Plant uptake and soil retention of radionuclides and metals in vineyard environments

Ljiljana Gulan[1], Jelena M. Stajic[2*], Biljana Milenkovic[2], Tijana Zeremski[3], Stanko Milic[3], Dragana Krstic[4]

[1]University of Priština in Kosovska Mitrovica, Faculty of Sciences and Mathematics, Lole Ribara 29, 38220 Kosovska Mitrovica, Serbia

[2]University of Kragujevac, Institute for Information Technologies, Kragujevac, Department of Science, Jovana Cvijica bb, 34000 Kragujevac, Serbia

[3]Institute of Field and Vegetable Crops in Novi Sad, Maksima Gorkog 30, 21000 Novi Sad, Serbia

[4]University of Kragujevac, Faculty of Natural Sciences, Radoja Domanovića 12, 34000 Kragujevac, Serbia

Corresponding author: J.M. Stajic, e-mail: stajicjelena11052012@gmail.com

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[*] Corresponding author: Jelena M. Stajic, e-mail: stajicjelena11052012@gmail.com

Abstract

In most European countries, each adult citizen drinks on average more than 20 litres of wine every year. Three popular wine-growing areas (Aleksandrovac, Topola and Orahovac) in Serbia were studied in order to investigate the abundance and uptake of elements from vineyard soil to plants. The specific activities of radionuclides (^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs and ^{7}Be) were measured in soil, leaves and grape berries. ^{226}Ra and ^{232}Th were positively correlated with silt and clay, and negatively correlated with sand content in soil. Specific activities of natural radionuclides were also negatively correlated with soil pH and $CaCO_3$. Significant correlations of ^{40}K and ^{137}Cs with organic matter in soil were found. Concentrations of fifteen metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Fe, K, Na, Ca, Mg and Hg) were also measured in soil samples as well as in grapevine leaves. Analyzed soils were rich in Ni, Cu, Co, Cr and Cd. High concentrations of Cu were probably caused by long-term use of Cu-based fungicides. Cu was correlated with Fe and organic matter content in soil. Soil-to-plant transfer factors (TF) were calculated to estimate the uptake of radionuclides and metals. Correlations obtained via PCA enable distinction between the sites Aleksandrovac and Topola relative to Orahovac. The first principal component (PC1) accounting for 30.70% of the total variance, correlated significantly with soil pH (H_2O), contents of $CaCO_3$, Na, Ca, ^{40}K and ^{226}Ra in soil as well as with ^{226}Ra, Na, Ca in plants and TF_{Ca}. The second principal component (PC2), with total variance of 17.21%, was mainly correlated with variables pertaining to Mg, Co and Cr in the soil and TF_K.

Keywords: vineyard, soil, radionuclide, metal, transfer factor, correlation

Introduction

According to WHO data, total alcohol per capita consumption in the world's population (aged 15+) is on average 6.4 litres of pure alcohol per year (WHO 2018). The highest consumption of alcohol (10 litres or more) is observed in countries of the European Region where wine is one of the most frequently consumed alcoholic beverages. In most European countries, each adult citizen drinks on average more than 20 litres of wine every year.

In addition to climate factors, agricultural practices, and different winemaking techniques, the quantity and quality of grape and wine production are also influenced by soil chemistry and geology (Blotevogel et al. 2019; Bramley et al. 2011; Styger et al. 2011). The mechanisms involved in transport of elements (nutrients as well as pollutants) from soil to vine leaves and grapes are rather complicated and still not completely understood (Blotevogel 2017; Gonzalez-Barreiro et al. 2015). Mineral nutrients play important roles in different biochemical processes in plants, acting like electron transporters, catalyzers, or regulators of osmotic pressure (Marschner and Marschner 2012). Interactions among plant nutrients can produce antagonistic or synergistic effects that can affect nutrient use efficiency (Rietra et al. 2017). Variations in element availability may influence the synthesis of aromatic compounds and polyphenol, sugar and essential amino acids in grapes, but it may also affect yeast fermentation and wine acidity (Brunetto et al. 2015; Pohl 2007; Pereira 1988). Transport and phytoavailability of elements depend not only on their content in soil but also on soil properties such as cation exchange capacity, pH, and organic matter content (Tyler and Olsson 2001).

All biological species have the ability to accumulate toxic heavy metals and radioactive isotopes found in nature. Naturally occurring radionuclides such as ^{226}Ra, ^{232}Th, and ^{40}K are present in all environments and their content in agricultural soils can sometimes be significantly

increased, e.g., due to the usage of phosphorus and potassium fertilizers. Different chemical forms of these natural radionuclides are incorporated in biological systems through the food chain and may affect human health. ^{7}Be is produced in the upper troposphere and lower stratosphere by the interaction of cosmogenic particles with nitrogen and oxygen. Because of short half-life (53.3 days), ^{7}Be does not penetrate deep into the soil profile, and surface vegetation is an effective trap for ^{7}Be bearing aerosols. On the other hand, ^{137}Cs is one the most important artificial radionuclides deposed onto the ground as a result of anthropogenic activities.

With 21,359 hectares of vineyards (Statistical Office of the Republic of Serbia 2019), and the production of about 198,000 tons of grapes every year, Serbia is among the first 20 wine-producing countries in the world (FAO 2015). The aim of this study was to investigate the concentrations of metals and radionuclides in 19 vineyards from three different wine-growing areas (Aleksandrovac, Topola and Orahovac) in Central Serbia and Kosovo. Soils, vine leaves, and grapes were analyzed, transfer factors were calculated and correlations between the elements in soil and leaves were investigated.

Experimental

Study area

Study area included grapevine plantations of well-known vineyards: Aleksandrovac and Topola in Central Serbia and Orahovac in Kosovo. Samples of soil, vine leaves and grapes were collected from 19 locations. The study included the following *Vitis vinifera* cultivars: *Riesling* (location No.1), *Cardinal* (No.2), *Semillon* (No.3), *Cabernet Sauvignon* (No.4,13,15, and 18),

Traminer (No.5), *Afus Ali* (No.6), *Muscat Hamburg* (No.7,12,16,17, and 19), *Merlot* (No.8 and 14), *Vranac* (No.9), *Smederevka* (No.10), *Prokupac* (No.11), according to the location numbers given in Tables 1-4. The last three vine types are autochthonous.

In terms of geology, Neogene and Quaternary overstep sequence cover areas of Topola and Aleksandrovac vineyards, while Orahovac lies in large Metohija Neogene and Quaternary basin which covers ultrabasic massif (Geological Atlas of Serbia 2002; Monthel et al. 2002). The terrains are mostly hilly with altitudes spanning from 250-700 m (in average 370 m) in Aleksandrovac, while Orahovac and Topola vineyards are situated at altitude of 477 m and 221 m, respectively. Moderate-continental climate with plenty of sunny days is extremely suitable for growing vines. The combination of relief, fertile land, altitude and climate characteristics induced high-quality wine-production.

Sampling

Soil, vine leaves and grapes were sampled before the grape harvest, in September of 2018. At each vineyard parcel, several surface subsamples of soil were taken by a spade and mixed into a composite sample. Leaves and grapes were collected from vine plants near the soil sampling sites. Samples were packed into plastic bags and transported to the laboratories for radioanalytical and physicochemical analysis.

Gamma spectrometry

Soil and leaf samples intended for gamma spectrometry were first air-dried at room temperature and then in oven until constant weight. Soil was ground in a glass mortar and passed through a 2 mm sieve. Grape berries were cleaned from pedicels, smashed and homogenized by blender. Samples were sealed in 450 mL Marinelli beakers and stored for a month in order to ensure radioactive equilibrium between ^{226}Ra and its progeny. Specific activities of natural radionuclides and ^{137}Cs in soil, leaves and grapes were measured using coaxial HPGe detector (GEM30-70 ORTEC, 30% relative efficiency and 1.65 keV FWHM for ^{60}Co at 1.33 MeV) placed in a 10 cm lead shield to reduce the background. Gamma spectrometric measurement of each soil sample was performed for 5 h, while leaves and grapes were measured for 48 h due to the low count rates.

The specific activity of ^{226}Ra was obtained using the gamma lines of ^{214}Pb (351.9 keV) and ^{214}Bi (609.3 keV and 1764.5 keV). The specific activity of ^{232}Th was estimated by the gamma lines of ^{228}Ac at 338.3 keV, 911.1 keV, and 968.9 keV and the line of ^{208}Tl at 583.0 keV. The gamma lines at 661.6 keV and 1460.7 keV were used for evaluating the activities of ^{137}Cs and ^{40}K, respectively. The specific activity of ^{7}Be was determined by the visible peak at 477.6 keV, with a decay correction to the time of sampling. Minimum detectable activities (MDAs) estimated by Currie's method (Currie 1968; Done and Ioan, 2016) were 0.44 Bq kg^{-3} and 0.40 Bq kg^{-3} for ^{226}Ra and ^{232}Th in leaves, respectively, and 0.13 Bq kg^{-3} for ^{226}Ra in grapes. The uncertainties of specific activities measured in leaves were in the ranges of 10-29% (for ^{226}Ra), 11-34% (for ^{232}Th), 3-4% (for ^{40}K) and 3-5% (for ^{7}Be). Specific activities of ^{226}Ra and ^{40}K were measured in grape samples with the uncertainties of about 5-28% and 1-2%, respectively. The uncertainties of all radionuclides measured in soil were below 10%.

Main physicochemical characteristics and metals in soils and plants

The vine leaf samples were washed with deionised water, wiped dry then air-dried and ground in a mill. Soil samples were air-dried, ground, and sieved, in accordance with ISO standard 11464:2006.

The pH value of the soil suspension in water and 1M KCl, organic matter content and the free $CaCO_3$ content were analyzed using standardized ISO methods: 10390:1994, ISO 14235:1998 and ISO 10693:1995 respectively. Particle size distribution was estimated after particle fractionation in following size fractions: coarse sand (200–2000 μm), fine sand (20-200 μm), silt (20 μm) and clay (2 μm). The fractionation was performed by the sieving and pipetting method (Van Reeuwijk, 2002).

Main physical and chemical characteristics of the soil are given in Table 1. The soil pH measured in 1M KCl solution ranged from moderately acidic (4.79) to neutral (7.43) and the average soil pH value per location was 5.8 in Aleksandrovac, 7.2 in Orahovac and 6.6 in Topola. The $CaCO_3$ content showed high heterogeneity and ranged from below detection limit (<0.2%) to 35.1% with the highest average content in samples from Orahovac (13.0%). Organic matter content ranged from 1.1 to 3.6% whereas the values between 2 and 3% are considered optimum for grapes (Dami et al., 2005). Clay content ranged from 8.8 to 47.9% relative to the particle size distribution with the greatest variation in samples from Orahovac (from 8.8 to 34.1%).

Fifteen elements (As, Cd, Co, Cr, Cu, Ni, Mn, Pb, Zn, Fe, K, Na, Ca, Mg and Hg) were determined in soils and grape leaves. The digestion of soil samples was performed in a microwave sample preparation system Milestone Ethos 1 by treating 0.5 g of dried soil samples with 9 mL of HNO_3 (concentrated, 65%) and 1 mL of HCl (concentrated, 37%), in a closed

7

teflon vessels at high pressure and temperature of 180°C for 25 minutes. Both acids used for digestion of soils were ultrapure grade. After digestion was finished, the vessels were allowed to cool and then uncapped. Digested samples were filtered and transferred in 50 mL flasks and diluted with deionized water. The vine leaves were dried at the temperature below 60°C to constant mass and homogenized in a mortar. 0.5 g of dried vine leaves were treated with a mixture of 10 mL of HNO_3 (concentrated, 65%) and 2 mL of H_2O_2 (concentrated, 30%) in a closed teflon vessels at high pressure and temperature using Milestone Ethos 1 digestion system. Analysis of heavy metals in prepared soil and vine samples was performed using ICP-OES (Varian Vista Pro-axial).

Quality assurance and quality control (QA/QC) were provided by analysis of certified reference materials SRM1515 (Apple leaves) and IRMM BCR 142R (Light sandy soils). Obtained results achieved adequate analytical accuracy and precision. Wavelengths used for analysis, method detection limits, reference materials recoveries and uncertainties are given in Table S1.

Total mercury content in soil and vine leaves was measured directly, using DMA 80 Direct Mercury Analyzer (Milestone), in accordance with US EPA Method 747, without any sample pretreatment except drying and grounding. The limit of detection for total mercury content was 0.0033 mg kg^{-1}. Quality control was periodically carried out with IRMM BCR reference materials 143R and deviations were within ±5 % of the certified values.

All reagents were analytical grade or better and blank samples were included in each extraction procedure. All calibration standards were prepared in the same acid matrix used for soil and leaves samples.

Data processing

IBM SPSS Statistics 20 software was employed for data processing. Shapiro-Wilk test was applied to check for the normality of data distribution. Since not all variables were normally distributed, nonparametric Spearman's rank correlation coefficient (*rho*) was used in correlation analysis. The significance was also estimated by *p*-value ($p<0.05$ was considered as statistically significant and $p<0.01$ was considered highly significant)."Principal component analysis (PCA) was conducted because it is a widely used and adaptive descriptive data analysis tool that permits identification of the structure of the interdependences between the main studied parameters. Before statistical analysis, in order to obtain symmetric distribution of data, which is not often present among the environmental variables, the data were log-transformed. The number of PCs extracted from the variables was determined by Kaiser's rule (Kaiser and Rice, 1974). Relationships between the samples were evaluated on the score plots, whereas the loading plots showed the extent to which each variable contributed to the sample separation (grouping). Statistical data interpretation for the principal component analysis, descriptive statistics and correlations were processed using STATISTICA for Windows version 13.0 (StatSoft, Germany).

Results and discussion

Radioactivity

Specific activities of radionuclides measured in vineyard soils, leaves and grape berries are presented in Table 2. The lowest levels of natural radioactivity in soil were measured in Orahovac. The average specific activities of ^{226}Ra, ^{232}Th and ^{40}K in the soils of Aleksandrovac

(34.9, 48.1 and 720 Bq kg^{-1}, respectively) were generally two times higher than those of Orahovac (16.2, 26.1 and 334 Bq kg^{-1}, respectively), but the same pattern could not be observed for leaves and grape samples. Artificial radionuclide ^{137}Cs, presumably originated from the Chernobyl nuclear accident, was detected in all soil samples in low levels (0.5 – 16.1 Bq kg^{-1}) which are typical for cultivated soils in these areas (Bikit et al. 2005). Average annual effective doses (D_E) in air (at 1 m above ground level) calculated based on specific activities of ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs in soil(UNSCEAR 2008; Kapdan et al. 2011) were 93.9, 46.6, and 83.8 μSv in the vineyards of Aleksandrovac, Orahovac and Topola, respectively. Cosmogenic radioisotope ^{7}Be was found in leaves (in the range of 133 – 291 Bq kg^{-1}) presumably as a consequence of atmospheric deposition.
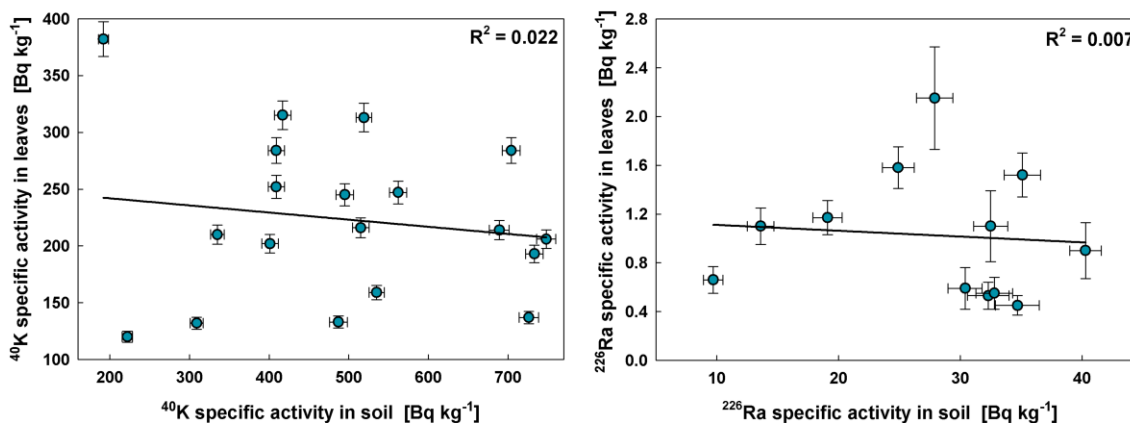
Fig. 1 Correlations between radionuclides (^{40}K and ^{226}Ra) in leaves and in soil samples

Transfer factors (TF) of elements (radionuclides as well as metals) were calculated by dividing concentrations of elements in plants by those in soils. The last four columns of Table 2 present soil-to-leaves (S-L) and soil-to-grape (S-G) transfer factors for ^{226}Ra and ^{40}K. As expected, soil-to-leaves transfer factors were higher than soil-to-grape TFs. S-L TF$_{K40}$ ranged from 0.19 to 1.99 and the average value obtained for Orahovac (0.75) was significantly higher

than that of Aleksandrovac (0.29) and Topola (0.51). According to the correlation analysis, there was a weak negative correlation between ^{40}K in leaves and in soil samples (Fig. 1). Evidently, these unexpected results support the fact that absorption, bioaccumulation, and distribution of radionuclides in plants are affected by many different factors (such as soil properties, vine types, local climate etc.) and cannot be readily predicted based on the radioactivity of underlying soil.

Correlations of radionuclides and physicochemical characteristics of soil were investigated, and the results are summarized in Table S2. Strong positive correlations between ^{226}Ra and ^{232}Th, as well as between ^{226}Ra and ^{40}K in soil can be explained by similar geochemical behavior of these natural radionuclides. Specific activities of natural radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) were negatively correlated with soil pH (Table S2). Natural radionuclides were also strongly negatively correlated with $CaCO_3$ indicating their binding with soil minerals other than calcite (Dragović et al. 2012). The correlations between radionuclides and soil particle size confirmed that coarse-grained soils have lower tendency for radionuclide adsorption than fine grained soils due to the larger soil particle surface area (Navas et al. 2002). ^{226}Ra and ^{232}Th were positively correlated with silt and clay, and negatively correlated with sand content in soil.
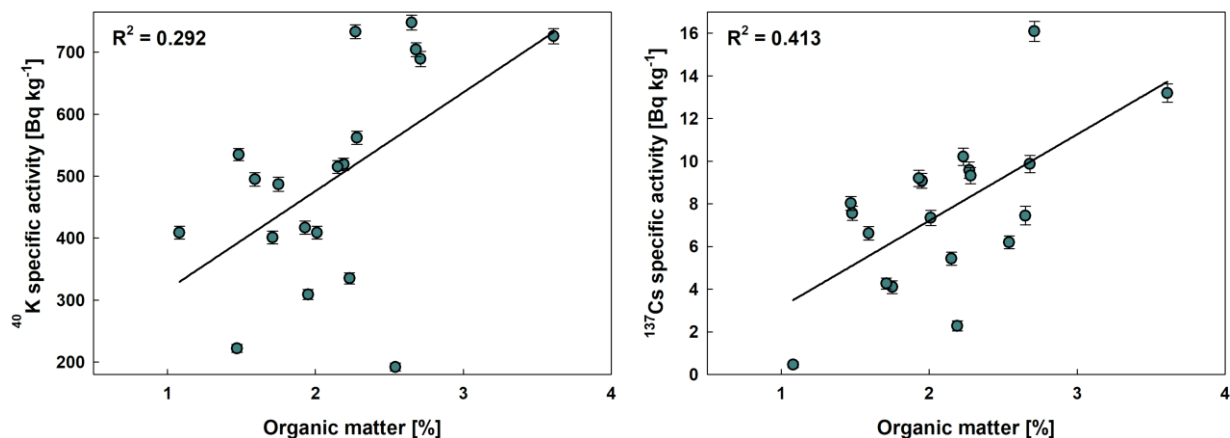
Fig. 2 Correlations of specific activities of ^{40}K and ^{137}Cs with organic matter

Organic matter is a very important characteristic of soil because it contains functional groups which have tendency to form soluble or insoluble compounds with radionuclides. This complexation controls the mobility of radionuclides in the environment, adsorption to soils and biological availability (Dragović et al. 2012). Organic matter decomposition changes soil property from an oxidizing to a reducing medium. Insoluble precipitates may be formed with carbonate, hydroxyl, phosphate or sulfide ions in alkaline soils (high pH), and thus reduce the availability of radionuclides for plants. Specific activities of ^{232}Th and ^{226}Ra measured in present study were not significantly correlated with organic matter content in soil. However, correlations between organic matter and specific activities of ^{40}K ($p<0.05$) and ^{137}Cs ($p<0.01$) are shown on Fig 2.

Metals

Metal concentrations measured in soil samples are presented in Table 3. In regulations for soil quality (Official Gazette 2018; VROM 2000) regulatory limits (target and intervention values) are defined for As, Cr, Cu, Pb, Ni, Co and Zn. In this study, the concentrations of Co higher than target value (9 mg kg^{-1}) were detected in almost all soil samples with the highest concentration of 15.4 mg kg^{-1} detected in the soil from Orahovac. Cd concentrations above target value (0.8 mg kg^{-1}) were detected in all soils sampled at Orahovac and ranged from 3.0 to 10.3 mg kg^{-1}. All analyzed soils are rich in Ni, especially at Orahovac where Ni concentration in soil exceeds intervention value of 210 mg kg^{-1}. Elevated concentrations of Cr (above target value of 100 mg

kg^{-1}) were detected only in soil samples from Orahovac. Chromium and nickel usually originate from the parent substrate on which the soil was formed. According to the Geochemical Atlas of Europe (Salminen et al. 2005), there are naturally elevated concentrations of Cr and Ni in the soil in different parts of the Balkan Peninsula since the soils are formed on ultramafic rocks rich on heavy metals. Some previous studies have reported the existence of mineral deposits rich in Cr and Ni near the Orahovac vineyards (Ruppert et al. 1996; Monthel et al. 2002). High positive correlation between Cr and Ni concentrations in analyzed soils (Spearman rho = 0.851) also indicate their natural origin (Ajmone-Marsan et al. 2008). Correlation analysis between radionuclides and metals in soil (Table S2) shows strong negative correlation of ^{40}K with Cr and Ni ($p<0.01$). This finding is in contradiction to the results reported by Dragović et al. (2012) and Van der Graaf et al. (2007) who have previously found positive correlations between ^{40}K and these metals. Vineyard soils in Orahovac are rich in Cd and since there is a strong positive correlation between Cd and Cr (Spearman rho = 0.690) and Cd and Ni (Spearman rho = 0.775) it can be assumed that Cd origin in analyzed soils is geochemical.

Worldwide, vineyard soils are usually polluted by Cu, up to several times higher than the regulated values, due to the long-term use of Cu-based fungicides (Duplay et al. 2014). Therefore, Cu can reach toxic levels inducing plant stress and reduction of soil fertility (McBride et al. 1981). In this study, Cu concentration in the soil samples was in the range of 33.7–451 mg kg^{-1}. According to Serbian Soil Quality Regulation, the target value for Cu (36 mg kg^{-1}) was exceeded in almost all samples while two samples from Aleksandrovac were above the intervention value (190 mg kg^{-1}). However, these concentrations were comparable with the data obtained for soils similarly treated by fertilizers and pesticides in other countries (Pueyo et al. 2004; Kelepertzis et al. 2015) and vineyard soils worldwide (Komárek et al. 2010). The

concentrations of Cu are significantly correlated with Zn (Spearman rho = 0.495) so the hypothesis reported by Komárek et al. (2010) that Cu and Zn originate from the same source (the frequent application of agrochemicals) could be confirmed. According to Spearman correlation analysis, Cu was moderately correlated with Fe (rho = 0.402) and strongly correlated with organic matter content in soil (rho = 0.675). This result is in line with the previous study of Parat et al. (2002) who suggested that Cu bounds to organic matter protecting it against biodegradation. The same study has also identified Fe as an important factor in Cu accumulation.

Cu, Mn, Ni, Zn, Fe, K, Na, Ca and Mg were detected in measurable concentrations in grapevine leaves (Table 4). According to Bravo et al (2017), soil pH has a significant influence on the uptake of heavy metals that have two or more oxidation states in the soil (i.e., Fe, Mn, Cu and Pb). In other cases, the uptake is mainly influenced by the ionic potential. In this study, the uptake of As, Cd, Co, Cr, Pb and Hg in grapevine leaves was low and the concentrations of these metals were below minimum detectable levels which are 0.987; 0.084; 0.084; 0.140; 0.086 and 0.0033 mg kg^{-1} respectively. This is in good agreement with the results obtained by Milićević et al (2018) who analyzed bioavailability of toxic elements for grapevines grown in Oplenac grapevine growing area. The low bioaccumulation of the elements in the grapevine is probably a consequence of the mainly neutral or alkaline pH value and low content of organic matter in soil, which does not accelerate the toxic elements' desorption from the soil matrix (Kabata-Pendias and Mukherjee 2007).

Transfer factors for metals are presented in Table 5. TF higher than 1 indicates that plant could be considered as accumulator of metal from soil. TF for Mn, Fe and K were less than 1 for all analyzed samples which in agreement with the results obtained by Bravo et al. (2017) who analyzed TF in 101 samples of grapevine leaves and concluded that although influenced by soil

pH grapevine leaves do not accumulate Mn, Fe, and K strongly enough to be considered as accumulators. Milićević et al. (2017) stated that some grapevine varieties including *Cabarnet Sauvignon* could be considered as accumulators of Zn from soil as their TF_{Zn} is greater than 1. This finding could not be confirmed in our study since the TF_{Zn} was in the range from 0.21 to 0.69 with only one exception for *Smederevka* variety grown in Orahovac (sampling site No. 10) where TF_{Zn} was 1.39.

The concentration of Cu in the leaf samples varied in a wide range from 22 mg kg^{-1} up to 2195 mg kg^{-1} and TF_{Cu} values which ranged from 0.10 to 59.82. Elevated Cu concentrations in soils which are result of frequent application of Cu-based fungicides could influence its content in the grapevine leaves due to increased Cu uptake by grapevine but copper is generally a slightly mobile element in plants as it is strongly bound by nitrogen and proteins (Komárek et al. 2010). Elevated concentrations of Cu in grapevine leaves and high TF_{Cu} are the result of foliar application of Cu-based fungicides which is also concluded by Milićević et al (2018) who analyzed correlation between different Cu fractions in soil and its quantity in leaves and grapes. The cultivars have been treated with fungicides 2-3 times during the vegetation period. These fungicides contained mostly copper sulphate (CuSO4), and they have been used for direct protection from *Botrytis cinerea*. An individual pattern of treatments derived by winegrowers could lead to an unclear situation about Cu concentrations in soils and leaves. This presumably caused a lack of soil-to-plant correlations.

Heavy metal concentrations measured in leaves in relation to the concentrations in soil are presented in Fig 3. Weak correlations have been found for the metals (Cu, Mn, Ni and Zn) in leaves and in soil (Spearman rho = -0.258, 0.037, 0.134, 0.175, respectively). Concentrations of Ca, Fe, Mg, and Na measured in leaves are also not strongly correlated with the concentrations in

soil (Spearman rho = -0.098, -0.058, 0.498, 0.421, respectively). These findings are in line with the fact that the mechanisms involved in the transport of elements from soil to vine leaves and grapes are rather complicated and affected by many different factors.
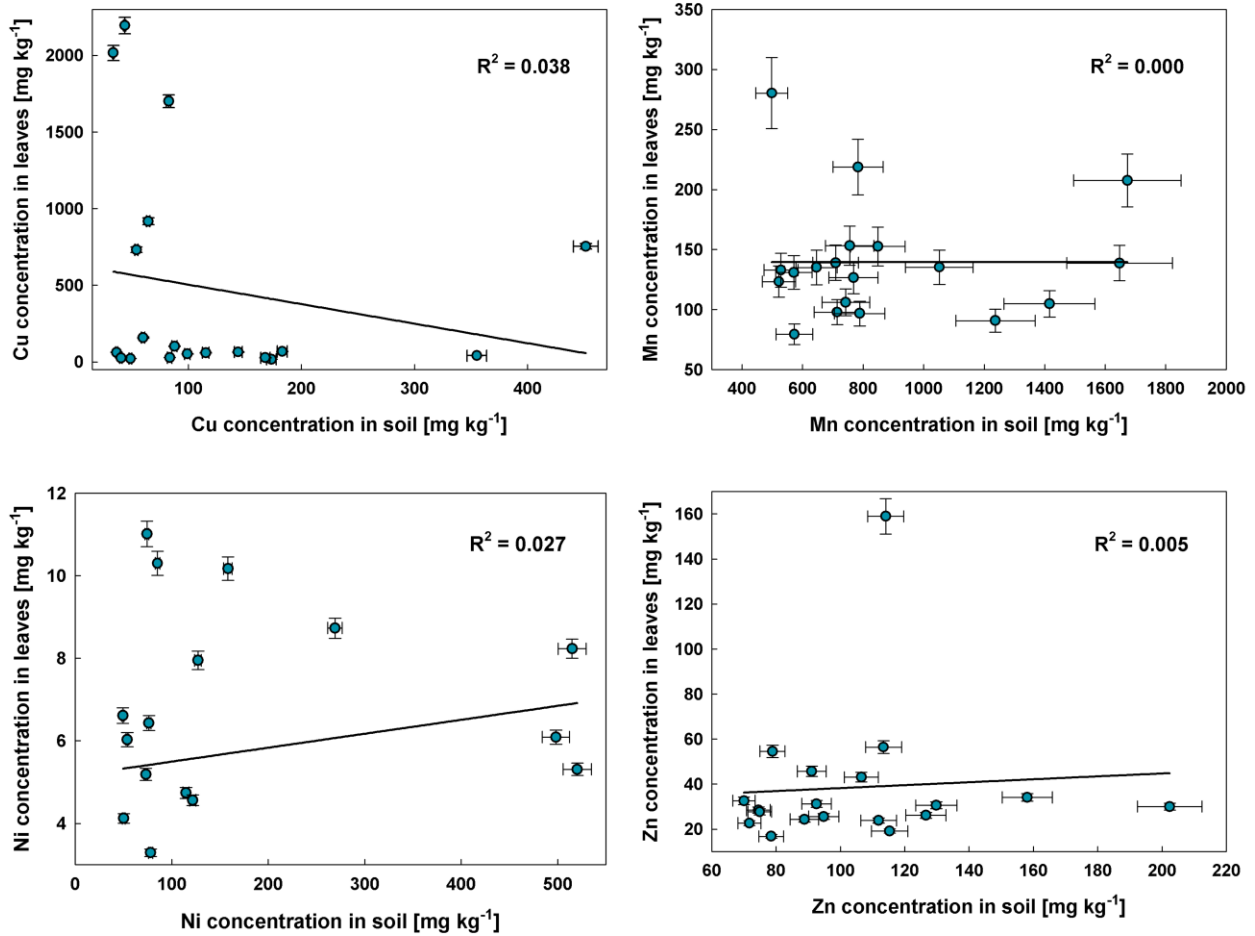

Fig. 3 Correlations between metal concentrations in leaves and soil samples

Principal Components Analysis (PCA)

PCA aims at finding and interpreting hidden complex, and possibly causally determined relationships between features in a dataset. Correlating features are converted to the so-called

factors which are themselves non correlated. PC and its eigenvalues identify the most important gradients in the dataset.

Clustering of samples based on their similarity were estimated on the score plots (Fig. 4A), whereas the loading plots (Fig. 4B) show how strongly each characteristic influences a principal component analyses and to which extend they contributed to the separation. PCA produced five principal components (PC/factor) with an eigenvalue greater than 1 and explanation of 76.15% in the total variance. Loading values of each principal component are shown in Table S3. The first two PCs had the greatest contribution to the variation. The first principal component (PC1) accounting for 30.70% of the total variance, correlated significantly with the pH (H_2O), contents of $CaCO_3$, Na, Ca, ^{40}K and ^{226}Ra in soil as well as with the TF_{Ca}, ^{226}Ra and plant Na and Ca. Radium is a member of the alkaline earth metals, a group which contains important elements for plant nutrition (calcium and magnesium). In the case of radium, strong correlations have been observed with calcium concentrations in plants, and with exchangeable potassium uptake (Mitchell et al. 2013). Calcium is known to be freely translocated in the xylem but discriminated against in the phloem. This is likely to be the case also for radium. If so, radium absorbed by leaves will be immobilised and accumulated in the specific leaves in which it is absorbed (Mitchell et al. 2013).

First principal component showed positive correlation with pH, $CaCO_3$, Ca, Na, Mg, and Cr in the soil as well as Na, Zn, Mg, Cr and Cu in plant. Also, positive correlations are distinctive for transfer factors of ^{40}K, ^{226}Ra, K, Mg and Cu (Table S3). Conversely, the first principal component showed negative correlation with the soil OM, Clay %, ^{40}K, ^{226}Ra, Zn, Pb and Cu. Negative correlation with the fine fractions silt and clay, pH and carbonates, as well as

radionuclides (^{40}K and ^{238}U), in the case of moraine soils, was observed also in Navas et al. (2018).

Since PC1 had the highest total variance its parameters were most important in assessing variations soil and plant relation. However, PC2 can also be used for describing additional gradients in dataset with total variance of 17.21%. PC2 was mainly correlated with variables pertaining to Mg, Co and Cr in the soil and TF of K. Accounting for 11.58% and 9.69% of the total variance, PC3 and PC4 substantially described the soil characteristics at the sampling locations. Similar PCA results for radionuclides in plants and soil characteristics were reported by Djelic et al. (2016). The different association of the investigated soil properties, concentrations of radionuclides in soils and plant transfer factor in examined sites might be due to the differential pedogenic and agroecological production conditions. Soil characteristics of stable elements in soil (OM, Clay content, content of K) are associated with the ^{40}K and ^{226}Ra in soil. On the contrary, association of the pH, CaCO$_3$ as well as Na in soil and plant content (majority of examined elements) as well as transfer factors of ^{40}K and ^{226}Ra, suggesting that those characteristics could influence plant uptake.
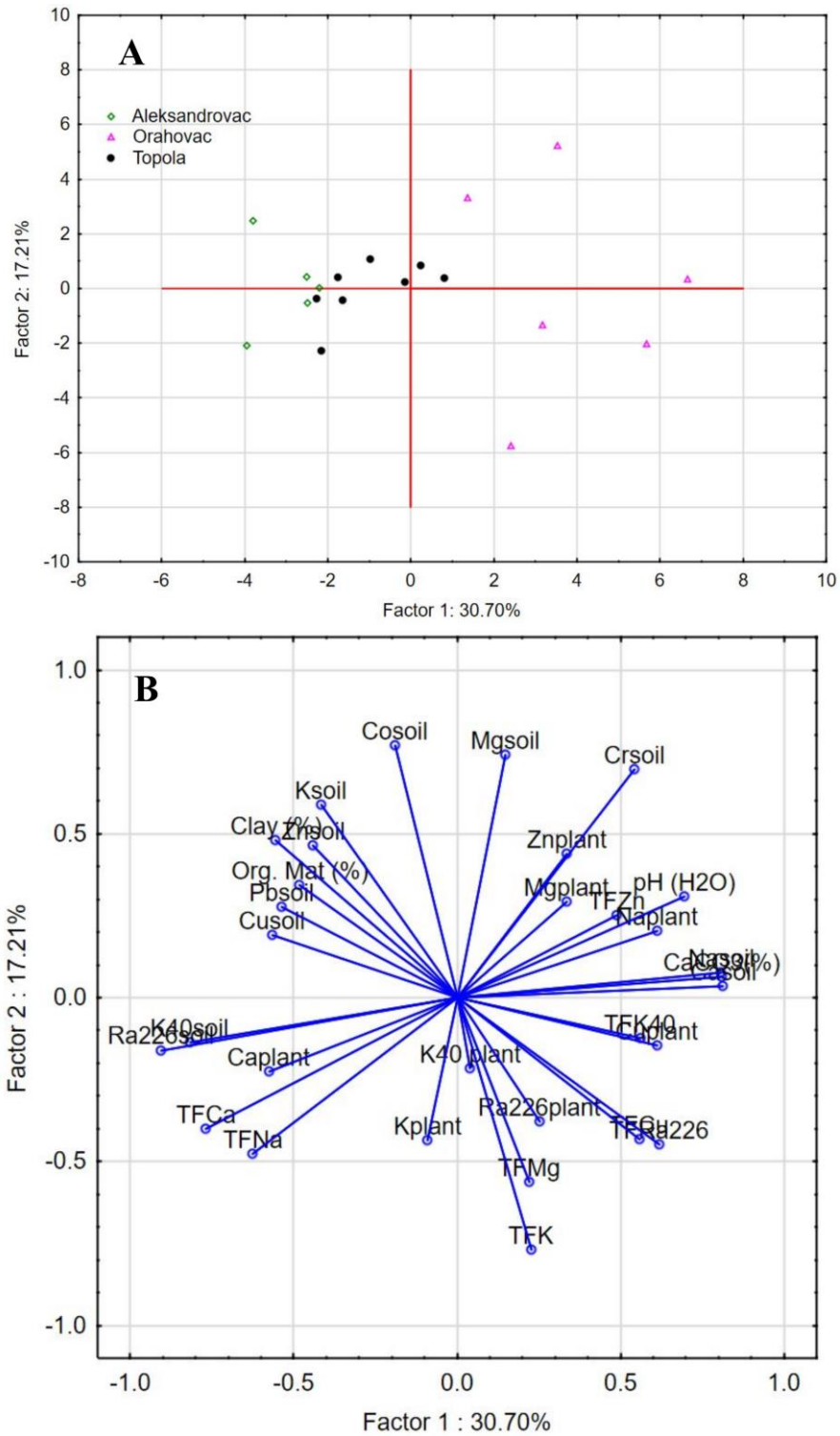
Fig. 4 Principal component analysis among soil characteristics, radionuclide content in plants,

soils and TF: A - projection of cases, B – projection of variables

The scatter plots of the first two PCs depicted the positions of analyzed sites and variables in the investigated properties space (Fig. 4A). PC1 enables distinction between the site Aleksandrovac and Topola relative to site Orahovac. Additionally, gradient of (negatively) correlated variables with the PC1 axis, showed that sites Aleksandrovac and Topola had a higher concentration of correlated variables. Biplot showing factor loadings is presented at Fig. 4B.

Obtained results imply that there are various atmospheric processes and accumulation mechanisms affecting radionuclide activity concentrations and metal content in plant samples. Table S3 and Fig 4 indicate that grape plants and underlying soils are most sensitive to the basic chemical properties from terrestrial sources such as pH, $CaCO_3$, Ca, Na, Mg, OM and Clay content.

Conclusion

Strong positive correlations were found between ^{226}Ra and ^{232}Th, as well as between ^{226}Ra and ^{40}K in soil, confirming similar geochemical behavior of these natural radionuclides. ^{226}Ra and ^{232}Th were positively correlated with silt and clay, and negatively correlated with sand content in soil, soil pH and $CaCO_3$. Significant correlations of ^{40}K and ^{137}Cs with organic matter in soil were observed.

All analyzed soils were rich in Ni, Cu and Co while elevated concentrations of Cr and Cd were detected only in soils in Orahovac. According to correlation analysis, it can be assumed that Cr, Ni and Cd in analyzed soils were probably of geochemical origin. Cu concentration in the soil samples exceeded the regulatory limit in almost all samples presumably because of long-term

24 use of copper fungicide. However, high values of TF_{Cu} in Orahovac (2.65 – 59.82) indicate that

25 Cu in leaves probably comes from the recent application of copper fungicides rather than from

26 the absorption from soil. Principal component analyses indicate that grape plants and underlying

27 soils are most sensitive to the basic chemical properties from terrestrial sources such as pH,

28 $CaCO_3$, Ca, Na, Mg, OM and Clay content.

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Declarations

33 **Ethics approval and consent to participate:** Not applicable

34 **Consent for publication:** Not applicable

35 **Availability of data and materials:** All data generated or analysed during this study are

36 included in this published article and its supplementary information file.

37 **Competing interests:** The authors declare that they have no competing interests.

41 **Authors' contributions:** LjG conceived and designed the study, collected the samples and wrote

42 a part of the manuscript. JMS and BM prepared the samples; measured specific activities of

43 radionuclides, performed statistical analysis and wrote the main part of the manuscript. TZ

44 determined metal concentrations and soil properties and provided appropriate discussion on the

45 subject. SM performed PCA analysis. DK provided HPGe detector efficiencies for gamma

46 spectrometry measurements. All authors read and approved the final manuscript.

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171   **Table 1.** Physical and chemical characteristics of analyzed soils

		pH (In KCl)	pH (In H₂O)	CaCO₃ (%)	OM (%)	Particle size distribution			
						Sand (2-0.2 mm) (%)	Fine sand (0.2-0.02 mm) (%)	Slit (0.02-0.002 mm) (%)	Clay (<0.002 mm) (%)
Aleksandrovac	1	6.02	7.28	nd	3.61	9.08	30.56	26.32	34.04
	2	4.79	5.78	nd	2.27	11.54	31.62	26.48	30.36
	3	5.95	6.85	nd	2.71	12.33	32.95	24.44	30.28
	4	6.44	6.99	0.08	2.68	11.65	29.39	29.44	29.52
	5	6.27	6.94	0.16	2.65	11.85	27.39	30.8	29.96
Orahovac	6	6.75	7.41	0.16	1.48	20.82	50.7	19.64	8.84
	7	7.17	8.04	3.76	1.08	6.58	36.66	23.28	33.48
	8	7.28	8.1	35.1	1.47	11.14	46.22	24.4	18.24
	9	7.43	8.11	25.91	2.54	23.12	44.52	16.96	15.4
	10	7.25	8.13	7.52	2.23	3.23	39.89	23.8	33.08
	11	7.16	8.26	5.43	1.95	5.91	37.65	22.36	34.08
Topola	12	7.2	8.16	5.85	1.75	12.41	26.95	25.68	34.96
	13	7.11	8.07	1.25	2.28	4.96	27.32	28.44	39.28
	14	7.27	8.15	10.86	1.93	6.62	24.3	31.08	38
	15	6.63	7.43	0.25	2.19	4.08	25.92	28.24	41.76
	16	5.09	6.37	nd	2.01	3.86	25.94	31.8	38.4
	17	6.48	7.53	0.42	1.59	3.1	27.54	33.4	35.96
	18	5.71	6.65	0.08	1.71	2.92	22.28	26.88	47.92
	19	7.26	8.11	7.52	2.15	6.41	24.51	30.52	38.56

172   nd – not detected

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Table 2. Specific activities and transfer factors for [226]Ra and [40]K

	No	SOIL [Bq kg⁻¹ d.w.]				LEAVES [Bq kg⁻¹ d.w.]				GRAPES [Bq kg⁻¹ w.w.]		TF$_{Ra226}$		TF$_{K40}$	
		^{226}Ra	^{232}Th	^{40}K	^{137}Cs	^{226}Ra	^{232}Th	^{40}K	^{7}Be	^{226}Ra	^{40}K	Soil to leaves	Soil to grapes	Soil to leaves	Soil to grapes
Aleksandrovac	1	34.9	43.1	726	13.2	nd	nd	137	222	0.18	195	-	0.01	0.19	0.27
	2	40.3	51.1	733	9.58	0.90	0.90	193	136	0.15	127	0.02	0.00	0.26	0.17
	3	32.5	44.8	689	16.1	1.10	nd	214	291	1.10	90	0.03	0.03	0.31	0.13
	4	32.3	50.7	704	9.87	0.53	0.44	284	208	2.62	100	0.02	0.08	0.40	0.14
	5	34.7	50.6	748	7.45	0.45	0.58	206	238	0.59	78	0.01	0.02	0.28	0.10
Orahovac	6	19.1	28.5	535	7.56	1.17	1.44	159	172	nd	145	0.06	-	0.30	0.27
	7	24.9	35.4	409	0.46	1.58	nd	284	206	nd	132	0.06	-	0.69	0.32
	8	9.7	16.0	222	8.02	0.66	nd	120	133	nd	148	0.07	-	0.54	0.67
	9	13.6	20.0	192	6.20	1.10	nd	382	162	nd	167	0.08	-	1.99	0.87
	10	16.9	28.2	335	10.2	nd	nd	210	189	nd	102	-	-	0.63	0.30
	11	13.2	28.4	309	9.08	nd	nd	132	179	nd	82	-	-	0.43	0.27
Topola	12	27.9	52.8	487	4.10	2.15	1.97	133	220	nd	92	0.08	-	0.27	0.19
	13	35.1	56.1	562	9.32	1.52	nd	247	194	0.86	102	0.04	0.02	0.44	0.18
	14	28.8	47.3	417	9.20	nd	nd	315	159	nd	117	-	-	0.76	0.28
	15	34.3	44.5	519	2.28	nd	1.33	313	250	nd	142	-	-	0.60	0.27
	16	32.4	55.2	409	7.34	nd	0.55	252	155	0.47	151	-	0.01	0.61	0.37
	17	41.9	68.1	495	6.62	nd	nd	245	200	0.40	151	-	0.01	0.50	0.31
	18	32.8	56.8	401	4.26	0.55	nd	202	182	1.31	94	0.02	0.04	0.50	0.23

| 19 | 30.4 | 49.5 | 515 | 5.43 | 0.59 | nd | 216 | 157 | 0.48 | 98 | 0.02 | 0.02 | 0.42 | 0.19 |

nd – not detected

Table 3. Concentration of elements in soil (in mg kg^{-1}).

		As	Co	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Ca	Fe	K	Mg	Na
Aleksandrovac	1	11.5	**10.6***	nd	90.4	**451****	0.059	743	**54***	17.8	**202***	8698	36000	9103	12280	325.1
	2	9.4	**10.4***	nd	75.2	**173***	0.047	768	**50.3***	20.8	94.8	5330	31790	6089	9735	244.2
	3	10.6	**10.7***	nd	54.5	**355****	0.079	522	**49.4***	17.3	106	5257	31670	6275	10770	268.1
	4	11.6	**10.8***	nd	76.9	**168***	0.046	849	**78.2***	23.9	113	5655	30700	6673	9945	309
	5	13.7	**11.1***	nd	69.9	**183***	0.071	646	**74.4***	19.6	115	4312	29700	7292	9793	299.8
Orahovac	6	6.7	7.2	nd	51.8	33.7	0.038	529	**76.4***	12.5	70	4592	20050	2529	6715	217.8
	7	13.5	**11.1***	**4.5***	**140***	**43.8***	0.031	783	**269****	14.6	78.9	24530	32420	7292	8271	748.2
	8	6.2	**11.0***	**8.0***	**159***	**64.6***	0.054	1647	**498****	13.6	74.5	138500	27970	4406	11390	3675
	9	5.6	6.2	**3.0***	87.7	**54.1***	**0.302***	498	**158***	14.3	91.1	113600	16870	5427	6986	2889
	10	8.4	**15.4***	**10.3***	**210***	**82.7***	0.072	1416	**520****	22.2	114	29550	35600	6172	16350	969.9
	11	9.4	**13.1***	**9.7***	**207***	**60.1***	0.09	1237	**515****	22.4	78.5	25750	33500	5983	14620	874.8
Topola	12	16.8	**10.6***	nd	93.1	**48.9***	0.046	756	**114***	24	74.9	29790	25750	7322	8442	1025
	13	11.3	**12.6***	nd	**109.0***	**83.6***	0.057	709	**127***	25.4	**158***	8568	25680	7191	7884	541
	14	10.5	**11.3***	nd	85.3	**87.8***	0.065	571	**115***	18.4	130	35060	22510	7744	6965	1447
	15	9.9	**12.8***	nd	82.8	**36.5***	0.043	573	**85.8***	22.7	88.8	5256	26360	6282	6713	412.1
	16	11.8	**12.0***	nd	76.8	**144***	0.035	1673	**85.3***	31.5	92.6	4503	28980	6229	6907	349
	17	11.5	**10.7***	nd	62.3	**99.2***	0.03	1052	**73.3***	27.6	71.7	5391	25450	4267	6027	351.5
	18	12.0	**12.3***	nd	100.0	**40.5***	0.036	714	**118***	21.8	127	5586	29560	6614	8228	347.1
	19	10.9	**10.6***	nd	88.7	**115***	0.06	789	**122***	20.2	112	32080	26370	6561	7384	1040

179 *exceeding target values
180 **exceeding intervention values (Official Gazette, 2018; VROM, 2000)
181 nd – not detected
182

183 **Table 4.** Concentration of elements in leaves (in mg kg^{-1})

		Cu	Mn	Ni	Zn	Ca	Fe	K	Mg	Na
Aleksandrovac	1	754	106	6.03	30.0	38540	115	5212	4546	190
	2	17.5	127	4.12	25.6	56300	219	8003	2837	211
	3	40.8	123	6.61	43.0	43680	241	4845	7110	184
	4	27.2	153	3.29	56.4	32040	394	6771	3419	224
	5	68.4	135	11.01	19.1	21970	348	4144	5623	161
Orahovac	6	2016	133	6.43	32.6	23620	199	5534	4956	220
	7	2195	219	8.73	54.5	30650	236	8145	4907	229
	8	918	139	6.09	28.4	20450	222	5827	5329	264
	9	731	280	10.17	45.7	29920	158	5526	4688	209
	10	1701	105	5.31	158.9	22620	269	4668	6377	266
	11	159	91	8.23	16.8	27740	329	4053	5250	208
Topola	12	22.2	153	nd	27.7	31280	784	3598	4600	200
	13	28.5	139	7.95	34.1	26920	1818	4903	4364	230
	14	102	131	4.74	30.6	29360	901	6383	3331	204
	15	62.3	79	nd	24.3	25070	263	7449	3065	199
	16	64.9	208	10.30	31.2	36760	229	5293	4728	226
	17	52.4	135	5.19	22.7	41400	147	6752	3435	186
	18	26.9	98	nd	26.1	29030	241	5203	4338	189
	19	60.2	97	4.56	23.8	41260	1780	5800	4151	235

184 nd – not detected

185

186   **Table 5.** Transfer factors from soil to leaves for metals

		TF_{Cu}	TF_{Mn}	TF_{Ni}	TF_{Zn}	TF_{Ca}	TF_{Fe}	TF_{K}	TF_{Mg}	TF_{Na}
Aleksandrovac	**1**	1.67	0.14	0.11	0.15	4.43	0.00	0.57	0.37	0.58
	2	0.10	0.16	0.08	0.27	10.56	0.01	1.31	0.29	0.86
	3	0.11	0.24	0.13	0.40	8.31	0.01	0.77	0.66	0.69
	4	0.16	0.18	0.04	0.50	5.67	0.01	1.01	0.34	0.72
	5	0.37	0.21	0.15	0.17	5.10	0.01	0.57	0.57	0.54
Orahovac	**6**	59.82	0.25	0.08	0.47	5.14	0.01	2.19	0.74	1.01
	7	50.11	0.28	0.03	0.69	1.25	0.01	1.12	0.59	0.31
	8	14.21	0.08	0.01	0.38	0.15	0.01	1.32	0.47	0.07
	9	13.51	0.56	0.06	0.50	0.26	0.01	1.02	0.67	0.07
	10	20.57	0.07	0.01	1.39	0.77	0.01	0.76	0.39	0.27
	11	2.65	0.07	0.02	0.21	1.08	0.01	0.68	0.36	0.24
Topola	**12**	0.45	0.20	-	0.37	1.05	0.03	0.49	0.54	0.20
	13	0.34	0.20	0.06	0.22	3.14	0.07	0.68	0.55	0.43
	14	1.17	0.23	0.04	0.24	0.84	0.04	0.82	0.48	0.14
	15	1.71	0.14	-	0.27	4.77	0.01	1.19	0.46	0.48
	16	0.45	0.12	0.12	0.34	8.16	0.01	0.85	0.68	0.65
	17	0.53	0.13	0.07	0.32	7.68	0.01	1.58	0.57	0.53
	18	0.67	0.14	-	0.21	5.20	0.01	0.79	0.53	0.54
	19	0.52	0.12	0.04	0.21	1.29	0.07	0.88	0.56	0.23

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