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CONCENTRATIONS OF MANGANESE AND IRON IN SOME WOODY AND HERBS PLANTS

ABSTRACT: Heavy metals are the substances that indicate environmental pollution. The plants polluted with heavy metals may endanger natural environment and cause health problems in humans. In our multidisciplinary research of the concentrations of pollutants in forest ecosystems and natural environment in Belgrade, we examined the contents of heavy metals essential for plants but harmful in greater concentrations on a long-term basis. The fact that heavy metals manganese and iron are accumulated in plants to the greatest extent focused our work on determination of the level of concentrations of Mn and Fe in the vegetative parts of 8 plant types on three locations on the Avala Mountain and one location in the centre of the city of Belgrade. The analyses of heavy metals contents in plants were performed by the method of flame atomic absorption spectrophotometry. The examination of the existence of important differences between the average values was performed by implementation of Duncan's test for the level of significance of 95%. The current contents of heavy metals in plants in the area of the protected natural resource *Avala* do not represent danger that would presently cause notable damage to forests but show the tendency of the increase of concentrations. Therefore, this issue should be constantly monitored.

KEY WORDS: Avala mountain, protected natural resource, concentrations Fe, Mn, woody, herbs plants

INTRODUCTION

As a two-million city, administrative, and tourist centre, Belgrade on one hand has a constant need for new areas for relaxation and recreation providing natural environment and esthetic framework. On the other hand, there is a permanent need for preservation of healthy environment in the manner of cherishing, preservation, and protection of already existent high-grade complexes.

One of such high-grade forest complexes and the only mountain near Belgrade, the favorite resort of inhabitants of Belgrade, is located as 16.5 km away from Belgrade, on the way to Kragujevac and overlooking the city and its surroundings as a guardian. Although only 511 m high (in the shape of an irregular cone), this mountain reigns the surrounding rolling terrain.

As a natural resource of common interest, it enjoys special protection. As a preserved part of nature park and landscape of outstanding features this area has permanent ecological, scientific, cultural, educational, health and recreational, as well as tourist significance.

Considering the current status of Belgrade's natural environment, the forests in the narrow as well the wider city zone must be given much greater importance.

As the causes and effects that endanger natural ecosystems of this area and their further development and natural environment are obvious to a certain extent, it was logical that our aim was to determine the pollution level of the protected area of *Avala*.

The protected natural resource *Avala* in accordance with the suggestion of the Institute for Nature Conservation of Serbia is declared the landscape of outstanding features.

According to the Special basis for management of forests (2008-2017) in the protected natural resource *Avala*, i.e., its part that is declared the landscape of outstanding features, is located on the territory Belgrade, municipality of Voždovac, and comprises certain parts of the cadastral municipalities of Beli Potok, Ripanj, Zuce, and Pinosava.

The total area of the protected natural resource is 489.13 ha; 74.35 ha (15.2%) is privately owned and 414.78 ha (84.8%) belongs to other forms of ownership.

MATERIALS AND METHODS

Bearing in mind the importance of the quality of natural environment in the areas intended for recreation, we studied the content of heavy metals (Fe and Mn) in plant leaves on the Avala Mountain. The samples for the analysis were collected from three locations with outstanding landscape features in the area of *Avala*.

The selected locations, according to the Special basis for management of forests (2008-2017) in the protected natural resource Avala, belong to management unit *Avala*: location 1 – at the road entering the area of the landscape of outstanding features *Avala*; location 2 – on the top of the Avala mountain (nearby the tower); and location 3 – on the downward road from the mountain (Stari Majdan).

After review and consideration of several potential locations, we selected the location 4 as a control location in the centre of Belgrade, at the Boulevard Despota Stefana where there is high traffic frequency.

MATERIALS AND METHODS

In the process of selecting plant species for the analysis, we performed a very detailed inventory list of all plant species present in this area. We selected 8 plant species: (1) *Tilia tomentosa* Mnch. – Silver Lime; (2) Pinus nigra Arn.

– European black pine; (3) *Plantago media* L. – Hoary plantain; (4) *Taraxacum officinale* Web. – common dandelion; (5) *Acer campestre* L. – Field Maple; (6) *Prunus avium* L. – wild cherry, sweet cherry, gean; (7) *Quercus petraea* (Matt.) Liebl. – sessile oak; and (8) *Pseudotsuga menziesii*; (9) *(Mirb.) Franco* – coast Douglas fir, common Douglas-fir, or Oregon Douglas fir.

For the purpose of control, we selected 4 plant species in the location 4 in the centre of the city as the representative sample.

Assuming again the fact that content of heavy metals in plants is directly dependant on distance from the road the plants were sampled in each location in the length of 200-300 m along the road and the depth of 15 m from the road. The samples of plant materials were collected on each location in the middle of vegetation period, at the beginning of July 2009.

For each species, only leaves were sampled and for that purpose 1-2 kg of material were collected from all locations. The samples were dried without previous washing until they became air-dry mass. The air-dry leaves were then dried further in dry kiln at 105^{o}C, ground, and used for laboratory analyses. Mn and Fe concentrations were determined by AAS method and expressed in μg/g of dry matter.

The analyses were performed in the laboratories of the Department for Biology and Ecology, Faculty of Natural Sciences in Novi Sad and the Institute for Lowlands Forestry and Environmental Protection in Novi Sad.

The obtained data on accumulation of heavy metals were processed by implementation of the standard statistical methods, variance analysis by LSD test for the level of significance $p=0.05$ and the testing of significance of the average values was performed by Duncan's test.

All tests were performed with the level of significance $p \leq 0.05$.

RESULTS AND DISCUSSION

Environmental pollution by chemical substances is one of the most important factors of degradation of certain components of ecosystem. Therefore, it is important to be aware of accumulation and toxic effects of heavy metals in plants from ecological point of view since this is the way heavy metals enter food chain (K a s t o r i , 1997, M e m o n et al., 2001).

The level of heavy metals accumulation in plant tissue is determined by numerous biotic and abiotic factors out of which the characteristic genotype is one of the most dominant (P a j e v i ć et al., 2008; N i k o l i ć et al., 2008). For some heavy metals there apply the interspecies calibration (B e r l i z o v et al., 2007). The accumulation of heavy metals in plant tissue points to the very important role of certain plant species as (bio)indicators of environmental pollution (T e n - H o u t e n , 1983; P r a s a d and F r e i t a s , 2003).

Nowadays, more attempts are made to use woody plants for monitoring environmental pollution. Critical values for individual heavy metal, plant resistance to their presence, cumulative and perhaps synergetic activities, and many other aspects that are very little known still present a problem.

Among heavy metals that are most dangerous for human organism are arsenic, cadmium, lead, nickel, manganese, mercury, and molybdenum even when they are present in a low level. Also very toxic but with special effect on plant growth are the zinc, lead, aluminum, boron, chromium, and iron (K a s - t o r i and P e t r o v i ć , 1993).

Heavy metals are the substances that signalize the issue of environmental pollution. There is still insufficient knowledge of their dispersion in nature and their role in environmental pollution.

MANGANESE CONCENTRATIONS IN PLANTS

Heavy metals contents in herbs, moss, lichen or fungi and needles and leaves of forest trees may be used as indicators of pollution of certain components of ecosystems (T y l e r , 1972). Among different plant species, there are differences in the uptake of heavy metals, which depends before all on their genetic characteristics, on the influence of the surface of root system and its capacity for absorption of ions, on the shape of root excretion and the speed of evapotranspiration (A l l o w a y , 1995).

Manganese represents an essential element for plants, which means that in certain concentrations it is necessary for regular functioning of plants since it activates a number of enzymes. It is also very important in the transmission of electrons during photooxidation of water in photosystem II (K a s t o r i , 2006). This element influences the level of phytohormone auxin and in that manner has an effect on elongation and plant growth. On the contrary, greater concentrations of manganese have adverse effects on plants.

The symptoms of toxicity of manganese appear on older leaves in the form of brown necrotic spots or there appear chlorotic spots near the tops of leaves. In dicotyledons, this causes the phenomenon of wavy leaves. The first signs of toxicity of manganese on plants are chlorosis and necrosis.

The role of manganese in life processes of plants is manifold, before all in activation of enzyme processes, the effect on pigment platelets (B o t r i l l et al., 1970), nitrogen metabolism or rather metabolism of amino acids and proteins.

There are no national regulations that refer to pollution of environment by manganese or heavy metals but there are standards and regulations in healthcare sector like The Rulebook on the quality of food and The Rulebook on the quantity of pesticides, metals, and metalloids that may be present in food products. In accordance with the regulations of the Federal Republic of Germany and the United States of America, the maximum allowed concentration of manganese in air amounts to 5 mg/m^3 of air (UNEP-UN/ECE 1994).

Some plant species are able to accumulate very high quantities of heavy metals in leaves before all (B a k e r and B r o o k s , 1989).

The results of laboratory analyses of manganese accumulation in the researching area (Fig 1,2,3,4) showed that concentration in the analyzed plant species differed depending on the location where samples were collected and depending on the plant species.

We found higher manganese concentration in plant species on the locations 1, 2, and 3 (locations on the Avala) compared to the location 4 in the centre of Belgrade.

The average least concentration of manganese at the control location in the centre of Belgrade in the Boulevard Despota Stefana amounting to 48 μg/g clearly showed that the increase of concentrations of manganese in plants was not directly related to traffic as the basic source.

The manganese contents depend on plant species and have a wide range; in accordance with the data provided by K á r p á t i et al. (1967) manganese contents in the dry matter of *Lemna trisulca* amounted to 34.600 ppm and in *Plantago altissima* only 10 ppm.

The concentrations of manganese in leaves of plants by locations (Fig. 1-4) clearly showed that woody plants appeared as hyperaccumulators of manganese; oak in the locations on the Avala Mountain and lime tree (*Tilia tomentosa)* on the location 4 appeared as hyperaccumulator of manganese in comparison to other analyzed species.

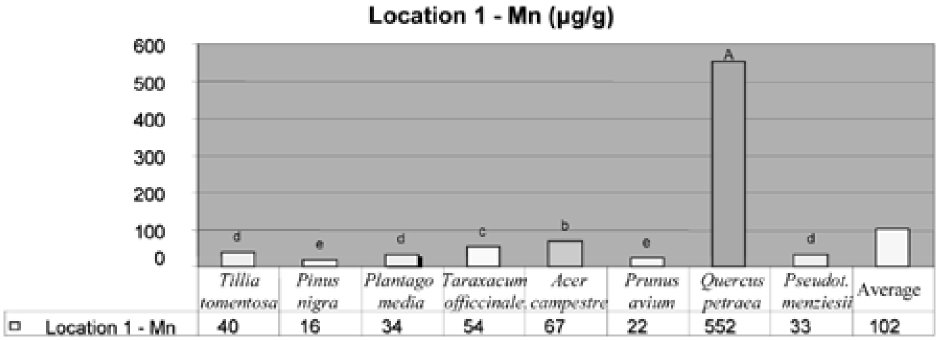


Fig. 1

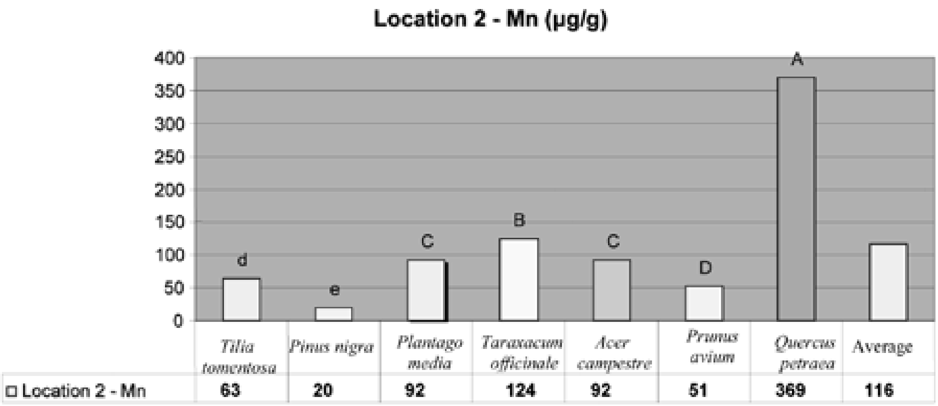
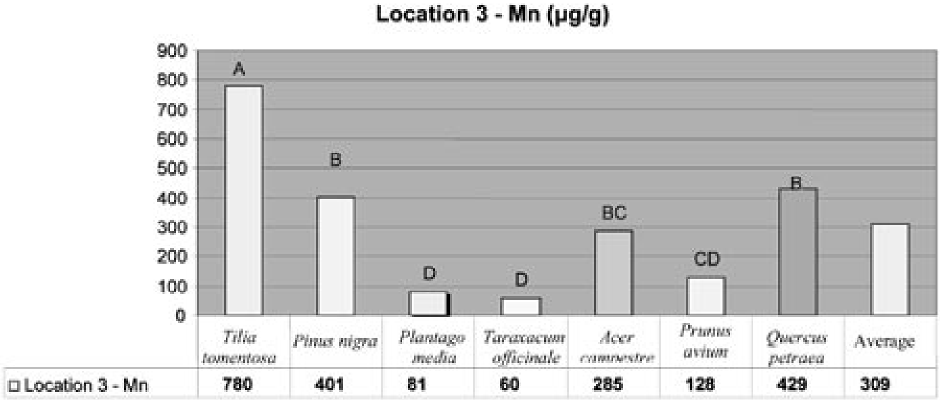


Fig. 2



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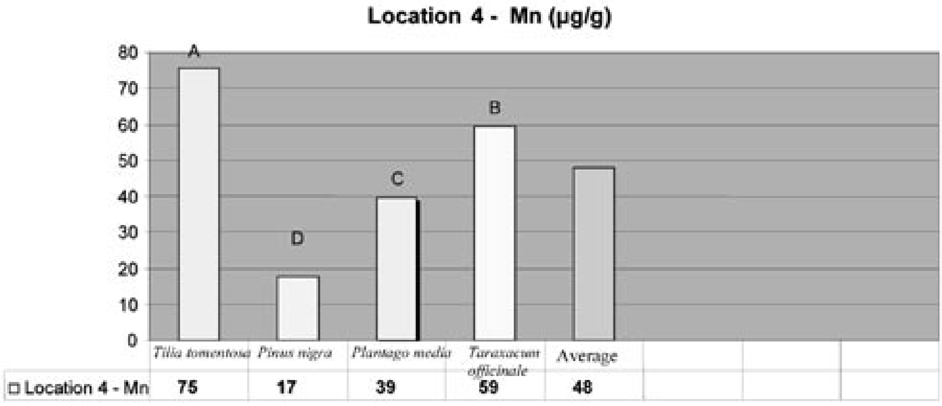

Fig. 4

The data obtained in our research on manganese concentrations by locations based of Duncan's test showed that the ranges varied on all locations from A to E.

Discussing the quantity of heavy metals in woody plants, we have to take into account that these data were obtained within a short time period of their life cycle. Manganese is transported through plants and mostly deposits in young plant organs (leaves), then in the bark, and the least deposits can be found in root or xylem juice (K a d o v i ć et al., 2002).

IRON CONCENTRATIONS IN PLANTS

Iron is a biogenic element present in plants in low quantities. It is polyvalent and has an effect on numerous physiological and biochemical processes. It has the capacity to form chelates, which are complex compounds of metals with certain organic compounds. Plants absorb iron from the soil in the form of ferrous ions (Fe^{2+}), ferric ions (Fe^{3+}), and in the form of iron chelates. Fe^{++} is physiologically active.

The high pH value, high concentration of phosphates and calcium ions influence the reduced uptake of iron. Iron plays a very important role in biosynthesis of chlorophyll, the first phases of photosynthesis, respiration, fixation of elemental nitrogen, reduction of nitrates and nitrites, metabolism of carbohydrates. It also affects cell division, elongation of plants, and root growth.

Iron contents in dry matter of plants have wide range from 50 to 1000 μg/g. Some plants are able to accumulate iron in significantly greater quantities so that for example leaves of spinach contains up to 3000 μg Fe g^{-1} of dry matter.

Distribution of iron within plants is very characteristic. In the aboveground plant parts, it is the most present in leaves then in stem and grain. Plants take out of the soil more Fe than any other microelement through their crops.

In case of surplus of Fe the growth of all vegetative organs is inhibited. Leaves become dark to blue-greenish, root gains umber color. The symptoms of surplus of Fe are usually followed by the signs of deficiency of phosphorous and manganese (S t a n k o v i ć, 2006).

The analysis of results (Fig. 5 to 8) showed that concentrations of iron by average values per locations ranged from 324 to 1065 μg/g.

Iron concentrations in plant leaves by locations (Fig. 5-8) clearly showed two herbs that appeared as hyperaccumulators of iron: hoary plantain (*Plantago lanceolata*) and common dandelion (*Taraxacum officinale*) in all locations. It is also necessary to point out that on location 2 on the Avala (Fig. 6) these two species showed very high values of iron concentrations: *Taraxacum officinale* 2425 μg/g and *Plantago lanceolata* 2765 μg/g. Such results are in line with the results of the research of heavy metals contents on Fruška Gora Mountain where comparing plant species it can easily be noted that common dandelion shows intensive uptake of iron with the value of 1428 ppm (S t a n k o v i ć , 2008).

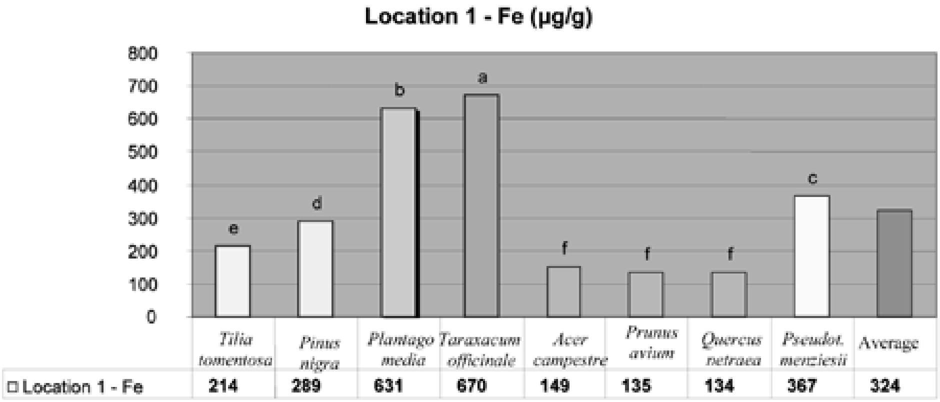

Fig. 5

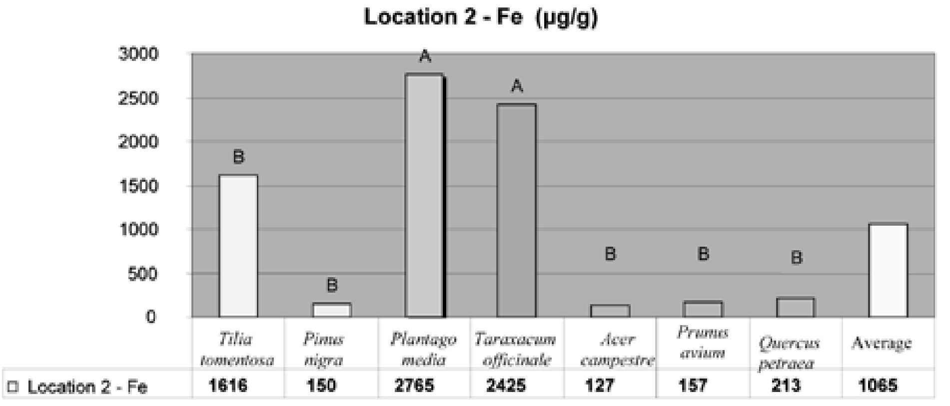

Fig. 6

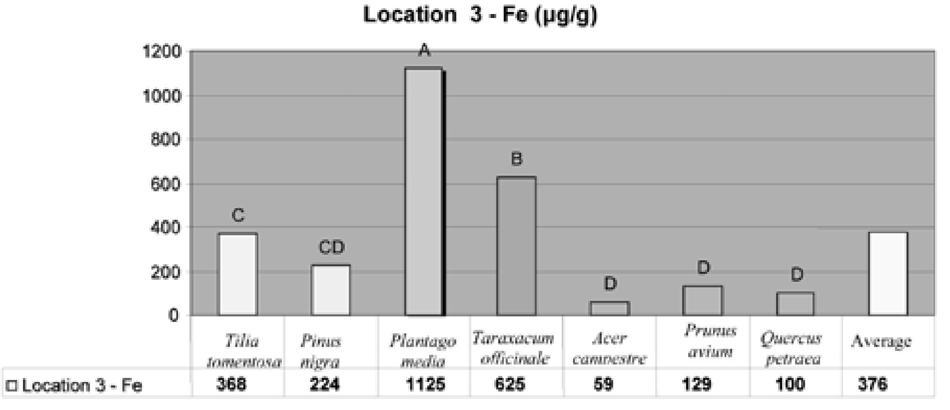

Fig. 7

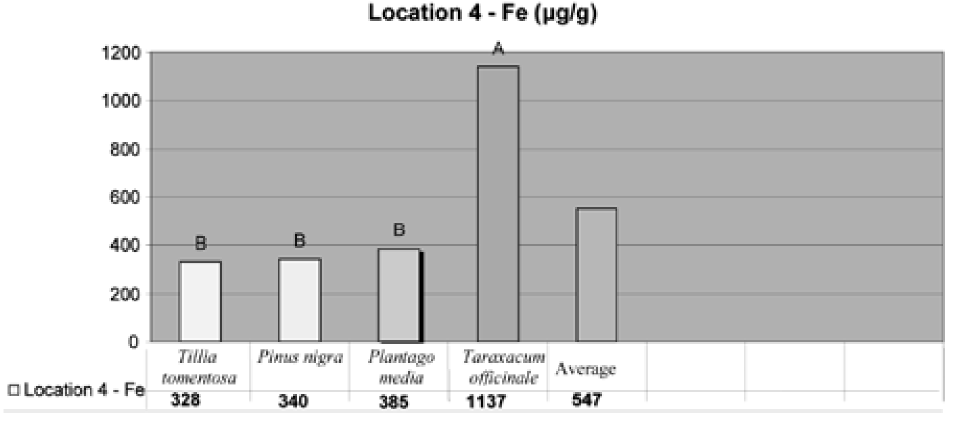

Fig. 8

It is important also to point out to the antagonism between iron and manganese i.e., the surplus of one element causes reduction of the other and vice versa.

In our study, this relation can be best seen on location 2 on the Avala (Fig. 2) where average values for manganese accumulation for all plants amounted to 116 μg/g and the average values for Fe amounted to 1065 μg/g (Fig. 6).

The antagonism of Fe and Mn was also clearly notable on location 4 in Belgrade where average values of Fe for all plants amounted to 547 μg/g (Fig. 8) while the values for Mn amounted to 48 μg/g (Fig. 4).

Regarding plant species by locations, we observed that the least range of variation in accordance with Duncan's test was present on location 4 from A-B, while on the locations on the Avala this range of variations was from A-F.

CONCLUSION

Based on the obtained results we conclude:

- Average manganese contents in leaves on all previously mentioned locations ranged from 48 μg/g on location 4 to 102 μg/g on location 1. The greatest manganese concentration was found in leaves of woody plants, namely (*Tillia tomentosa*) 780 μg/g, and then Sessile Oak (*Quercus petraea*) 552 μg/g. The least concentrations of manganese from all locations, and especially location 1, were found in European black pine (*Pinus nigra*) 16 μg/g.
- Average iron contents in leaves on all previously mentioned locations ranged from 324 μg/g on location 1 to 1065 μg/g on location 2;
- The greatest iron concentration was found in the leaves of herbs on location 2 on the Avala with especially high values amounting to 2425 μg/g found in common dandelion (*Taraxacum officinale*) and 2765 μg/g in hoary plantain (*Plantago media*);
- The least quantity of average accumulated iron among all locations and especially on location 3 was found in sessile oak (*Quercus petraea*) amounting to 100 μg/g and on the same location in field maple (*Acer campestre*) we measured the least values of only 59 μg/g;
- On the basis of all the above mentioned and as a result of this research manganese and iron clearly appeared as antagonists;
- On the basis of the obtained results of the research for all analyzed species on all locations in general it might be concluded that traffic was not the basic polluter but that the increased concentrations of manganese and iron in plants in this complex were, besides natural contents in soil, caused by some other sources of emission.

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КОНЦЕНТРАЦИЈА МАНГАНА И ГВОЖЂА У НЕКИМ ВИШЕГОДИШЊИМ ДРВЕНАСТИМ И ЗЕЉАСТИМ ВРСТАМА

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Резиме

Авала као заштићено природно добро површине од 489 ha од изузетног је значајаса различитих аспеката за становнике Београда, стога ову планину треба сачувати од контаминације полутантима пре свега антропогеног утицаја као што је на пример интензиван саобраћај. Нарочито је интересантно пратити садржај тешких метала у биљкама као и неке друге полутанте (PAH-ове).

Циљ овог рада усмерен је на утврђивање степена концентрације Mn и Fe у листовима 8 врста биљака од тога 6 дрвенастих (*Tilia tomentosa* Mnch., *Pinus nigra* Arn., *Prunus avium* L., *Quercus petraea* (Matt.) Liebl, *Pseudotsuga menziesii*) и две зељасте (*Plantago media* L., *Taraxacum officinale* Web.).

Биљке су узорковане на три локалитета на Авали и једном локалитету у центру Београда. Садржај тешких метала одређен је методом атомске апсорбционе спектрофотометрије (AAS).

Резултати истраживања за акумулацију мангана на испитиваном подручју указују да је већа концентрација мангана на локалитетима на Авали, него на локалитету у центру Београда, а то јасно показује да повећање концентрације мангана у биљкама није директно везано за саобраћај као основни извор него земљиште. Највећа акумулација мангана нађена је код биљака храста и липе а гвожђе код боквице и маслачка на свим локалитетима. У овим истраживањима јасно је уочљив и антагонизам између гвожђа и мангана. Најјасније је то видљиво на локалитету 4 у центру Београда, где су просечне вредности за све биљке код Fe износиле 547 μg/g, док су вредности за Mn на истом локалитету 48 μg/g.

Тешки метали у биљкама на подручју заштићеног природног добра „Авала" за сада не представљају опасност за настанак видљивих оштећења шуме, али показују тенденцију повећања концентрација, те их треба интезивно пратити.