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Uptake of some heavy metal(oid)s by sunflower

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ABSTRACT

Plant parts of sunflower (*Helianthus annuus* L.): root, stem, leaf, and seed, as well as the soil on which this plant culture was grown were analyzed for the content of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn using Optical emission spectrometry with inductively coupled plasma (ICP-OES). The samples were prepared by wet digestion. To assess the degree of bioaccumulation in plant parts and the translocation of the examined elements from the roots to the above-ground plant parts, the Biological Concentration Factor (BCF), Mobility Ratio (MR), and Translocation Factor (TF) were calculated. BCF and MR values are less than 1 for all elements while TF (*leaf/root*) values for As, Cd, Cu, Fe, and Mn and TF (*stem/root*) values for Cu are higher than 1.

Keywords: sunflower, soil, heavy metal(oid)s, ICP-OES, bioaccumulation, translocation

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Introduction

Heavy metal(oid)s are considered to be the most common pollutants of the environment and their increased presence is a consequence of anthropogenic activities, such as mining (melting and galvanization of heavy metals), industrial waste, sewage sludge, exhaust emissions from vehicles, as well as agricultural activities: application of phosphate fertilizers, manure, and pesticides (Rai et al., 2019; Rezaeian et al., 2020; Sheoran et al., 2016).

A group of researchers from China conducted research with four commercial oil crops (rapeseed, sunflower, peanut, and sesame seeds) to use these agricultural species in the process of phytoremediation of agricultural soil contaminated with cadmium and lead due to mining activities. In a one-year field experiment, they applied three, so-called rotation systems (after harvesting the oilseed rape, sunflower, peanut, and sesame were planted separately and then harvested). In this experiment, 458.6 g/ha of Cd and 1264.7 g/ha of Pb were extracted by dry biomass in an oilseed rape-sunflower rotation system (Yang et al., 2017).

Liang et al. (2011) determined the content of Cd, Cr, and Pb in parts of sunflower (root, stem, leaf, and seed) as well as in the soil where sunflower was grown. This research showed that the use of wastewater for irrigation increased the heavy metal concentration in soil and plants.

Since sewage sludge is one of the potential pollutants of agricultural soil with heavy metals, Chen et al. (2010) provided a health risk assessment of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in maize, sunflower, and cotton seeds grown in China. These authors used High-Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) to determine the content of heavy metals in the seeds of these crops. Sunflower seeds had the highest content of all tested metals.

Nehnevajova et al. (2005) examined the influence of fertilizers (ammonium sulfate and ammonium nitrate) on the uptake of Zn, Cd, and Pb by 15 varieties of sunflower using Flame Atomic Absorption Spectrometry (FAAS). They observed that sulfate improved the extraction of Zn and Pb while nitrate was most effective for Cd.

The aim of this work is to determine the content of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the root, stem, leaf, and seed of sunflower, as well as in the soil on which this crop was grown, using Optical emission spectrometry with inductively coupled plasma (ICP-OES).

Experimental

The soil and plant material of sunflowers were sampled from an agricultural field in Deliblato Sand of the Republic of Serbia during the harvest of sunflowers in the autumn (September 2021) (Figure 1). Sampling was carried out from five different places along the diagonal of the field. Representative homogeneous samples from these soil and plant material subsamples were made.

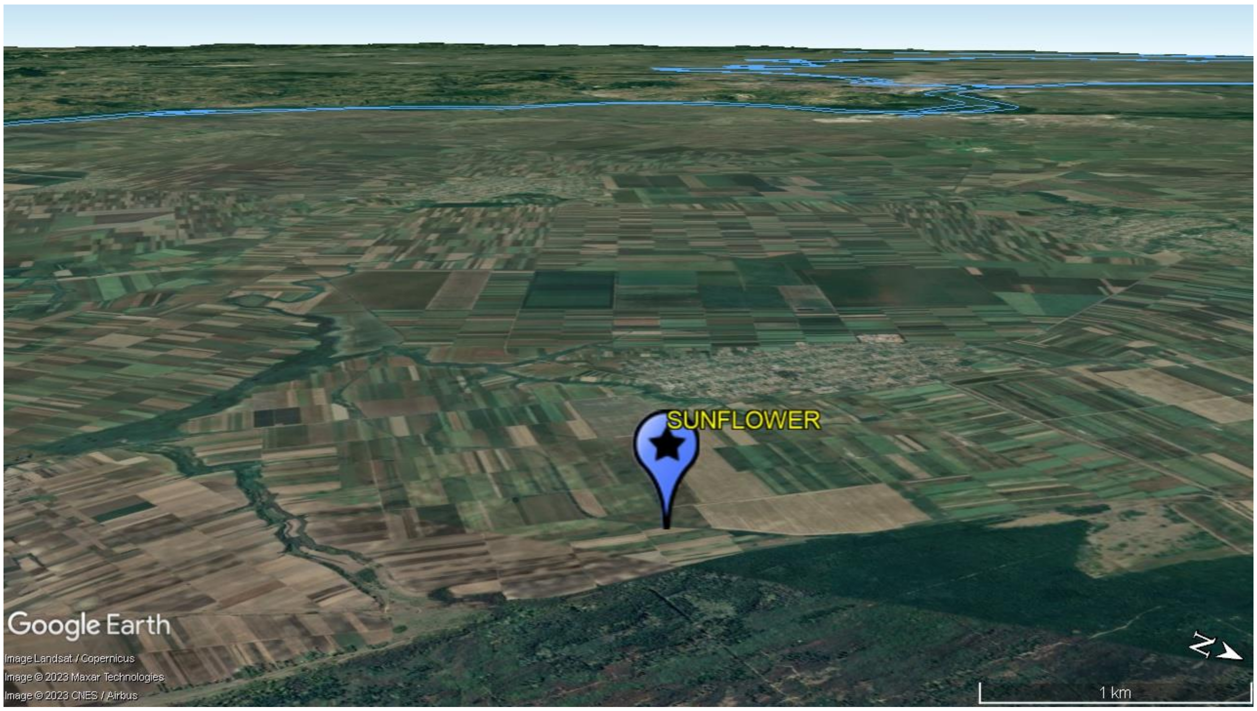

Figure 1. Agricultural field from which the soil and plant materials were sampled

Plant parts were divided into subsamples: root, stem, leaf, and seed. Sunflower roots were washed first with tap water and then deionized water, while the above-ground parts were analyzed unwashed. All plant material was air-dried for about 15 days, ground in a blender, and dried in the dryer at 65 °C for 8 hours.

The soil was air-dried for about 15 days, sifted through a sieve (2 mm diameter), and dried at 95 °C for 8 hours.

Preparation of soil sample for ICP-OES analysis

About 1 g of dry soil sample was measured into 100 mL conical flasks and 16 mL of *aqua regia* was added (mixture of conc. HNO_3 (Macron) and conc. HCl (Sigma-Aldrich), in a ratio 1:3, v/v) and left for about half an hour at room temperature. The contents were heated in a sandy bath for an hour at about 190 °C almost to dryness, cooled to room temperature, and 6 mL of conc. H_2O_2 (Sigma-Aldrich) was added. The contents were reheated to a smaller volume. After cooling, 5 mL of deionized water was added. The contents were filtered through the filter paper (blue tape), and the filtrate was collected into 25 mL volumetric flasks and filled up to the mark with deionized water (Addis & Abebaw, 2017).

Preparation of plant material for ICP-OES analysis

About 1 g of sunflower root, stem, leaf, and seed samples were weighted into 100 mL conical flasks and 15 mL of conc. HNO_3 was added, and the contents were left at room temperature for about 30 minutes. The samples were then heated almost to dryness on a hot plate for about 1 hour. 5 mL conc. H_2O_2 was added to the cooled samples, evaporated again, and after cooling, 5 mL of deionized water was added to each conical flask. The samples were filtered through the filter paper (blue tape), and the filtrates were collected into 25 mL volumetric flasks and filled up to the mark with deionized water (Bargagli et al., 2000).

Parameters of ICP-OES instrument and characteristics of the calibration curve

The contents of the tested elements in soil and plant material samples were determined by the ICP-OES technique (iCAP 6000 series, ThermoScientific, Cambridge, United Kingdom) at the following optimal instrument parameters: flush pump rate-100 rpm, analysis pump rate-50 rpm, RF power-1150 W, nebulizer gas flow-0.7 L/min, coolant gas flow-12 L/min, auxiliary gas flow-0.5 L/min, plasma view-axial, washing time-30 s.

Multielement certified standard solution IV (Al, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Tl, V, and Zn; TraceCERT, Fluka Analytical, Switzerland) was used.The correlation coefficient (r), the limit of detection (LOD), and the limit of quantification (LOQ) of the working calibration curve for each tested element are shown in Table 1.

Table 1. The correlation coefficient (r), the limit of detection (LOD), and the limit of quantification (LOQ) of the calibration curve for each tested element

Element/ λ (nm)	r	LOD (ppm)	LOQ (ppm)	Element/ λ (nm)	r	LOD (ppm)	LOQ (ppm)
As 189.042	0.99993	0.00281	0.00936	**Fe 259.940**	0.99992	0.00052	0.00174
Cd 226.502	0.99985	0.00018	0.00061	**Mn 257.610**	0.99988	0.00012	0.00039
Co 228.616	0.9999	0.00029	0.00095	**Ni 231.604**	0.99989	0.00044	0.00146
Cr 267.716	0.99976	0.00063	0.00211	**Pb 220.353**	0.99993	0.00184	0.00613
Cu 324.754	0.99989	0.00062	0.00205	**Zn 202.548**	0.99977	0.00012	0.00029

Assessment of the bioaccumulation and transfer of tested elements

The degree of bioaccumulation of the studied elements in plant parts of sunflower is shown by bioaccumulation factors (BAFs) through the *Biological Concentration Factor* (BCF)-the ratio of metal(oid) concentration in the root and the concentration in the soil and *Mobility Ratio* (MR)-the ratio of metal(oid) concentration in the above-ground plant part and the concentration in the soil. The distribution of elements from the root to the above-ground parts of the sunflower is shown *via Translocation Factor* (TF)-the ratio of metal(oid) concentration in the above-ground plant part and the concentration in the root (Alagić et al., 2015; Antoniadis et al., 2017; Dimitrijević et al., 2016; Rai et al., 2019; Retamal-Salgado et al., 2017; Tošić et al., 2016).

Results and Discussion

The content of elements in soil samples and sunflower parts

The content of the studied elements in the plant parts of sunflowers, as well as in the soil on which this agricultural crop was grown are listed in Table 2. The most abundant element in the soil sample is Fe (7300 mg/kg) while the least abundant is Cd (1.12 mg/kg). None of the tested elements exceeds the maximum allowable concentration (MAC value) in the soil sample so the soil can be considered uncontaminated ("Official Gazette of the RS", No. 23/94, 1994).

The order of occurrence of the examined elements in the plant parts is quite uniform. The most abundant are Fe, Mn, Zn, and Cu, and the least abundant are Cd, As, and Co. It is interesting that the highest concentrations of essential metals Cu and Zn are in the seed; the largest part of Co, Cr, Ni, and Pb are retained in the roots, and the highest concentrations of Cd, Fe, and Mn are in the leaf. Concentrations of As, Cd, Co, Mn, Ni, Pb, and Zn in all plant parts are within normal concentrations in plant tissue. Chromium and iron concentrations in roots and leaves are, according to some studies, above normal concentrations, but certainly below phytotoxic values. The Cu content in the seeds is at the upper limit of normal concentrations in plant tissue (Alloway, 2013; Kabata-Pendias & Pendias, 2001; Nagajyoti et al., 2010; Vamerali et al., 2010) (Table 3).

In many published papers, the influence of different fertilizers on the uptake of some elements, as well as the influence of different pollutants, has been reported. Mineral fertilizers increase the bioavailability of microelements. Nehnevajova et al. (2005) examined the effect of sulfate and nitrate fertilizers on some microelements' adoption. Although the concentration of Cd in the soil in this paper is slightly higher (1.12 mg/kg) than the concentration in the work of

Nehnevajova et al. (2005) (0.9 mg/kg), the Cd concentrations are several times higher in the plant shoots grown in the presence of the mentioned fertilizers.

Liang et al. (2011) analyzed agricultural soil which was continuously contaminated with wastewater for at least 20 years through irrigation of agricultural crops grown on it. The concentrations of Cr and Pb were approximately two times higher than the concentration of these metals in the soil that was the subject of this study. Also, concentrations of these elements in sunflower stems and seeds are also approximately two times higher than the concentrations of these metals in sunflower parts in this paper. Thus, it can be concluded that sunflower has certain uptake abilities towards Pb and Cr.

The contents of Pb and Cd in the soil analyzed by Yang et al. (2017) are several times higher (Pb - about 40 times and Cd - about 9 times) than the contents of these metals in the soil analyzed in this paper. Also, concentrations of these heavy metals in the root, stem, leaf, and sunflower seeds are many times higher (even 700 times for Cd in the stem) than the concentrations in this paper, which is expected considering the degree of pollution of agricultural soil located near the mining district in southern China. This is just another confirmation that sunflower has a great affinity for Pb and Cd.

Table 2. The content of elements in the soil and parts of sunflower (mean value $\pm SD$, mg/kg dry matter)

El.	Soil	MAC (mg/kg)	Root	Stem	Leaf	Seed
As	6.693±0.008	25*	0.48±0.02	n.d.	0.49±0.03	n.d.
Cd	1.12±0.02	3*	0.1024±0.0000	0.0175±0.0000	0.140±0.003	0.082±0.003
Co	9.7±0.2	/	1.01±0.02	0.090±0.005	0.95±0.05	0.055±0.003
Cr	12.8±0.4	100*	4.74±0.09	0.30±0.02	4.3±0.2	0.25±0.02
Cu	19.8±0.3	100*	3.38±0.06	3.8±0.1	6.7±0.2	14.3±0.6
Fe	7300±100	/	770±10	50±2	890±40	33±2
Mn	294±4	1500-3000**	25.0±0.5	6.6±0.2	113±4	10.9±0.4
Ni	27.0±0.2	50*	4.87±0.04	0.45±0.02	4.3±0.2	1.30±0.01
Pb	17.4±0.3	100*	2.35±0.04	0.29±0.02	1.25±0.03	0.20±0.02
Zn	37.1±0.2	300*	9.62±0.03	4.50±0.04	8.3±0.2	22.7±0.2

* "Official Gazette of the RS", No. 23/94, (1994)
** Kabata-Pendias (2011)
n.d. – not detected

Chen et al. (2010) determined the contents of some heavy metals in sunflower seeds grown on soil contaminated with sewage sludge. The concentrations of Cd, Cu, Zn, Ni, and Pb were 2-3 times higher while the concentration of Cr was almost 20 times higher than the concentrations in this paper. The largest difference for Cr is most likely due to the high content of Cr in the soil (173.30 mg/kg).

Table 3. Normal concentrations and toxicity thresholds for the investigated metal(oid)s in plant tissue (mg/kg dry matter)

Element	Normal concentration	Toxicity threshold	Element	Normal concentration	Toxicity threshold
As	0.02-7[a]	5[c]	**Fe**	140[a]	/
Cd	0.1-2.4[a,b]	5-10[c] 10-20[d] 5-30[b]	**Mn**	15-100[a]	170-2000[c] 300-500[b]
Co	0.1-10[b]	/	**Ni**	1[a] 0.02-5[b]	20-30[c] 10-100[b]
Cr	0.2-1[a] 0.03-14[b]	5-30[b]	**Pb**	1-13[a] 0.1-10[d]	10-20[c] 30-300[b]
Cu	4-15[a,b]	5-40[b] for leaf 100-400[b] for root	**Zn**	8-100[a]	150-200[c,d] 100-500[b]

[a]Nagajyoti et al. (2010), [b]Alloway (2013), [c]Vamerali et al. (2010), [d]Kabata-Pendias & Pendias (2001)

Assessment of the bioaccumulation capacity of sunflower according to the tested elements

The ability of the sunflower to accumulate the tested elements in the root was assessed using the BCF values shown in Figure 2.

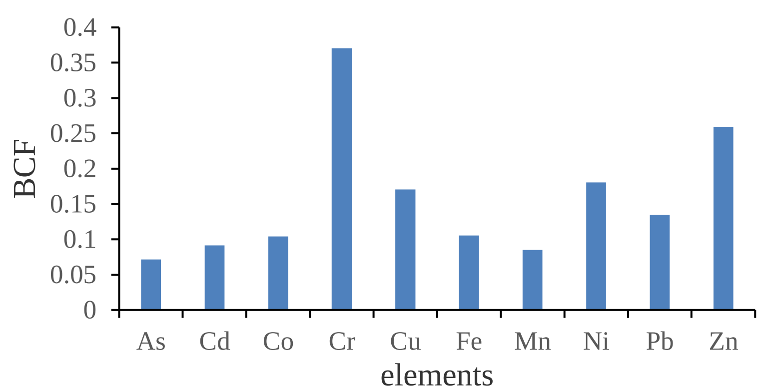

Figure 2. BCF values for sunflower root

The bioaccumulation ability of sunflower root according to the tested elements grows in the sequence As<Mn<Cd<Co<Fe<Pb<Cu<Ni<Zn<Cr. The BCF values are quite less than 1, which indicates a low accumulation of these metals in sunflower roots. Chromium is the metal that the sunflower plant deposits mostly in the root. Yang et al. (2017) have shown in their field experiment that the BCF values for Pb were very low while those values for Cd were higher than 1 in all plant parts except seed. Liang et al. (2011) calculated the BCF values for sunflower root for Cr, Pb, and Cd and according to their results, the highest BCF value was reported for Cr.

Assessment of the uptake of studied elements by above-ground parts of sunflower from the soil

Figure 3 shows a histogram with the MR values for the sunflower stem and leaf. Obtained values are less than 1, which means that the contents of the elements in the stem and leaf are less than the contents in the soil. The MR factor for *leaf/soil* is higher than the *stem/soil* factor for all elements. Yang et al. (2017) reported that the MR values (*leaf/soil*) for Cd and Pb are also higher than the MR (*stem/soil*) values. Liang et al. (2011) showed that the MR (*stem/soil*) for sunflowers follows the next order: Cd<Pb<Cr which is consistent with the results in this study.

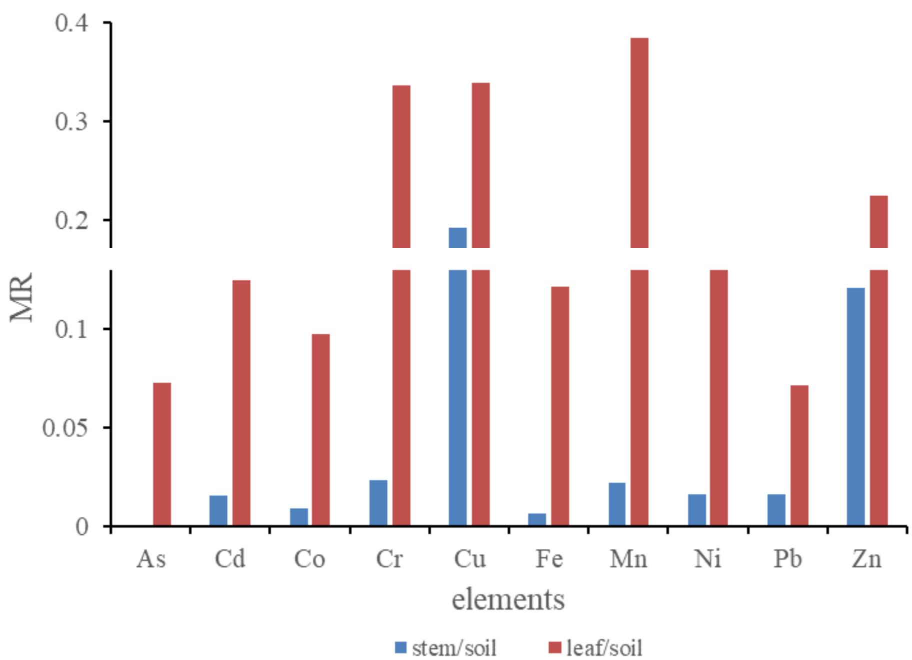

Figure 3. MR values for sunflower parts

Assessment of the distribution of tested elements from the roots to the above-ground parts of the sunflower

In general, the TF (*leaf/root*) values are higher than the TF (*stem/root*) values for all elements (Figure 4). The TF factors for *leaf/root* are higher than 1 for As, Cd, Cu, Fe, and Mn while TF is higher than 1 for *stem/root* for Cu only. The highest TF values are for Mn and Cu, 4.52 and 1.98 respectively. Copper and manganese are cofactors of the enzymes Cu/Zn-SOD and Mn-SOD (superoxide dismutase, SOD), and their significant role in the antioxidant system of the plant is directly related to the significant translocation of these metals in the above-ground parts of sunflower. Iron is slightly less common in superoxide dismutase (Fe-SOD), but it is present in redox enzymes (Fe-S proteins), which is also related to the noticeable transfer of this metal from the root to the leaf (Nagajyoti et al., 2010).

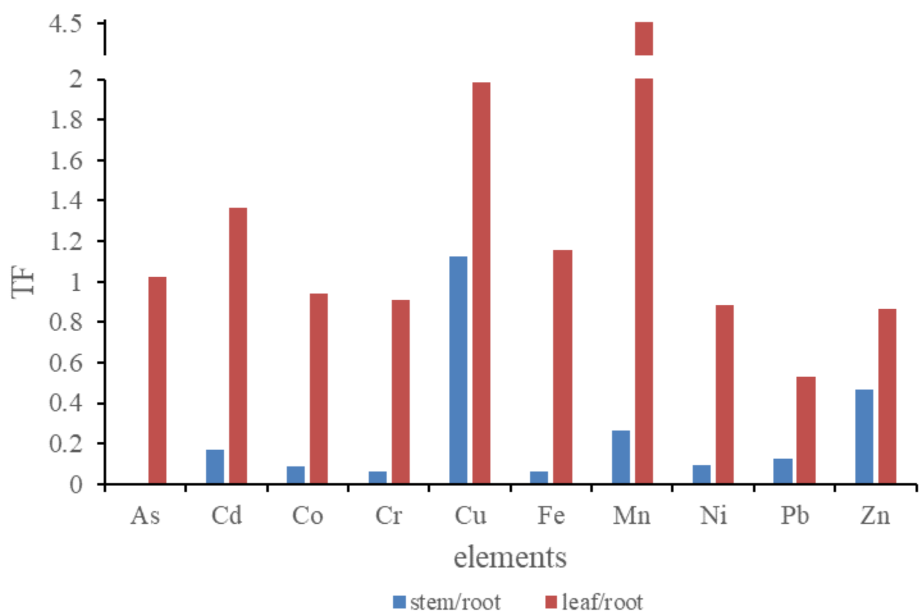

Figure 4. TF values for sunflower parts

Conclusion

The most abundant elements in soil and plant parts of sunflowers are Fe, Mn, Zn, and Cu, and the Cd, As, and Co are the least abundant. All soil concentrations are below the MAC values, and plant parts concentrations are within normal concentrations or at the upper limit of normal concentrations in plant tissue but certainly below phytotoxic values. The order of presence of the examined elements in the studied parts of the plant is different for different metal(oid)s. The calculated factors show that Cr is mostly deposited in the roots as well as MR (*leaf/soil)* and TF (*leaf/root)* are higher than the corresponding values for the *stem/soil* and *stem/root* systems for all elements which is probably a consequence of the specificity of the plant species itself as well as potential foliar uptake. A good translocation from the root to the leaf was observed for As, Cd, Cu, Fe, and Mn and to the stem for Cu.

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Conflict-of-Interest Statement

None.

References

Addis, W., & Abebaw, A. (2017). Determination of heavy metal concentration in soils used for cultivation of *Allium sativum* L. (garlic) in East Gojjam Zone, Amhara Region, Ethiopia. Cogent Chemistry, 3(1), 1–12. doi: 10.1080/23312009.2017.1419422

Alagić, S. Č., Tošić, S. B., Dimitrijević, M. D., Antonijević, M. M., & Nujkić, M. M. (2015). Assessment of the quality of polluted areas based on the content of heavy metals in different organs of the grapevine (*Vitis vinifera*) cv Tamjanika. Environmental Science and Pollution Research, 22(9), 7155–7175. doi: 10.1007/s11356-014-3933-1

Alloway, B. J. (2013). Heavy metals in soils (3rd ed.). London: Springer.

Antoniadis, V., Levizou, E., Shaheen, S. M., Ok, Y. S., Sebastian, A., Baum, C., Prasad, M. N. V., Wenzel, W. W., & Rinklebe, J. (2017). Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation–A review. Earth-Science Reviews, 171, 621–645. doi: 10.1016/j.earscirev.2017.06.005

Bargagli, R., Borghini, F., & Celesti, C. (2000). Elemental composition of the lichen *Umbilicaria decussata*. Italian Journal of Zoology, 67(1), 157–162. doi: 10.1080/11250000009356371

Chen, Z.-F., Zhao, Y., Zhu, Y., Yang, X., Qiao, J., Tian, Q., & Zhang, Q. (2010). Health risks of

heavy metals in sewage-irrigated soils and edible seeds in Langfang of Hebei province, China.

Journal of the Science of Food and Agriculture, 90(2), 314–320. doi: 10.1002/jsfa.3817

Dimitrijević, M. D., Nujkić, M. M., Alagić, S. Č., Milić, S. M., & Tošić, S. B. (2016). Heavy metal contamination of topsoil and parts of peach-tree growing at different distances from a smelting complex. International Journal of Environmental Science and Technology, 13(2), 615–630. doi: 10.1007/s13762-015-0905-z

Kabata-Pendias, A. (2011). Trace elements in soils and plants (4th ed.). CRC Press.

Kabata-Pendias, A., & Pendias, H. (2001). Trace elements in soils and plants (3rd ed.). Boca Raton: London, New York, Washington.

Liang, J., Chen, C., Song, X., Han, Y., & Liang, Z. (2011). Assessment of heavy metal pollution in soil and plants from Dunhua sewage irrigation area. International Journal of Electrochemical Science, 6(11), 5314–5324.

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters, 8(3), 199–216. doi: 10.1007/s10311-010-0297-8

Nehnevajova, E., Herzig, R., Federer, G., Erismann, K.-H., & Schwitzguébel, J.-P. (2005). Screening of sunflower cultivars for metal phytoextraction in a contaminated field prior to mutagenesis. International Journal of Phytoremediation, 7(4), 337–349. doi: 10.1080/16226510500327210

"Official Gazette of the RS", No. 23/94 (1994). Rulebook on allowable quantities of dangerous and hazardous matters in soil and irrigation water and methods for their testing.

Rai, P. K., Lee, S. S., Zhang, M., Tsang, Y. F., & Kim, K.-H. (2019). Heavy metals in food crops:

Health risks, fate, mechanisms, and management. Environment International, 125, 365–385. doi: 10.1016/j.envint.2019.01.067

Retamal-Salgado, J., Hirzel, J., Walter, I., & Matus, I. (2017). Bioabsorption and bioaccumulation of cadmium in the straw and grain of maize (Zea mays L.) in growing soils contaminated with cadmium in different environment. International Journal of Environmental Research and Public Health, 14(11), 1–15. doi: 10.3390/ijerph14111399

Rezaeian, M., Moghadam, M. T., Kiaei, M. M., & Zadeh, H. M. (2020). The effect of heavy metals on the nutritional value of alfalfa: comparison of nutrients and heavy metals of alfalfa (*Medicago sativa*) in industrial and non-industrial areas. Toxicological Research, 36(2), 183–193. doi: 10.1007/s43188-019-00012-6

Sheoran, V., Sheoran, A. S., & Poonia, P. (2016). Factors affecting phytoextraction: A review. Pedosphere, 26(2), 148–166. https://doi.org/10.1016/S1002-0160(15)60032-7

Tošić, S., Alagić, S., Dimitrijević, M., Pavlović, A., & Nujkić, M. (2016). Plant parts of the apple tree (*Malus* spp.) as possible indicators of heavy metal pollution. Ambio, 45(4), 501–512. doi: 10.1007/s13280-015-0742-9

Vamerali, T., Bandiera, M., & Mosca, G. (2010). Field crops for phytoremediation of metal-contaminated land. A review. Environmental Chemistry Letters, 8(1), 1–17. doi: 10.1007/s10311-009-0268-0

Yang, Y., Zhou, X., Tie, B., Peng, L., Li, H., Wang, K., & Zeng, Q. (2017). Comparison of three types of oil crop rotation systems for effective use and remediation of heavy metal contaminated agricultural soil. Chemosphere, 188, 148–156. doi: 10.1016/j.chemosphere.2017.08.140