Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 89 (12) 1629–1645 (2024)
JSCS–5811
Original scientific paper
Published 11 November, 2024

Assessment of the concentration of toxic metals (aluminum, cadmium and manganese) in the soil and evergreen plant species at the Sastavci surface mine and its vicinity

MILICA TOMOVIĆ[1]*, JOVANA GRAHOVAC[2], JELENA DODIĆ[2], MARIJA RADOJKOVIĆ[2#], NATAŠA ELEZOVIĆ[1] and KRSTIMIR PANTIĆ[1]

[1]University of Priština in Kosovska Mitrovica, Faculty of Technical Sciences, Knjaza Miloša 7, 38220 Kosovska Mitrovica and [2]Faculty of Technology Novi Sad, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

(Received 1 April, revised 30 April, accepted 18 June 2024)

Abstract: The study aims to determine the concentration of Al^{3+}, Cd^{2+} and Mn^{2+} in the soil and parts of evergreen plant species – juniper and white pine – at the surface mine Sastavci (Badanj) and its vicinity in order to determine the possibility of using evergreen plants as an ecological indicator or for phytoremediation. Globally, as a result of various anthropogenic activities such as traffic, agricultural activities, waste incineration, industrial production, mining, *etc*., it represents a serious problem leading to pollution with toxic and potentially toxic metal cations. One of the more innovative techniques used for the remediation of mining areas is phytoremediation. By applying phytoremediation, certain plant species in polluted areas have the ability to act as accumulators or hyperaccumulators, absorbing toxic metals from the soil through the plant roots and transporting them to the upper parts. This research has been conducted to determine the concentration of Al^{3+}, Cd^{2+} and Mn^{2+} at the surface mine itself and its surroundings, as well as to monitor the distribution of metal cations in the system of roots, branches, needles, and fruits of the evergreen plant species – white pine and juniper. The results showed that the sampled soil was contaminated with Cd in zones I and II for both plant species, since the concentrations exceeded the limit values, while the concentration of Cd in zone III, as well as in the control zone was below the determination limits for both plant species. The concentration of Mn in the soil from the white pine and juniper zone was above the world average in all three zones, as well as in the control zone itself. The soil was most enriched with the analysed elements in the surface mine of zonec I and II. According to the analysis of elements in the parts of white pine, roots, branches, needles and fruits, the highest concentration of Al was detected in the root in zone I, while the lowest concentration was recorded in the fruit

* Corresponding author. E-mail: milica.tomovic@pr.ac.rs
# Serbian Chemical Society member.
https://doi.org/10.2298/JSC240401063T

(cones) in the control zone, an increased concentration of Cd was recorded in the branches in zones I and II, and the highest concentration of Mn was recorded in needles in zone II. The highest Al concentration was recorded in the juniper root in zone I and the lowest in the juniper fruit in the control zone, the Cd concentration was the highest in the juniper root zone I, and the lowest in the juniper fruit and the highest Mn concentration was recorded in the juniper needles in zone I. Based on the obtained values of the coefficient of biological absorption, it can be concluded that white pine is not suitable for phytoextraction or phytostabilization of the tested elements. The analysis of biological factors (bioconcentration, translocation and bioaccumulation factor) indicated a possible usage of juniper in phytoextraction for Cd only.

Keywords: trace elements; ICP-OES; ICP-MS; juniper; white pine; phytoremediation.

INTRODUCTION

The quantity of heavy metals originating from natural sources is almost negligible, when compared to the quantity of heavy metals generated as a result of anthropogenic activities. Trace elements – heavy metals, represent pollutants of significant concern due to their potentially harmful effects on the environment.[1–3] Long-term and excessive intake of these elements can burden the environment, as they enter and circulate within biogeochemical cycles. Due to their inability to degrade, these elements accumulate through the food chain, and depending on their concentration and toxicity, they pose a risk to human health as well as to ecosystems.[3–5] Heavy metals cannot be degraded through physical or biological processes, which makes them more persistent in soil. These metals can remain in the soil for extended periods, accumulating and causing harmful effects on ecosystems and human health.[6] For the removal of heavy metals from contaminated areas, people employ various techniques. These techniques can often be combined, depending on the specific contamination conditions and the goals of remediation. Phytoremediation has proven to be one of the best solutions, as technological methods have shown to be ineffective and uneconomical.[7] Phytoremediation is an ecological method that applies plant species to remove or reduce the contamination of heavy metals from soil. The plant species used in phytoremediation have the ability to accumulate heavy metals from the soil through processes such as phytoextraction or phytostabilization.[8] Different plant species have varying abilities to absorb pollutants from the soil, including heavy metals. These diverse capabilities of plants to absorb pollutants play a crucial role in preserving the environment from the harmful effects of pollutants.[9,10] Some heavy metals pose a significant problem worldwide due to their toxicity and ability to induce cytotoxic and mutagenic effects on all living organisms, including plants.[11–17] Some plant species have developed tolerance and resistance to high concentrations of heavy metals. They can absorb and accumulate large amounts of heavy metals in their tissues without significant negative effects on their growth and development.[18–20] For the subject of investigation in this study, two evergreen plant species were selected - juniper and white pine. Juniper belongs to the group of long-lived plant species, as its needle-like leaves function throughout the year. Previous research has shown that juniper is a promising candidate for phytoremediation.[21] The use of juniper as a plant for phytoremediation and the restoration of contaminated soil has proven to be promising. Juniper possesses specific properties of heavy metal accumulation, meaning it can uptake and concentrate large amounts of these metals from the environment into its tissues. Juniper is also known for its rapid biomass growth, which is an additional advantage in its use for phytoremediation.[22] Juniper is ideal for phytostabilization of contaminated soil due to its deep root system, high tolerance to heavy metals, and ability to grow in nutrient-poor soils.[23] The second evergreen plant species examined in this study is the white pine. White pine is widely distributed and often used to monitor changes in the environment due to its extensive prevalence compared to its relatives.[24] White pine is a conifer that thrives on various types of soil, including dry, moist, rocky, and sandy soils, as well as marshy areas. It grows in diverse conditions, ranging from fertile to dry and infertile habitats.[25,26] The needles of the white pine have the ability to absorb and retain heavy metal cations from the surrounding environment, making them important indicators of environmental conditions. By studying the content of heavy metals in the needles of the white pine, we can obtain information about the degree of pollution and the quality of the environment. White pine is known for its efficient abilities in absorbing heavy metals from the soil.[27,28] Establishing surface mines represents one of the greatest sources of changes in the natural environment. This can lead to catastrophic consequences, including the release of heavy metals into the environment.[29–31] The aim of the research was to evaluate the content of elements (Al^{3+}, Cd^{2+} and Mn^{2+}) in soil and parts of white pine and juniper (root, branches, needles and fruits) in order to study their potential use in phytoremediation and the possibility of using evergreen plants as an ecological indicator.

EXPERIMENTAL

Description of the investigated area

Since the 1920s, the first explorations of lead-zinc ore deposits began in the vicinity of Raška. Mining has a long history in this part of Serbia. In the medieval period, mining was one of the most significant economic activities in the territory of present-day Serbia, and Mount Kopaonik was known for its rich mineral deposits. The lead–zinc ore deposit of Sastavci (Badanj) is located at the source of the Radišićka River, on the slopes of Mount Karač (916 m) and Šanac (1098 m), in an altitude zone ranging from 720 to 905 m above sea level. The estimates determine that this deposit contains approximately 364,000 tons of ore with an average content of 2.05 % lead and 5.59 % zinc. On the mine site, a high content of Au was discovered, but the content of As was also high, leading to the cessation of exploitation. Although mining is no longer a dominant industry in this region, one of the problems that remains as a consequence of exploitation is tailings, an unusable material that remains as residual toxic waste after ore processing. Mine tailings can contain various harmful substances and metals that pose a potential threat to the surrounding soil and water systems. While surface mines lead to soil degradation, they often contain heavy metal cations that accumulate through the food chain, causing toxicity and posing a serious threat to animals and human populations.

Sampling of soil and plant material

White pine and juniper, which were used for the purpose of this research, were selected for sampling based on several criteria. These plant species are perennial and are adapted to different living conditions, which allows them to survive and thrive. When it comes to long-term anthropogenic pollution, these plants can provide some useful information since they are perennial plants and have the ability to accumulate pollutants over time. This means that the presence of certain toxic elements in white pine and juniper tissues may indicate the presence or history of pollution in the area. White pine and juniper have an important role in human nutrition and medicine. If white pine and juniper grow in polluted areas, there is a risk that toxic elements accumulate in their tissues. If these plants are used for food or medicinal purposes, there is a possibility that toxic elements can be transferred to the human body, which can be harmful to health.

Description of the zones and places of sampling of soil and plant material for the Sastavci (Badanj) surface mine and its vicinity

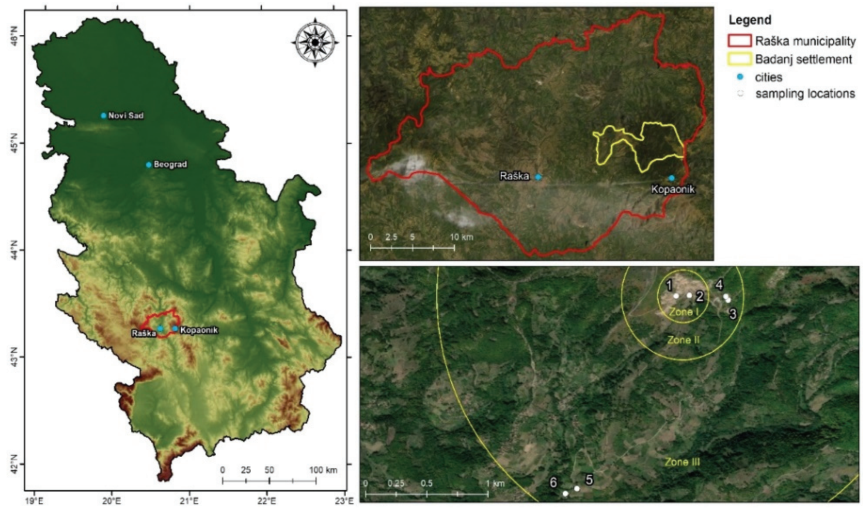


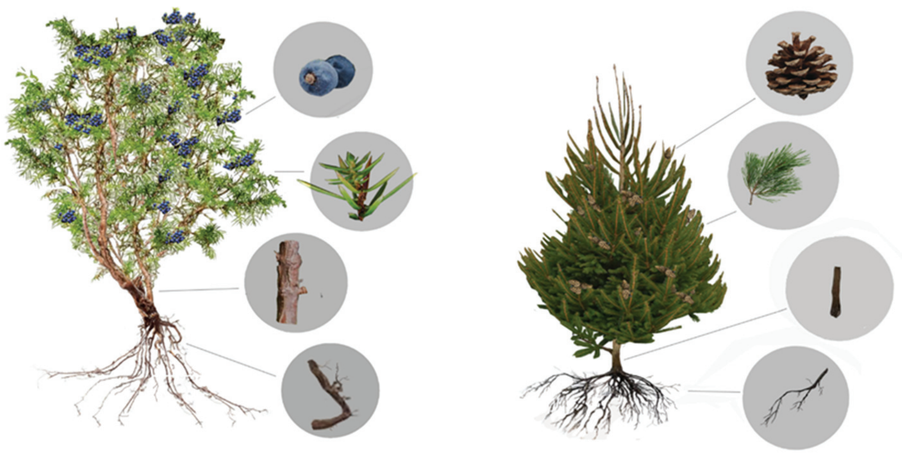
Fig. 1. Map of the surveyed area with sampling locations of soil and plant material by zones of the Sastavci (Badanj) surface mine (points 1, 3 and 5 are samples of white pine; points 2, 4 and 6 are samples of juniper).

The sampling of soil and plant material was conducted in three different zones (6 sampling sites) with varying degrees of contamination. The sampling locations were selected based on the assumption that the concentration of metal cations would decrease with the distance from Sastavci (Badanj) surface mine. For soil sampling, a stainless-steel probe was used, and soil samples were taken from a depth of 20 cm, where the highest concentration of roots was observed. After the composite samples were collected, the removal of leaves, stones, twigs, and other visible impurities was performed. The sampling locations of plant material and soil (Fig.

1) are divided into different sampling zones. Samples were collected at the primary source of pollution, *i.e.*, at the surface mine, Zone I. This part represents the most polluted area. The samples were collected in the immediate vicinity of the surface mine, representing a secondary source of pollution, Zone II. A lower degree of pollution is expected in this zone, when compared to Zone I. Samples collected in the tertiary zone are located at a distance of 1,700 m from the surface mine, Zone III. Here, the degree of pollution is expected to be lower compared to the previous two zones. The control sampling zone is located 5 km straight-line distance from the Pb-Zn surface mine near the village of Kneževići. This zone is considered uncontaminated.

Description of the sampling procedure of plant material and soil

The indigenous plant species used for analysis were in good condition, without the presence of visible signs of disease or pests, which was important in order to ensure quality and representative samples for analysis. These precise measures were taken to ensure maximum accumulation of metal cations in the selected plant species and to obtain accurate analysis results. Soil samples were collected at a depth of 20 cm and weighed approximately 500 g. At the same depth, roots up to 1 cm in diameter were sampled. For juniper, samples were collected at a height of 50–70 cm, and for white pine at a height of approximately 1.50–1.80 cm. Samples were collected from different sides of each plant and weighed 4–5 g. When it comes to sampling mature juniper berries and pine cones, those with similar shape and colour were selected. Samples for both plant species were collected from the same branches. Sampling procedure was applied according to the given protocol, whereby soil and various parts of plants (roots, branches, needles and fruits) were prepared as composite samples (Fig. 2).[32] This sampling methodology was used to ensure the representativeness of samples for the detection of concentrations of metal cations in soil and various parts of plants.



a) b)

Fig. 2. Sampling scheme (roots, branches, needles and (fruits) cones); a) juniper and b) white pine.

Materials and methods

For the investigation of this locality and the investigation of the persistence of toxic elements in the soil and parts of white pine and juniper, sampling was carried out that was adapted to the morphology of the terrain and wild plant species, whereby a total of 6 soil samples and 24 samples, parts of white pine and juniper (roots, branches, needles and (fruits) cones) in three different zones. Microwave dissolution of soil and plant material samples was performed at the Faculty of Chemistry in Belgrade. The content of major elements in traces was determined using two analysis methods: inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). These methods enable precise measurement of concentrations of various elements in the samples, which is crucial for assessing contamination. Microwave digestion was performed in SpeedWave XPERT instrument, manufactured by Berghof. About 0.4 g of sample was measured in Teflon cuvettes. 6 ml of purified nitric acid and 2 ml of hydrogen peroxide (30 %, Fluka) were added. Purified nitric acid was made through purification of HNO_3 (65 % p.a., Sigma Aldrich), on Berghof-purification apparatus-BSB-939-IR. Degradation of samples was performed according to Microwave Digestion of Soil according to EPA 3051A, Application Note Environment & Geology, Digestion, Berghof (https://www.berghof-instruments.com/en/application/microwave-digestion-of-soilaccording-to-epa-3051a/). After completion of the program and cooling of the cuvettes, the samples were quantitatively transferred and diluted with ultra-pure water (Milli Q water, Thermo Scientific, UK) in volumetric flasks of 50 ml. All samples were filtered with Syringe filters (25 mm, PTFE membrane 0.45 μm). 3 elements were analysed in samples. On ICP-OES (ICP-OES, iCAP 6500 Duo, Thermo Scientific, UK) Al was analysed, and on ICP-MS (ICP-MS, iCAP Qc, Thermo Scientific, UK) Cd and Mn were analysed. Standard series were made from internal standards of 1000 μg L^{-1}, and diluted with ultra-pure water to appropriate concentration. The data on the concentration of each element were obtained on the basis of three measurements. For the analyses, calibration solutions were made from the standard stocks (Multi-Element Plasma Standard Solution 4, Specture®, Alfa Aesar; Major Elements Stock, EPA Method Standard, VHG Labs, Merck). The determination of soil pH values, both active (pH (H_2O)) and potential acidity of the soil (pH (KCl)), was conducted in accordance with ISO standard 10390:2005.[33] For this purpose, the Orion Star A221 instrument by Thermo Scientific was used. The determination of pH values was carried out in a suspension of 1g soil and 100 ml distilled water or 1g soil and 1 mol L^{-1} solution of KCl, using the Orion Star A221 instrument, Thermo Scientific. It is important that the soil has an optimal pH value between 6.5 and 7.8 because this provides ideal conditions for the absorption of nutrients, access to water, and good root ventilation, contributing to a healthy and improved plant growth.[34,35] The attached soil samples were dried at a temperature of 105±5 °C in a drying oven, to a constant mass. The gravimetric method of mass loss (*LOI* – loss on ignition) was used to determine the content of organic matter in the soil after drying. The samples were weighed on an analytical balance, brand KERN model ABJ-NM/ABS-N, then they were transferred to porcelain containers and placed in an annealing furnace (high-temperature furnace, VTP-1,2, Elektron), where the soil samples were annealed for of 2 h in which the temperature gradually increased to 440 °C. In soil samples, the content of organic matter was determined based on mass loss at high temperature.[36] Organic matter in soil originates from various residues, including animal and plant materials, and plays a crucial role in maintaining soil quality and the circulation of nutrients within it. The content of organic matter in the soil has a great influence on maintaining the biological productivity of the soil.[37] The enrichment factor is a method used to estimate the degree of contamination of soil and plant material in the investigated area compared to an uncontaminated area.[32,38,39] To determine the degree of soil contamination, there are five categories, each of which represents a different degree of enrichment, EF < 2 no or minimal enrichment, $2 \leq EF < 5$ moderately enriched, $5 \leq EF < 20$ significant enrichment, $20 \leq EF < 40$ very high enrichment and *EF* > 40 extremely high soil enrichment.[40] The value of the bioconcentration factor (*BCF*) is defined as the ratio of the concentration of elements in the roots of the plant to the concentration of elements in the soil. It is considered that the accumulation of elements from the soil in the roots occurs when the *BCF* value is > 1.[41-44] Biological absorption coefficient (*BAC*) is defined as the ratio of the concentration of elements in plant leaves to the concentration of elements in the soil. *BAC* values are classified into five groups: *BAC*, 10–100 (intense absorption), *BAC*, 1–10 (strong absorption), *BAC*, 0.1–1 (medium absorption), *BAC*, 0.01–0.1 (weak absorption) and *BAC*, 0.001–0.01 (very weak absorption).[45] The translocation factor (*TF*) is defined as the ratio of the total concentration of elements in the root and the concentration in the aerial part of the plant. It is considered that the translocation of elements is efficient from the roots to the aerial part of the plant when the value is >1.[42,43,46–48]

RESULTS AND DISCUSSION

In Table I, the data on the content of organic matter in the root zone of the evergreen plant species of white pine and juniper in the researched area are presented. One of the key factors is the OM content influencing the capacity of soils to sustain biological productivity and to maintain the environmental quality.[49] The organic matter content in the soil ranged from 4.78 to 15.96 %. Based on these results, it can be concluded that the highest percentage of soil had a moderate content of organic matter, while three sampled soil locations had a high content of organic matter.[50] The highest concentration of organic matter in the soil was recorded in the root zone of white pine sample 5, while the lowest concentration of organic matter was in the root zone of juniper sample 2.

TABLE I. Organic matter content (*OM*) in soil from the root zone of white pine and juniper in the researched area

Sampling zone	Sampling number	Organic matter, *OM* / %	Average
I	S 1 (White pine)	11.13	7.955
	S 2 (Juniper)	4.78	
II	S 3 (White pine)	6.95	7.515
	S 4 (Juniper)	8.08	
III	S 5 (White pine)	15.96	14.09
	S 6 (Juniper)	12.22	

Table II presents the pH values of active and potential soil acidity from the root zone of white pine and juniper. Soil pH plays the most important role in determining metal morphology, mineral surface solubility, migration and ultimate bioavailability.[51,52] One of the most frequently measured parameters is soil pH, considering its influence on behaviour and condition bioavailability of elements in soil.[53] In the 6 to 7 range, soil pH is generally optimal for plant growth because more plant nutrients are readily available in this pH range.[54] According to the acidity classification categories of soil,[54] the sampled soil can be classified as very strongly acidic to slightly acidic. Based on the comparison of soil pH values in the investigated area, we can see that the highest soil acidity was in the I zone, sample

2, while the least acidity was in III zone, sample 6. Samples 1, 4 and 6 had a ΔpH value (pH(H_2O) – pH(KCl)) slightly above 1 at the sampling sites, indicating a tendency of soil acidification at these sampling locations.

TABLE II. Soil acidity from the root zone of white pine and juniper in the studied area; ΔpH = pH(H_2O) – pH(KCl)

Sampling zone	Sampling number	pH(H_2O)	pH (KCl)	ΔpH
I	S 1 (White pine)	5.77	4.72	1.05
	S 2 (Juniper)	4.72	4.01	0.71
II	S 3 (White pine)	6.07	5.43	0.64
	S 4 (Juniper)	6.11	5.03	1.08
III	S 5 (White pine)	6.16	5.29	0.87
	S 6 (Juniper)	6.33	5.19	1.14

Fig. 3 shows the concentrations of elements Al^{3+}, Cd^{2+} and Mn^{2+} in the root zone soil of white pine and juniper and they are also presented in the Table III. The obtained concentrations of the examined elements were compared with the corresponding remediation values and threshold values prescribed by the Regulation of the Republic of Serbia.[55]

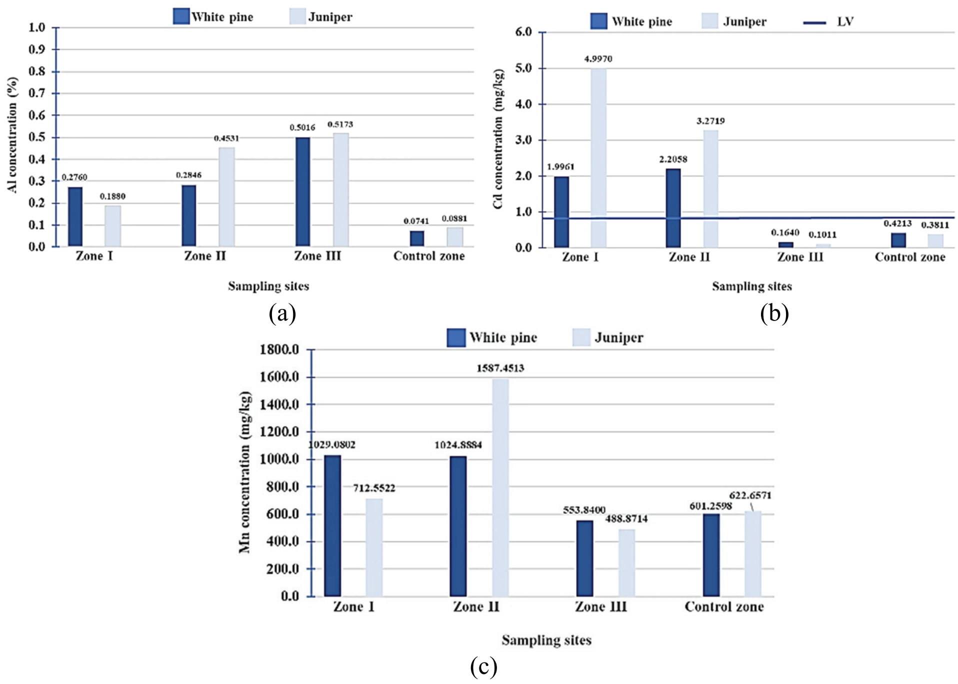


Fig. 3. Concentrations of metal cations a) Al, b) Cd and c) Mn in the root zone of white pine and juniper at 6 sampled locations (solid line represents the threshold value according to the Regulation of Serbia (Regulation No. 30/2018-50, 2018)).

TABLE III. The concentrations (mg kg^{-1})of elements Al^{3+}, Cd^{2+} and Mn^{2+} in the root zone soil of white pine and juniper

Sampling zone	Sampling number	Al	Cd	Mn
I	S 1 (White pine)	0.2760	1.9961	1029.0802
	S 2 (Juniper)	0.1880	4.9970	712.5522
II	S 3 (White pine)	0.2846	2.2058	1024.8884
	S 4 (Juniper)	0.4531	3.2719	1587.4513
III	S 5 (White pine)	0.5016	0.1640	553.8400
	S 6 (Juniper)	0.5173	0.1011	488.8714
Control	White pine	0.0741	0.4213	601.2598
	Juniper	0.0881	0.3811	62.6571

The concentrations of aluminium in the soil from the root zones of the analysed plant species are lower than the average values (1–5 %), indicating a relatively low concentration of aluminium in the soil or the presence of factors that reduce these concentrations. Slightly higher aluminium values were observed in Zone III for both plant species. Fig. 3b shows the concentration of cadmium in the soil from the root zone of white pine and juniper. The prescribed limit values for cadmium in the soil according to the Regulation of the Republic of Serbia are 0.8 mg kg^{-1}.[55] The world average concentration of cadmium in the soil is 0.41 mg kg^{-1}.[56] Cd concentrations that exceeded the limit values were recorded for both plant species in zones I and II, while in soil samples from zone III as from the control zone, the Cd concentration was below the determination limits for both plant species. There are no defined limits and remediation values for manganese in the soil according to the Regulation of the Republic of Serbia, while the world average concentration of manganese in the soil is from 411 to 550 mg kg^{-1}.[56] The concentrations of manganese in the soil from the root zones of white pine and juniper were above the global average in all three zones, as well as in the control zone.

The values of enrichment factors for Al^{3+}, Cd^{2+} and Mn^{2+} in the soil of white pine and juniper are presented in Table IV. The enrichment factors for aluminium were greater than 2, indicating enrichment or contamination of soil with aluminium. The presence of aluminium can be considered anthropogenic at all sampling locations, although there are differences in aluminium concentrations depending on the sampling location. Enrichment of soil with cadmium was observed for both plant species in Zones I and II, while there was no soil enrichment with cadmium for white pine and juniper in Zone III. Most soil samples belong to the category of moderate to significant enrichment with cadmium. The enrichment factor values indicate no soil enrichment for most samples, while moderate enrichment with manganese was observed in juniper soil in Zone II. Table V presents a literature review of the range of element concentrations in plant leaves.

Analysis of the concentration of Al, Cd and Mn (Fig. 4 and Table VI) was conducted on various parts of the white pine at the surface mine Sastavci (Badanj) and its vicinity. The highest concentrations of Al were detected in the roots of the white pine in Zone I, while the lowest concentration was observed in the fruit (cone) in the control zone. For most samples of plant material, the concentration of Cd was below the detection limit (< 0.2 mg kg^{-1}). The World Health Organization (WHO) has established permissible levels for Cd herbal materials, which amount to 0.3 mg kg^{-1}.[58] The content of these metals in unwashed pine needles was 0.1-2.4 mg kg^{-1} for Cd.[59] However, an increased concentration of Cd was observed in the branches of the white pine in Zone I and Zone II. Regarding Mn, the highest concentrations were found in the needles of the white pine in Zone II, while the lowest concentrations were observed in the control zone.

TABLE IV. Enrichment factor for soil in the White Pine and Juniper Zone Sastavci (Badanj)

Element	Zone I		Zone II		Zone III	
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Al	3.7249	2.1341	3.8403	5.1431	6.7695	5.8713
Cd	4.7380	13.1120	5.2357	8.5854	0.3893	0.2653
Mn	1.7115	1.1444	1.7046	2.5495	0.9211	0.7851

TABLE V. Concentration ranges of the elements in mature leaves (mg kg^{-1} dw);[57] dw – dry weight basis, and „-“ not defined

Element	Deficient	Sufficient or normal	Excessive or toxic	Tolerable in agronomic crops
Cd	–	0.05–0.2	5–30	0.05–0.5[a]
Mn	10-30	30-300	400-1000	300

[a]Fresh weigh basis

TABLE VI. Concentration (mg kg^{-1}) of Al, Cd and Mn in parts of the white pine

Sampling zone	Sampling number	Al	Cd	Mn
I	Root	593.1935	1.0142	93.3293
	Branch	307.7305	3.7611	96.8308
	Needle	183.2863	0.9624	301.8593
	Strobilus	221.4027	0.7828	65.0804
II	Root	63.6972	1.7570	56.3886
	Branch	192.7475	3.8288	164.2559
	Needle	120.9598	1.7201	738.1713
	Strobilus	112.0603	0.2243	64.8791
III	Root	135.0197	0.1560	9.7610
	Branch	216.4097	0.2316	88.7822
	Needle	449.4844	0.0512	602.5080
	Strobilus	506.1707	0.0930	123.9799
Control	Root	82.0100	0.2200	22.7200
	Branch	70.9300	0.3400	30.7000
	Needle	110.9300	0.4100	35.6100
	Strobilus	33.0900	0.1100	25.1200

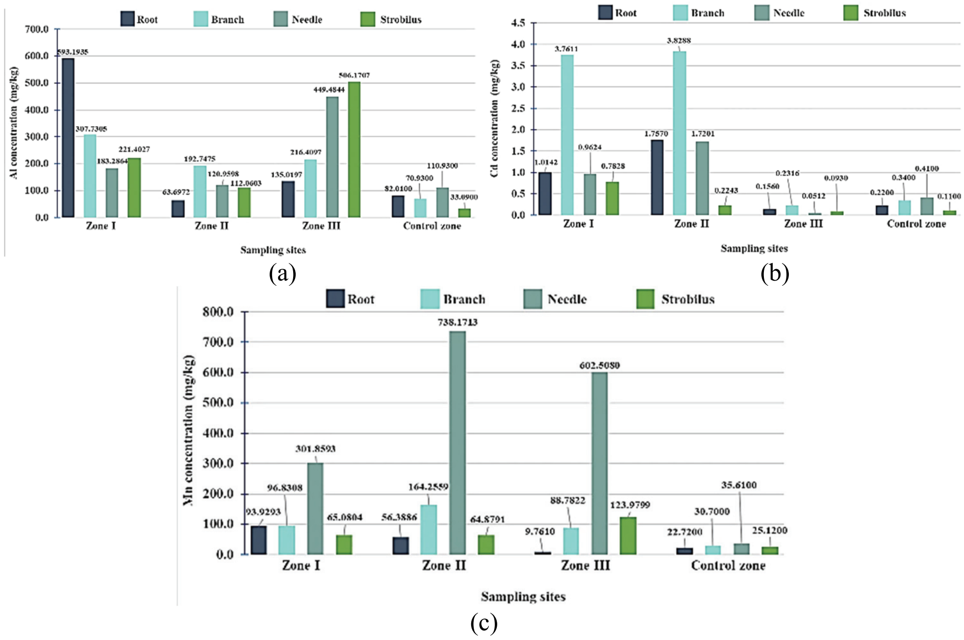


Fig. 4. Concentration (mg kg^{-1}) for a) Al, b) Cd and c) Mn in the root and above-ground parts of the white pine.

In the examined area, concentrations of Al vary in the juniper (roots, branches, needles, and fruit). The highest concentration of aluminium was observed in the roots of juniper in the first zone, while the lowest was in the juniper fruit in the control zone. Concentrations of Cd in the juniper, examined both at the open pit and its immediate surroundings, also vary. The highest concentration of Cd was found in the roots of spruce in Zone I, while the lowest was in the juniper fruit in zone III. Regarding Mn, the highest concentrations were observed in the juniper needles in the first zone of the examined area, while the lowest concentrations were detected in the control zone (Fig. 5 and Table VII).

Table VIII displays the values of biological factors for white pine. It can be observed that for Al, Cd and Mn, the criterion BCF > 1 and TF > 1 does not exist in any zone or sample. When it comes to aluminium, cadmium and manganese, we can conclude that white pine is not suitable for phytoextraction or phytostabilization of the examined elements, under the given conditions of the Sastavci (Investigation area) surface mine and its immediate vicinity.

Based on the tabular data for juniper in phytoextraction (Table IX), the criterion BCF > 1 and TF > 1 is fulfilled only for Cd, sample 6, zone III. Based on the BAC values, which were less than 1, it can be concluded that juniper excludes the examined elements. In the case of Cd and Mn, the BAC value was greater than 1, indicating the potential accumulation of these elements in juniper needles.

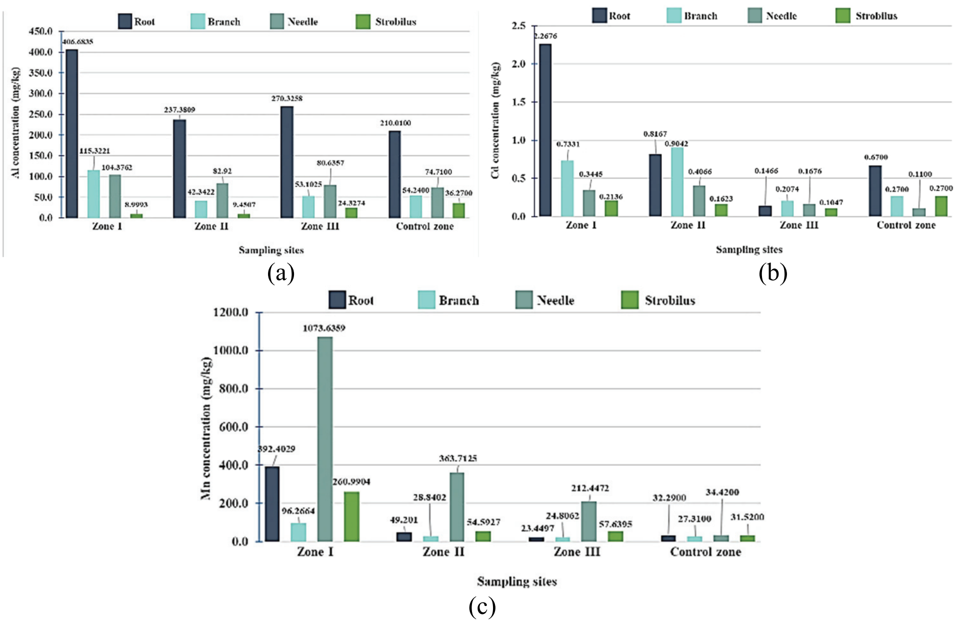


Fig. 5. Concentration (mg kg^{-1}) of: a) Al, b) Cd and c) Mn in parts of the juniper.

TABLE VII. Concentration (mg kg^{-1}) of Al, Cd and Mn in parts of the juniper

Sampling zone	Sampling number	Al	Cd	Mn
I	Root	406.6835	2.2676	392.4029
	Branch	115.3221	0.7331	96.2664
	Needle	104.3762	0.3445	1073.6359
	Strobilus	8.9993	0.2136	260.9904
II	Root	237.3809	0.8167	49.201
	Branch	42.3422	0.9042	28.8402
	Needle	82.92	0.4066	363.7125
	Strobilus	9.4507	0.1623	54.5927
III	Root	270.3258	0.1466	23.4497
	Branch	53.1025	0.2074	24.8062
	Needle	80.6357	0.1676	212.4472
	Strobilus	24.3274	0.1047	57.6395
Control	Root	210.0100	0.6700	32.2900
	Branch	54.2400	0.2700	27.3100
	Needle	74.7100	0.1100	34.4200
	Strobilus	36.2700	0.2700	31.5200

TABLE VIII. Bioconcentration factor (BCF), translocation factor (TF), and biological absorption coefficients (BAC) for white pine

Factor	Sampling site	Al	Cd	Mn
BCF	Sample 1	0.2149	0.5081	0.0913
	Sample 3	0.0224	0.7965	0.0550

TABLE VIII. Continued

Factor	Sampling site	Al	Cd	Mn
BCF	5	0.0269	0.9512	0.0176
TF	1	0.3090	0.9489	**3.2137**
	3	**1.8990**	0.9790	**13.0908**
	5	**3.3290**	0.3282	**61.7261**
BAC	1	0.0664	0.4821	0.2933
	3	0.0425	0.7798	0.7202
	5	0.0896	0.3122	**1.0879**

TABLE IX. Bioconcentration factor (*BCF*), translocation factor (*TF*) and biological absorption coefficients (*BAC*) for juniper

Factor	Sampling site/Elements	Al	Cd	Mn
BCF	2	0.2163	0.4538	0.5507
	4	0.0524	0.2496	0.0310
	6	0.0523	**1.4500**	0.0037
TF	2	0.2567	0.1519	**2.7361**
		0.3493	0.4979	**7.3924**
		0.2983	**1.1432**	**9.0597**
BAC	2	0.0378	0.1726	1.0433
	4	0.0291	0.1843	0.3549
	6	0.0161	**1.0220**	0.3836

CONCLUSION

The exploitation of natural resources can have significant negative consequences on soil, plant and animal life, and the environment in general. The results indicate that there have been exceedances of the threshold values for elements in the soil, particularly for Cd in zones I and II for both plant species. Enrichment factors, which were mostly in the categories of moderate and significant enrichment, were observed in most soil samples from the root zones of white pine and juniper for Al, Cd, and Mn (only one sampled location). We conclude that Al, Cd and Mn in the soil from the root zones of white pine and juniper originate from the exploitation process of Pb–Zn ore. The natural origin was determined for manganese, while the enrichment was detected in only one sample, indicating that the exploitation contributed to the increase in the concentration of this element. For the Sastavci (Badanj) surface mine, the values of the bioconcentration factor (*BCF*) for the examined elements were <1, indicating very low uptake of elements from the soil through the roots of white pine. Based on the values of the bioconcentration factor for juniper, *BCF* >1 was observed for Cd, while for other elements, the bioconcentration factor value was <1. Based on the obtained values of the biological absorption coefficient, the absorption intensity ranged from very weak to strong intensity for Mn in white pine needles, while for juniper, the absorption of elements from the soil to the juniper needles was observed for Cd and Mn. The criteria for the possibility of using juniper in the phytoextraction process, *BCF* > 1 and *TF* > 1, were achieved only for Cd. Given that the research was conducted on a surface mine of lead-zinc ore, there is a possibility that an increased concentration of other toxic elements may be found on the surface mine, as well as in its immediate surroundings. Given that for this research we used wild evergreen plant species, which belong to the group of tolerant plants, which managed to develop and survive in the polluted area and which did not prove to be good candidates for phytoremediation of the investigated elements, further research can be carried out in order to examination of some other wild plant species such as wild cherry, fern, oak, since these plant species also survive in such a polluted area. The final research should provide a scientific contribution to the assessment and/or rehabilitation of such areas, using appropriate plant species for the phytoremediation process in the form of erosion reduction, reforestation and environmental preservation.

И З В О Д

ПРОЦЕНА КОНЦЕНТРАЦИЈЕ ТОКСИЧНИХ МЕТАЛА (АЛУМИНИЈУМ, КАДМИЈУМ И МАНГАН) У ЗЕМЉИШТУ И ЗИМЗЕЛЕНИМ БИЉНИМ ВРСТА НА ПОВРШИНСКОМ КОПУ САСТАВЦИ И ОКОЛИНИ

МИЛИЦА ТОМОВИЋ[1], ЈОВАНА ГРАХОВАЦ[2], ЈЕЛЕНА ДОДИЋ[2], МАРИЈА РАДОЈКОВИЋ[2], НАТАША ЕЛЕЗОВИЋ[1] и КРСТИМИР ПАНТИЋ[1]

[1]*Универзитет у Приштини са привременим седиштем у Косовској Митровици, Факултет техничких наука, Ул. Књаза Милоша 7, 38220 Косовска Митровица,* [2]*Технолошки факултет Нови Сад, Универзитет у Новом Саду, Булевар цара Лазара 1, 21000 Нови Сад*

У раду је спроведено истраживање у циљу утврђивања концентрације Al^{3+}, Cd^{2+} и Mn^{2+} у земљишту и деловима зимзелених биљних врста – клеке и белог бора – на површинском копу Саставци (Бадањ) и његовој околини и његовој околини у циљу утврђивања могућност коришћења зимзелених биљака као еколошког индикатора или за фиторемедијацију. На глобалном нивоу, као резултат различитих антропогених активности као што су саобраћај, пољопривредне активности, спаљивање отпада, индустријска производња, рударење, итд., представља озбиљан проблем који доводи до загађења токсичним и потенцијално токсичним катјонима метала. Једна од иновативнијих техника која се користи за санацију рударских подручја је фиторемедијација. Применом фиторемедијације одређене биљне врсте на загађеним подручијима имају способност да делују као акумулатори или хиперакумулатори, апсорбују токсичне метале из земљишта кроз корен биљке и транспортује их у горње делове. Ово истраживање је спроведено у циљу одређивања концентрације Al^{3+}, Cd^{2+} и Mn^{2+} на самом површинском копу и његовој околини, као и праћења дистрибуције металних катјона у систему корен, гране, иглице и плодови зимзелених биљних врста – бели бор и клека. Резултати су показали да је узорковано земљиште контаминирано Cd у зони I и II за обе биљне врсте, јер су концентрације прелазиле граничне вредности, док је концентрација Cd у зони III као и у контролној зони била испод граница одређивања за обе биљне врсте. Концентрација Mn у земљишту из зоне белог бора и клеке била је изнад светског просека у све три зоне, као и у самој контролној зони. Земљиште је највише обогаћено анализираним елементима у површинском копу I и II зоне. Анализом елемената у деловима белог бора, корену, гранама, иглицама и плодовима, највећа концентрација Al је откривена у корену у зони I, док је најмања концентрација забележена у плоду (шишаркама) у контролној зони,

повећана концентрација Cd забележена је у гранама у зонама I и II, а највећа концентрација Mn забележена је у иглицама у зони II. Највећа концентрација Al забележена је у корену клеке у зони I, а најмања у плоду клеке у контролној зони, концентрација Cd је највећа у зони корена клеке I, а најмања у плоду клеке и највећа концентрација Mn забележена је у иглицама клеке у зони I. На основу добијених вредности коефицијента биолошке апсорпције, може се закључити да бели бор није погодан за фитоекстракцију или фитостабилизацију испитиваних елемената. Анализа биолошких фактора (биоконцентрација, транслокација и фактор биоакумулације) указала је на могућу употребу клеке у фитоекстракцији само за Cd.

(Примљено 1. априла, ревидирано 30. априла, прихваћено 18. јуна 2024)

REFERENCES

1. L. Järup, *Brit. Med. Bull.* **68** (2003) 167 (https://doi.org/10.1093/bmb/ldg032)
2. B. Wei, L. Yang, *Microchem. J.* **94** (2010) 99 (https://doi.org/10.1016/j.microc.2009.09.014)
3. N. B. Milosavljević, M. Đ. Ristić, A. A. Perić-Grujić, J. M. Filipović, S. B. Štrbac, Z. Lj. Rakočević, M. T. Kalagasidis Krušić, *J. Haz. Mat.* **192** (2011) 846 (https://doi.org/10.1016/j.jhazmat.2011.05.093)
4. Z. Cong, S. Kang, Y. Zhang, X. Li, *App. Geochem.* **25** (2010) 1415 (https://doi.org/10.1016/j.apgeochem.2010.06.011)
5. V. D. Nica, M. Bura, I. Gergen, M. Harmanescu, D-M. Bordean, *Chem. Cent. J.* **6** (2012) 55 (https://doi.org/10.1186/1752-153x-6-55)
6. J. Suman, O. Uhlik, J. Viktorova, T. Macek, *Front. Plant Sci.* **1476** (2018). (https://doi.org/10.3389/fpls.2018.01476)
7. A. S. Mussina, G. U. Baitasheva, M. S. Kurmanbayeva, G. J. Medeuova, A. A. Mauy, E. M. Imanova, A. Zh. Kurasbaeva, Z. S. Rachimova, Y. S. Nurkeyev, K. Orazbayev, *Israel J. Ecol. Evol.* **64** (2018) 35 (http://doi.org/10.1163/22244662-06303005)
8. S. Adiloğlu, *Heavy Metal Removal with Phytoremediation*. in *Advances in Bioremediation and Phytoremediation*, Ed. N. Shiomi, InTech, (2018). (https://doi.org/10.5772/intechopen.70330)
9. Y. Hu, Z. Nan, J. Su, N. Wang, *Env. Sci. Poll. Res.* **20** (2013) 7194 (https://doi.org/10.1007/s11356-013-1711-0)
10. E. Osma, M. Elveren, G. Karakoyun, *Air Qual. Atm. Health* **10** (2017) 85 (https://doi.org/10.1007/s11869-016-0410-7)
11. M. P. Waalkes, *Mut. Res. – Fund. Mol. Mech. Mutagen.* **533** (2003) 107 (https://doi.org/10.1016/j.mrfmmm.2003.07.011)
12. J. Ding, G. He, W. Gong, W. Wen, W. Sun, B. Ning, S. Huang, K. Wu, C. Huang, M. Wu, W. Xie, H. Wang, *Can. Epid. Biomark. Prevent.* **18** (2009) 1720 (https://doi.org/10.1158/1055-9965.EPI-09-0115)
13. H. Chen, N. C. Giri, R. Zhang, K. Yamane, Y. Zhang, M. Maroney, M. Costa, *J. Biol. Chem.* **285** (2010) 7374 (https://doi.org/10.1074/jbc.M109.058503)
14. T. Schwerdtle, F. Ebert, C. Thuy, C. Richter, L. H. F. Mullenders, A. Hartwig, *Chem. Res. Tox.* **23** (2010) 432 (https://doi.org/10.1021/tx900444w)
15. Y. Asara, J. A. Marchal, E. Carrasco, H. Boulaiz, G. Solinas, P. Bandiera, M. A. Garcia, C. Farace, A. Montella, R. Madeddu, *Int. J. Mol. Sci.* **14** (2013) 16600 (https://doi.org/10.3390/ijms140816600)
16. M. Ovečka, T. Takáč, *Biotec. Adv.* **32** (2014) 73 (https://doi.org/10.1016/j.biotechadv.2013.11.011)

17. M. E. Morales, R. S. Derbes, C. M. Ade, J. C. Ortego, J. Stark, P. L. Deininger, A. M. Roy-Engel, *PLoS One* **11** (2016) e0151367 (https://doi.org/10.1371/journal.pone.0151367)
18. H. Jia, D. Hou, D. O'Connor, S. Pan, J. Zhu, N.S. Bolan, J. Mulder, *J. Haz. Mat.* **389** (2020) 121849 (https://doi.org/10.1016/j.jhazmat.2019.121849)
19. L. Wang, D. Hou, Z. Shen, J. Zhu, X. Jia, Y.S. Ok, F. M. G. Tack, J. Rinklebe, *Crit. Rev. Env. Sci. Tech.* **50** (2020) 2724 (https://doi.org/10.1080/10643389.2019.1705724)
20. D. O'Connor, X. Zheng, D. Hou, Z. Shen, G. Li, G. Miao, S. O'Connell, M. Guo, *Env. Int.* **130** (2019) 104945 (https://doi.org/10.1016/j.envint.2019.104945)
21. L. Ahrens, M. Shoeib, T. Harner, S. C. Lee, R. Guo, E. J. Reiner, *Env. Sci. Techn.* **45** (2011) 8098 (https://doi.org/10.1021/es1036173)
22. Li X. Zhang, X, Li, B, Wu, Y, Sun, H, Yang, Y. *Env. Sci. Poll. Res.* **24** (2017) 21660 (https://doi.org/10.1007/s11356-017-9781-z)
23. I. D. Pulford, C. Watson, *Env. Int.* **29** (2003) 529 (https://doi.org/10.1016/s0160-4120(02)00152-6)
24. E. Baltrenaite, P. Baltrenas, D. Butkus, A. Lietuvninkas, *Phytoremediation* (2015) 21 (https://doi.org/10.1007/978-3-319-10395-2_2)
25. C. Kole, Genome Mapping and Molecular Breeding in Plants, Springer, Berlin, 2007.
26. R. Muilu-Mäkelä, J. Vuosku, E. Läärä, M. Saarinen, J. Heiskanen, H. Häggman, T. Sarjala, *Plant Physiol. Biochem.* **88** (2015) 70 (https://doi.org/10.1016/j.plaphy.2015.01.009)
27. M. Pajak, W. Halecki, M. Gąsiorek, *Chemosphere* **168** (2017) 851 (https://doi.org/10.1016/j.chemosphere.2016.10.125)
28. M. Mleczek, P. Goliński, B. Waliszewska, A. Mocek, M. Gąsecka, M. Zborowska, Z. Magdziak, W.J. Cichy, B. Mazela, T. Kozubik, A. Mocek-Płóciniak, W. Moliński, P. Niedzielski, *J. Env. Sci. Health, Part A* **53** (2018) 1029 (https://doi.org/10.1080/10934529.2018.1471116)
29. A. Aidosov, G. Aidosov, N. Zaurbekov, N. Zaurbekova, G. Zaurbekova, I. Zaurbekov, *Ekoloji* **28** (2019) 349
30. G. Cheloni, V. I. Slaveykova, *Environments* **5** (2018) 1 (https://doi.org/10.3390/environments5120138)
31. FAO, Status of the World's Soil Resources. Google Scholar, (2015).
32. M. D. Mingorance, B. Valdés, S. R. Oliva, *Env. Int.* **33** (2007) 514 (http://dx.doi.org/10.1016/j.envint.2007.01.005)
33. ISO 2005, International Organisation for Standardisation, Soil Quality: Determination of pH, 10390:2005. ISO, Geneva.
34. N. S. Eash, T. J. Sauer, D. O'Dell, E. Odoi, Soil Science Simplified. Sixth edition. John Wiley & Sons, Inc., Hoboken, New Jersey (2016)
35. A. Zseni, H. Goldie, I. Bárány-Kevei, *Acta Carsologica* **32/1**(5), (2003) 57 (https://doi.org/10.3986/ac.v32i1.364)
36. K. R. Reddy, Organic matter determination. In: Engineering properties of soils based on laboratory testing, Illinois, Chicago. Chicago, Illinois: Department of Civil and Materials Engineering University of Illinois at Chicago, (2002) 13-19
37. Y. Mao, S. Sang, S. Liu, J. Jia, *Comptes Rendus Biologies* **337** (2014) 332 (https://doi.org/10.1016/j.crvi.2014.02.008)
38. S. R. Oliva, A .J. F. Espinosa, *Microchem. J.* **86** (2007) 131 (https://doi.org/10.1016/j.microc.2007.01.003)
39. E. O. Fagbote, E. O. Olanipekun, *Am.–Euras. J. Sci. Res.* **5** (2010) 241 (https://idosi.org/aejsr/5(4)10/4.pdf)

40. A. Enuneku, E. Biose, L. Ezemonye, *J. Env. Chem. Eng.* **5** (2017) 2773 (https://doi.org/10.1016/j.jece.2017.05.019)
41. A. Christou, C. P. Theologides, C. Costa, I. K. Kalavrouziotis, S. P. Varnavas, *J. Geochem. Exp.* **178** (2017) 16 (https://doi.org/10.1016/j.gexplo.2017.03.012)
42. R. E. Mendoza, I. V. García, L. de Cabo, C. F. Weigandt, A. F. de Iorio, *Sci. Tot. Env.* **505** (2015) 555 (https://doi.org/10.1016/j.scitotenv.2014.09.105)
43. J. Nouri, B. Lorestani, N. Yousefi, N. Khorasani, A. H. Hasani, F. Seif, M. Cheraghi, *Env. Earth Sci.* **62** (2011) 639 (https://doi.org/10.1007/s12665-010-0553-z)
44. A. A. Radojevic, S. M. Serbula, T. S. Kalinovic, J. V. Kalinovic, M. M. Steharnik, J. V. Petrovic, J. S. Milosavljevic, *Env. Sci. Poll. Res.* **24** (2017) 10326 (https://doi.org/10.1007/s11356-017-8520-9)
45. P. J. C. Favas, J. Pratas, M. N. V. Prasad, *Int. J. Env. Sci. Tech.* **10** (2013) 809 (https://doi.org/10.1007/s13762-012-0115-x)
46. D. Yildirim, A. Sasmaz, *J. Geochem. Expl.* **182** (2017) 228 (https://doi.org/10.1016/j.gexplo.2016.11.005)
47. D. Marbaniang, S. S. Chaturve*, Int. J. Sci. Res. Manag. (IJSRM)*, **2** (2014) 965 (https://ijsrm.net/index.php/ijsrm/article/view/668)
48. S. Shiyab, *Agriculture* **8** (2018) 29 (https://doi.org/10.3390/agriculture8020029)
49. Y. Mao, S. Sang, S. Liu, J. Jia, *Comptes Rendus Biologies* **337** (2014) 332 (https://doi.org/10.1016/j.crvi.2014.02.008)
50. USDA. Soil quality information sheet, Soil quality indicators: Organic matter. Washington D.C.: United States Department of Agriculture (USDA), Natural Resources Conservation Service (NRCS) (1996)
51. G. Du Laing, D. R. J. Vanthuyne, B. Vandecasteele, F. M. G. Tack, M. G. Verloo, *Environ. Pollut.* **147** (2007) 615 (https://doi.org/10.1016/j.envpol.2006.10.004)
52. F. R. Zeng, S. Ali, H. T. Zhang, Y. B. Ouyang, B. Y. Qiu, F. B. Wu, G. P. Zhang, *Environ. Pollut.* **159** (2011) 84 (https://doi.org/10.1016/j.envpol.2010.09.019)
53. S. Bravo, J. A. Amorós, C. Pérez-de-los-Reyes, F. J. García, M. M. Moreno, M. Sánchez-Ormeño, P. Higueras, *J. Geochem. Expl.* **174** (2017) 79 (https://doi.org/10.1016/j.gexplo.2015.12.012)
54. USDA, Soil Quality Indicators: pH. Soil quality information sheet. Natural resources conservation service, U.S. Department of agriculture, (1998)
55. Uredba br. 30/2018-50; UREDBU o graničnim vrednostima zagađujućih, štetnih i opasnih materija u zemljištu 30/2018-50. „Službeni glasnik Republike Srbije” (2018)
56. A. Kabata-Pendias Trace elements in soils and plants (4th ed.) CRC Press, Boca Raton, Florida, (2010) (https://doi.org/10.1201/b10158)
57. A.Kabata-Pendias, H. Pendias, Trace Elements in Soil and Plants (3rd ed.), Boca Raton: CRC Press, (2000) (https://doi.org/10.1201/9781420039900)
58. WHO. WHO guidelines for assessing quality of herbal medicines with reference to contaminants and residues. Geneva: World Health Organization (2007)
59. M. Pająk, W. Halecki, M. Gąsiorek, *Chemosphere* **168** (2017) 851 (https://doi.org/10.1016/j.chemosphere.2016.10.125).