mean value").^[50]

The CF values reveal that the most contaminated soil on the Mt. Medvednica is situated in the area of the abandoned mines (the location 1 represents "Zrinski mine", while and point 2 stands for "French mine"), whose concentrations are taken from previously published results,^[60,62] while the topsoil samples that were taken from forests and tested in this work show CFs values that are far below than those that originate from the historical mines areas. The points that show $CF \geq 6$, namely, points 16 and 17 are situated near a local road and a quarry, while point 7 is situated in the wider area of the abandoned "French mine".

CONCLUSION REMARKS

Pseudo-total mass fractions of 25 chemical elements (major elements and trace metal(loid)s) as well as organic carbon was analysed in this work.

Table 6. Sampling points in the Medvednica area with *considerable contamination degree* ($CF = 3...6$) and *very high contamination degree* ($CF \geq 6$). The sampling point labels correspond to those given in Figure 2.

Sampling points	As	Cd	Ni	Pb	Zn
1		6.5		232.5	10.7
2				96.2	
3					5.4
4					8.3
5				3.2	
6					4.0
7				7.3	
8				3.4	3.3
9					3.2
10	6.4			3.3	
11					3.1
12				3.9	
13	3.3				
14				3.4	3.8
15	7.2		9.3	3.7	4.5
16			11.2		
17	5.0				

The pseudo-total content of the elements: As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, and Zn increases with increasing pH value, but significant correlation was found only between pH value and Ca, Cr, Mg, Mn, Pb, Sr, and Zn.

Pseudo-total mass fraction values that have been found for the elements Cd, Co, Cu, and Mo – whose maximum allowed concentrations (MAC) are prescribed by Croatian national directives (NN 71/2019)^[31] – are lower than their MACs in all the tested samples. On the other hand, Cr, Ni, Pb, Zn, and As in some samples were found in concentrations that are higher than the prescribed MAC values. The sampling points where these elevated concentrations were found they are situated in the vicinities of anthropogenically influenced areas (e.g. villages, hamlets, roads). Also, in some cases, somewhat of an influence of abandoned mines should not be neglected.

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