

## The content of Cd and Pb in undeveloped and shallow soils and plant material in the area of national park Tara

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### Abstract

Ultramafic (serpenites) are a group of igneous or metamorphic rocks, which are characterized by high concentrations of Mg, Fe, Ni, Cr, and Co, along with low concentrations of Ca, P, and K, contain less than 45% silicon (SiO<sub>2</sub>). Tara Mountain is natural good of western Serbia where areas under serpentinites occupy 28%. Researchers agree that the flora of serpentine areas is unique and botanically very important. The specificity of the flora and the development of vegetation on serpentinites are characterized by special mechanisms of plant species adaptation to increased concentrations of some heavy metals in the soil with low content of essential elements (nutrients). This paper examines the influence of serpentinite geological substrate on the occurrence of certain plant species in the initial stages of plant community development. The soil was mainly sampled in rock crevices in the early phases of soil development (*Lithosols*) where the influence and origin of the metals from the rock can be considered the most obvious. Content of cadmium (Cd) and lead (Pb) in geological substratum, soil and plants biomass is analysed in order to differentiate levels and extents of natural and anthropogenic pollution and also deposition data from the EMEP program (European Monitoring and Evaluation Programme). Results show that the content of lead and cadmium in the soil and plant samples are higher than the content in the corresponding rock sample, except for two soil samples, in which the content of Cd is lower. This suggest that the origin of the increased Pb and Cd content might be from anthropogenic sources. Deposition (data from EMEP program) of Cd and Pb, which was analysed for the period from 1990-2018, indicate significant cumulative effect. The values of cumulative deposition in research area have a value of 91,51 kg/km<sup>2</sup> lead, while the value of cadmium is 1665 g/km<sup>2</sup>, which classifies NP Tara in above-average polluted area in R. Serbia.

*Keywords:* serpentinite, heavy metals, parent material, soil, EMEP, deposition

### Introduction

Ultramafic (serpenites) are a group of igneous or metamorphic rocks, which are characterized by high concentrations of Mg, Fe, Ni, Cr, and Co, along with low concentrations of Ca, P, and K, contain less than 45% silicon (SiO<sub>2</sub>). Soils on serpentinites are rich in chromium, nickel, manganese, zinc, cobalt, lead, etc. Determining the content of metals in the geological substratum, eg. potential natural soil pollution, as well as anthropogenic pollution of soil by heavy metals is important regarding plant species usage growing on such area. Due to intensive use of medicinal plants in modern pharmacology, but also in the traditional lifestyle, there is a need to monitor the levels of elements in the herb of these plants,

especially potentially toxic to health, such as mercury, lead and cadmium (Obratov-Petkovic et al., 2008).

Serpentine soils have properties that are highly unfavourable for most plants. They are often characterized by gravelly texture, low clay content, shallowness, susceptible to erosion and with a low content of organic matter (Farag, 2013). Strongly serpentized rocks are more susceptible to mechanical breakdown and disintegration, as well as to chemical decomposition involving considerable changes in chemical and mineralogical composition (Knežević et al., 2009). High concentrations of heavy metals (nickel, chromium, lead, cobalt, cadmium...) in serpentine soils were responsible for their infertility. Vegetative cover at serpentine sites is usually scarcer than the surrounding areas and is characterized by obligate and facultative serpentinophytes. Due to high levels of metal concentrations, plants accumulate them, which require different adaptation mechanisms to reduce their harmful effect (Farag, 2013).

The main goal of this paper is to determine the degree of influence of the parent substrate and potential anthropogenic pollution on the content of non-essential toxic metals in poorly developed soils on serpentinites. In order to determine the potential transfer of these metals in the environment, the contents in the soil, aboveground and belowground biomass were analysed. In order to define "natural pollution" rates through weathering, content of microelements in the geological substratum were analysed. Atmospheric deposition data from EMEP program were analysed.

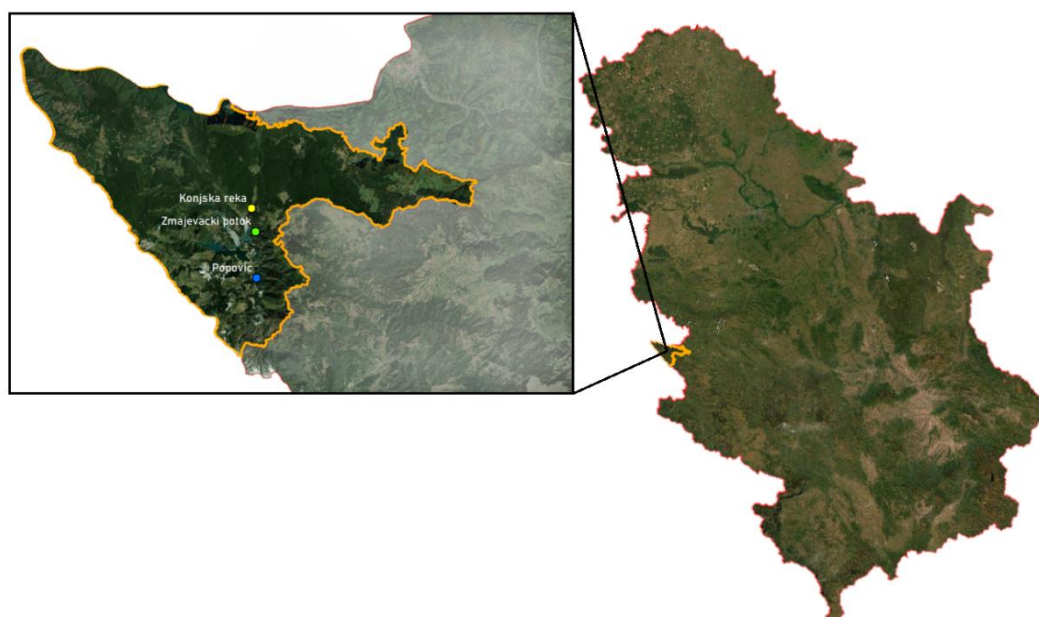
## Material and Methods

### *Research area and sampling method*

Geological substratum, soil, and plant biomass samples were collected in the NP Tara at 3 localities. Konjska reka (43°53'53.5"N, 19°25'01.0"E), Zmajevacki potok-Trenice (43°53'1.5"N, 19°25'4.6" E) and Popovici (43°51'18.7"N, 19°24'49.8"E) (Figure 1). The total number of samples is: 3 of geological substratum, 17 samples of soil, 15 samples of below ground biomass and 17 samples of above ground biomass. Plant samples were collected under favourable weather conditions using appropriate equipment, according to plant abundance and cover. The research was performed for 9 plant species: *Dorycnium pentaphyllum* subsp. *germanicum* (Gremli) Gams, *Asperula purpurea* (L.) Ehrend., *Odontarrhena muralis* (Waldst. & Kit.) Endl., *Thymus* sp., *Vaccinium myrtillus* L., *Euphorbia glabriflora* Vis., *Cytisus procumbens* (Waldst. & Kit. ex Willd.) Soil analysis were performed according to standard JDPZ methods (eng. Yugoslav Society of Soil Science); (Bošnjak et al., 1997). The content of cadmium and lead in geological substratum, soil and biomass were determined according to the standard ISO (ISO 11466:1095 Soil quality, 1995) procedure and measured by the AAS method.

Lead (Pb) and cadmium (Cd) have no established biological functions and are considered as non-essential, toxic elements (Grozdic, 2015; Tchounwou et al., 2012). In accordance with the Regulation on limit values of pollution, harmful and dangerous substances in soil (Official Gazette of the Republic

of Serbia 30/2018 and 64/2019) obtained results were compared with the limit and remediation values of dangerous and harmful substances and values that can indicate significant soil contamination.



**Figure 1.** Research area and sampling locations

### ***Deposition data - EMEP***

The European monitoring and evaluation programme for transboundary long-range transported air pollutants (EMEP) started in 1977. EMEP programme is focused on assessing the transboundary air pollution: (1) collection of emission data, (2) measurements of air and precipitation quality and (3) modelling of atmospheric transport and deposition of air pollutants. The Meteorological Synthesizing Centre-East (MSC-E) of the EMEP program is focused on heavy metals, whose data were used in this paper (<https://www.emep.int/>). Lead and cadmium deposition data were downloaded and processed, in order to determine the connection whether the metals are anthropogenic or of natural origin, for the period 1990 to 2018, for the entire Republic of Serbia, therefore, and three sampling locations in the NP Tara.

## **Results and Discussion**

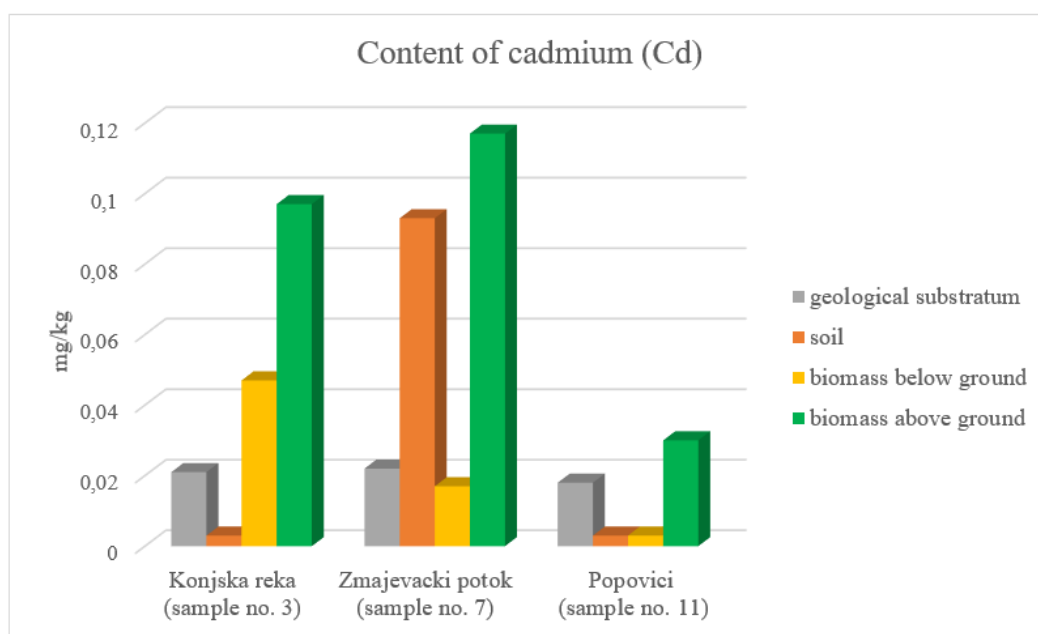
### ***Chemical properties of soil***

At the Konjska reka site, all samples show a weakly alkaline reaction, with a mean value of 7.46. At the Zmajevacki potok site, the soil is moderately acidic to neutral with a mean value of 6.52 (Knezevic et al., 2016). At the third sampling location (Popovici) soil is included in the class of weakly to moderately alkaline, with a maximum measured value of 8.27. The soil is carbonate-free, so it can be concluded that the alkaline reaction of the soil is caused by a high level of magnesium. The soil at

Konjska reka and Popovici site has moderate to high content of humus, and the soil in Zmajevacki potok is considered semi-peat soil with an average humus content 19.42% (Knezevic et al., 2016).

### **Cadmium (Cd)**

Cadmium shows a constant concentration in geological substratum, and its value is around 0.02 mg/kg. The maximum measured concentration of cadmium in the soil is 0.18 mg/kg, the minimum – 0.003, while the limit value according to the Regulation is – 0.80. The concentration of 0.003 mg/kg was measured in all samples of lithosol, and slightly higher in the samples of cambisol – 0.093 and 0.186. In biomass below ground the lowest concentration (0.003 mg/kg) was measured in *Thymus* sp. and *Euphorbia glabriflora*, and the highest (0.083) in the species *Odontarrhena muralis* and *Dorycnium pentaphyllum* subsp. In biomass above ground the lowest contents (0.003 mg/kg) are found in the species *Thymus* sp. and *Asperula purpurea*, and the maximum measured concentration (0.12 mg/kg) was in the sample of blueberry (*Vaccinium myrtillus*) (Figure 2).



**Figure 2.** Cadmium contents in the tested samples distributed by localities

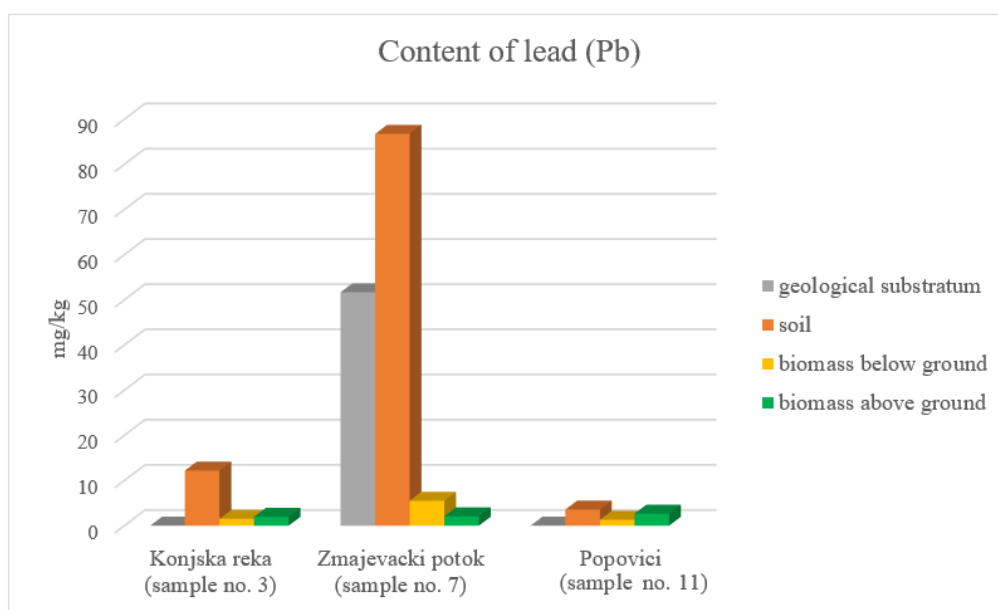
According to Kastori (1993) the average cadmium content in plants is 0.05-0.2 mg/kg, while the toxic value of Cd is estimated at 3-30 mg/kg. None of the tested plant species has a concentration close to toxic. In the soil as well, the concentration is lower than the prescribed limit and from the concentrations measured in other serpentine areas found in the literature sources. Jovanovic (2019) have recently shown that cadmium concentrations in the soil layer of 0–15 cm, are much higher, about 6.5 times, than in layer of 15–35 cm, which indicates that the reason for the high concentration of deposition.

### Lead (Pb)

Lead concentration of 0.02 mg/kg was measured in geological substratum from Konjska reka and Popovici, while concentration of 54.72 mg/kg was measured in Zmajevacki potok.

The maximum measured concentration of lead in the soil is 86.74 mg/kg, while the limit value according to the Regulation is 85. This is the only sample where the value exceeded the limit, and it is a sample of soil under the blueberry (*Vaccinium myrtillus*). However, even the minimum measured concentration in soil (0.94 mg/kg), as in all other samples, is significantly higher than that measured in the corresponding rock sample, which suggests that the presence of lead is not the result of weathering but anthropogenic origin.

This assumption is supported by the constant contents of this metal in both below ground (average 1.81 mg/kg) and above ground (average 2.56 mg/kg) plant biomass which may further indicate that this accumulation process is not naturally. None of the species, which occur naturally in this area, did not show increased accumulation as a mechanism of adaptation, when the presence of lead would be the result of natural, pedogenetic processes (Figure 3).



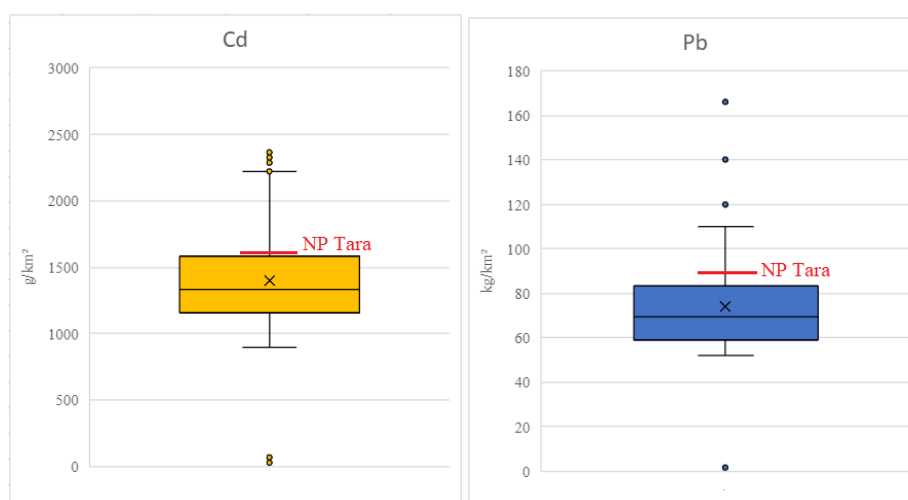
**Figure 3.** Lead contents in the tested samples distributed by localities

The measured concentration of lead in geological substratum, as well as in the soil where lithosol is present, is significantly lower than some previous measurements (Oze et al., 2020; Brankovic et al., 2016; Obratov-Petkovic et al., 2008; Vasic, 2017), while in the samples of rocks and soil from Zmajevacki potok it is almost double higher. According to the research of Jovanovic (2019) the values of lead at the same location (Zmajevacki potok) on the same geological substratum reach much higher values (228,75 mg/kg).

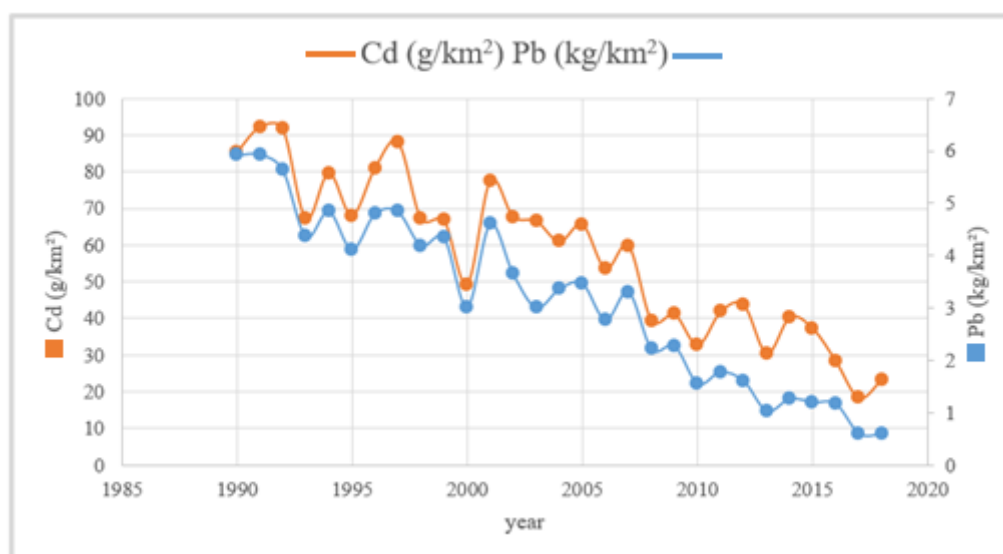
The content of Pb in the plant biomass is constant and it is in accordance with the other published data (Arsenijević et al., 2011; Kucukbay et al., 2010). According to Kabata-Pendias (2011), the Pb content in plants is in the range of 0.05-3.0 mg/kg, therefore, the tested samples do not deviate much from the average.

### *Deposition data trends-EMEP*

According to the European Program for Monitoring and Evaluation of Deposition Values (EMEP), the cumulative values of Cd and Pb deposition for the period 1990-2018 were obtained, presented for the whole R. Serbia (Figure 4). The values of cumulative deposition in the research area has value above the 75th percentile, ie, the value of lead is 91.51 kg/km<sup>2</sup>, while the value of cadmium is 1665 g/km<sup>2</sup>. Figure 5 shows the values by years for both heavy metals, for those pixels that correspond to the sampling location. Although the values have a declining trend, over the years, with slight oscillations, in both cases (Cd and Pb), there is a significant cumulative effect achieved by deposition, where the aboveground parts of vegetation implies the first level of deposition of dry and wet atmospheric deposition (Kadovic et al., 2002).



**Figure 4.** Cumulative values of Cd and Pb deposition for the period 1990-2018 in R. Serbia and mountain Tara



**Figure 5.** Pb and Cd values for the period 1990-2018 in the research area

## Conclusion

Serpentine participates in the geological substratum of the Republic of Serbia, mainly in the western and central part of the country, forming the base of many mountain massifs. The specificity of this substrate and the vegetation that grows on it is the motive for their better understanding. As previously said, one of the characteristics of the soils formed on serpentinite is high content of metals, so the plants that grow on such terrains accumulate them.

Unlike other metals, cadmium and lead are non-essential, exclusively toxic elements. They occur naturally in very small quantities, so their toxic effect results from anthropogenic influence.

The summarized result of this paper is reflected in a couple of key points. The content of lead and cadmium in the soil and plant biomass, compared to samples of geological substratum indicate that the pollution is anthropogenic origin. Values of lead concentrations regarding pollution are clear, since it exceeds the limit values according to the Regulation (Official Gazette of the Republic of Serbia 30/2018 and 64/2019), regarding cadmium it could be notified the same origin of pollution. Although cadmium concentrations in soil and plants are below the limit values (Official Gazette of the Republic of Serbia 30/2018 and 64/2019; Kastori, 1993), the presence of light anthropogenic pollution should not be neglected and have to be monitored in future. Also, the confirmation of these results are the cumulative values obtained by the EMEP program which only confirm the measured results, where the values for research area are above-average polluted region in R. Serbia, which should not be because it is a protected area.

Monitoring of heavy metals in contaminated soils and plant is one of the most significant nature conservation challenges. Such studies should provide guidelines for further control of pollutant

emissions and ratification of existing protocols on air pollution by heavy metals especially in protected areas.

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## Sadržaj Cd i pb u nerazvijenim zemljištima na serpentinitu i biljnom materijalu na području Nacionalni park Tara

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### Izvod

Ultramafiti (serpentiniti) predstavljaju grupu magmatskih ili metamorfnih stena, koje se karakterišu visokim koncentracijama Mg, Fe, Ni, Cr i Co, kao i niskim koncentracijama Ca, P i K, sadrže manje od 45 % silicijuma (SiO<sub>2</sub>). Planina Tara predstavlja prirodno bogatstvo zapadne Srbije gde površine pod serpentinitima zauzimaju 28%. Istraživači se slažu da je flora serpentinskih područja jedinstvena i botanički veoma važna. Specifičnost flore i razvoj vegetacije na serpentinitima karakterišu posebni mehanizmi prilagođavanja biljnih vrsta na povećanu koncentraciju nekih teških metala u zemljištu sa niskim sadržajem esencijalnih elemenata (hranljivih materija). Cilj ovog rada je da se ispita uticaj serpentinske geološke podloge na pojavu određenih biljnih vrsta u početnim fazama razvoja biljnih zajednica. Zemljište je uglavnom uzorkovano iz stenskih pukotina što predstavlja rane faze razvoja zemljišta (*Litosol*) gde se uticaj i poreklo metala iz stene mogu smatrati najočiglednijim. Analiziran je sadržaj kadmijuma (Cd) i olova (Pb) u geološkoj podlozi, zemljištu i biomasi biljaka, kako bi se odredio nivo i opseg prirodnog i antropogenog zagađenja kao i podaci o depoziciji iz EMEP programa (European Monitoring and Evaluation Programme). Rezultati pokazuju da je sadržaj olova i kadmijuma u uzorcima zemljišta i biljaka veći od sadržaja u odgovarajućem uzorku stena, što ukazuje da je poreklo povećanog sadržaja Pb i Cd može biti iz antropogenih izvora. Depozicija (podaci iz EMEP programa) Pb i Cd, koja je analizirana za period od 1990. do 2018. godine, ukazuje na značajan kumulativni efekat. Kumulativne vrednosti na istraživanom području iznose 91,51 kg/km<sup>2</sup> olova, dok je vrednost kadmijuma 1665 g/km<sup>2</sup>, što NP Tara svrstava u natprosečno zagađeno područje u R. Srbiji.

*Ključne reči:* serpentinit, teški metali, geološka podloga, zemljište, EMEP, depozicija

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