INTERNATIONAL CONFERENCE

MEĐUNARODNA KONFERENCIJA

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

PROCEEDINGS

KNJIGA RADOVA

Under the auspicies of the
MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

Pod pokroviteljstvom
MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

May 16-19, 2022 : : Divčibare, Serbia

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

INTERNATIONAL Conference YUCORR (23 ; 2022 ; Divčibare)
Meeting point of the science and practice in the fields of corrosion, materials and environmental protection [Elektronski izvor] : proceedings = Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine : knjiga radova / XXIII YuCorr International Conference = XXIII YuCorr [Jugoslovenska korozija] Međunarodna konferencija, May 16-19, 2022, Divčibare, Serbia = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.]] ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] ; [editors, urednici Miroslav Pavlović, Marijana Pantović Pavlović, Miomir Pavlović]. - Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2022 (Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM). - 1 elektronski optički disk (CD-ROM) ; 12 cm
Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Radovi na engl. i srp. jeziku. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts.
ISBN 978-86-82343-29-5
а) Премази, антикорозиони -- Зборници б) Превлаке, антикорозионе -- Зборници в) Антикорозиона заштита -- Зборници г) Животна средина -- Заштита -- Зборници д) Наука о материјалима -- Зборници
COBISS.SR-ID 68624905

XXIII YUCORR – International Conference | *Međunarodna konferencija*

PUBLISHED AND CD BURNED BY | *IZDAVAČ I NAREZIVANJE CD*
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

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SCIENTIFIC AREA | *OBLAST:* CORROSION AND MATERIALS PROTECTION **|** *KOROZIJA I ZAŠTITA MATERIJALA*

PAGE LAYOUT | *KOMPJUTERSKA OBRADA I SLOG:* *Dr Marijana Pantović Pavlović*

CIRCULATION | *TIRAŽ:* **200** copies **|** *primeraka*
PUBLICATION YEAR | *GODINA IZDANJA:* **2022**
ISBN 978-86-82343-29-5

Synthesis : : Materials : : Corrosion : : Environment : : Energy

XXIII YuCorr

Analyse : : Discover : : Coat : : Green : : Protect : : Save : : Sustain

May 16-19, 2022, Divčibare, Serbia

Ovaj PDF fajl sadrži elektronsku Knjigu radova prezentovanih u okviru Međunarodne konferencije **XXIII YuCorr.** U knjizi su **plavom bojom** obeleženi aktivni linkovi ka pojedinim njenim delovima, iz Sadržaja do naznačenih stranica.

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ORGANIZATORI XXIII YUCORR-a

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Udruženje Inženjera Srbije za Koroziju i Zaštitu Materijala

INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE

Institut za Hemiju, Tehnologiju i Metalurgiju, Univerzitet u Beogradu

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Cu, Mn, Pb and Zn concentrations in bark of different tree species as indicator of atmospheric pollution

Dragana Pavlović*, Marija Matić, Olga Kostić, Dimitrije Sekulić, Natalija Radulović, Miroslava Mitrović, Pavle Pavlović

Department of Ecology, Institute for Biological Research "Siniša Stanković", - National Institute of the Republic of Serbia, University of Belgrade, Bulevar despota Stefana 142, 11000 Belgrade, Serbia

Corresponding_author: dragana.pavlovic@ibiss.bg.ac.rs

Abstract

Quality of urban air is one of the most challenging environmental problems in the 21st century. The use of higher plants, especially different parts of trees, for air monitoring purposes is becoming more and more widespread. In this study, the bark of Acer platanoides L., Acer pseudoplatanus L. and Betula pendula Roth was examined in order to evaluate their ability for biomonitoring purposes in the three urban municipalities in Belgrade city which is affected by different industrial activities and traffic. The concentration of Cu, Mn, Pb and Zn were measured using ICP-OES. The results obtained in this study indicate the regularity in the spatial distribution of the examined elements, ie the highest concentrations were measured in the tree bark from the park in the municipality of Palilula. It was established that the bark of A. platanoides and A. pseudoplatanus retain higher concentration of Cu, Pb and Mn in relation to the bark of B. pendula, but that the accumulation potential of examined species depends not only on the characteristics of the bark, but also on specific habitat conditions. The bark of B. pendula showed good potential for Zn accumulation. Based on the obtained data, it can be concluded that the bark of the examined species can be used as indicator of long-term air pollution, whereby the bark of A. platanoides and A. pseudoplatanus were more efficient as indicators of Cu, Mn and Pb accumulation, and the bark of B. pendula as an indicator of Zn. The use of different parts of plants for the purpose of biomonitoring can reach its full potential in areas where there is no developed network of monitoring stations for air quality.
Keywords: *tree bark; urban parks; air pollution indicators; dedicious trees*

Introduction

Urbanization and industrialization combined with increase in vehicular traffic provided easier and comfortable life of inhabitants in the cities. However, such trend represent a serious threat to environment in both developing and developed countries [1]. Air pollution in urban areas is one of the most urgent environmental problems since it poses serious threats to human health [2]. World Health Organization estimated that air pollution was responsible for more than 550 000 premature deaths in the Europe, almost 6 600 of which were attributed to air pollution in Serbia. The main sources of air pollution in Serbia include the energy sector (thermal power plants, heating plants and individual household heating), the transport sector, waste dump sites and industrial activities (oil refineries, the chemical industry, mining and metal processing and the construction industry), [3]. Particulate matter (PM) emitted from these sources is toxic and contributes to the degradation of air quality [2,4]. Toxic elements associated with PM are considered as one of the most serious environmental pollutants due to their persistence in the environment, bioaccumulation and high toxicity [5,6,7].

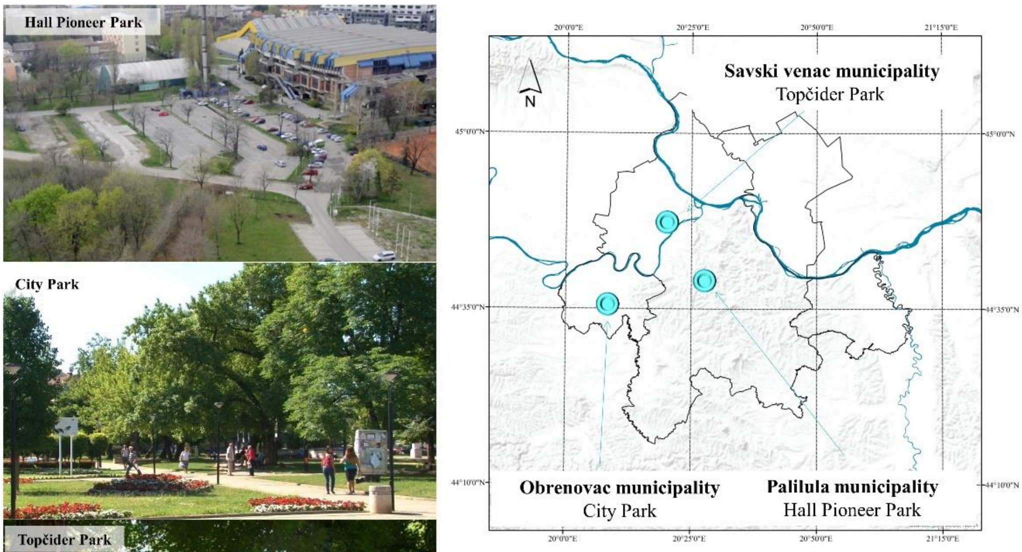
The vegetation in urban environment is identified as suitable for capturing PM from the atmosphere and can be used for monitoring elemental deposition [8,9]. For instance, McPherson et al. [10] found that 234 tons of PM in Chicago can be removed if 11% of the city area was covered by trees, while Yang et al. [11] found that 772 tons of PM in Beijing were removed in one year by city vegetation.

Previous studies also showed that trees and their different parts can be used for monitoring elemental deposition from the atmosphere [6,9,12-15]. Tree bark is often used to assess the levels of toxic elements in the atmosphere [9,12-14,16]. Because it accumulates airborne contaminants in the outer layers and provides information about the long-term air pollution, via dry and wet deposition. Bark with a rough surface is a more effective trap for atmospheric particles than smooth bark because the surface of such tree bark is very porous and enables efficient accumulation and retention of toxic substances [17].
The aim of this study was: (1): to determine the levels of potentially toxic elements (Cu, Mn Pb and Zn) accumulation in bark of *Acer platanoides* L., *Acer pseudoplatanus* L. and *Betula pendula* Roth. which grow in urban parks in three Belgrade municipalities exposed to a different source of pollution; and (2) to compare their accumulation ability for biomonitoring purposes in the urban areas.

Materials and methods

Sampling site description

The research was conducted in urban parks located in three Belgrade municipalities (Palilula, Obrenovac and Savski venac) exposed to airborne and element pollution from industrial activities and traffic. In Palilula municipality, the dominant pollution source is traffic exhaust. Sampling was performed in the “Hall Pioneer” park (44°48'51'' N, 20°28'58'' E). In Obrenovac municipality, the dominant pollution source is the “Nikola Tesla A” thermal power plant (TENT A) with ash and slag dump sites and sampling was performed in the “City Park” (44°39’16’’ N, 20°12’50’’ E). In Savski venac municipality sampling was performed in “Topčider Park” (44°46’57’’ N, 20°25’23’’ E), which is located in a zone of mixed oak forest (Quercetum farinetto cerris Rud.) in an area without a direct source of pollution (Figure 1). Parks were chosen as research sites since the population in cities, spend most of their free time in such places.



Municipalities	Sampling sites
Palilula	Hall Pioneer Park (44°48'51" N, 20°28'58" E)
Obrenovac	City Park (44°39'16" N, 20°12'50" E)
Saavski venac	Topčider Park (44°46'57" N, 20°25' 23" E)

Figure 1. *Map of the selected urban sampling parks in three Belgrade municipalities*

Sample collection and analysis

Determination of potentially toxic elements (PTEs) content in the bark of *Acer platanoides* L., *Acer pseudoplatanus* L. and *Betula pendula* Roth. was conducted from three to five randomly chosen trees at each sampling site. The flakes of the bark layer from each tree, about 4-5 mm in thickness and of about 1×3 cm^2 were carefully removed with a stainless steel knife at an average height of 1.5 m above the ground (in all directions around a tree) and mixed into a composite bark sample, resulting in one composite bark sample per sampling site. The bark samples were kept in a paper envelope and then placed in a polythene bag before transportation to the laboratory. In the laboratory, unwashed bark was dried to a constant weight of 75° C (Binder, Tuttlingen, Germany). Dried samples were ground with a stainless-steel mill and sieved through a 2.0 mm stainless-steel sieve.

For the element analysis, 0.3 g of bark samples were digested in a microwave (CEM, 39 MDS-2000), using a mixture of 9 ml of 65% HNO_3 and 3 ml of 30% H_2O_2. The final extracts were filtered into 50 mL polyethylene volumetric flasks, and then diluted to the mark with deionized water. All samples were analysed in five replicates, and results were presented as mean values, with standard deviation (SD). The concentrations of Cu, Mn, Pb and Zn in the samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Spectro Genesis Fee, Spectro-Analytical Instruments GmbH, Kleve, Germany). Quality control was performed using standard reference material (Beach leaves - BCR-100, IRMM certified by EC-JRC). The recovery values found were within 95-110% of the certified values for all the elements measured. Element concentrations were expressed in milligrams per kilogram of dry weight (mg kg^{-1} d.w.). The detection limits (mg kg^{-1}) for the elements were as follows: Cu - 0.006; Mn - 0.003; Pb - 0.038 and Zn - 0.002.

Data analysis

The results were analyzed using one-way analyses of variance (ANOVA) by computing the statistical significance of the PTEs concentrations with respect to their locations.

Species description

Three different species (*Acer platanoides* L., *Acer pseudoplatanus* L. and *Betula pendula* Roth.) of trees with different bark features (degree of roughness) were selected for this study (Figure 2).

Acer platanoides L. (**Norway maple)**, belongs to the genus *Acer* which belongs to the family Sapindaceae in the order Sapidales. Norway maple is a fast-growing medium sized tree growing up to 30 m in height and up to 100 cm in diameter. The crown is rounded and symmetrical, often as broad as the tree is tall. The leaves are palmately lobed, wider than long, about 8-16 cm long and 10-18 cm wide. Each leaf has 5 to 7 lobes that often have bristle-tipped teeth. Bark is grey and smooth when young, while older trees have dark grey bark with shallow, intersecting ridges in a regular, often diamond-shaped pattern. Unlike many other maples, mature trees do not tend to develop a shaggy bark. Under ideal conditions in its native range, Norway maple may live up to 250 years, but often has a much shorter life expectancy, sometimes only 60 years. Norway maple is the most widespread native maple in Europe. The Norway maple is able to grow well across a wide range of soil conditions, shade, drought and pollution. However, it thrives best in deep, fertile, moist soils, which are adequately drained and with a sub-acid pH. Exposure and strong calcareous soils are well tolerated. It is intolerant to low soil nitrogen conditions, high evapo-transpiration or prolonged drought and it is rare on acidic soils (pH~4). The Norway maple has been used extensively as an ornamental, shade and street-side tree because of its attractiveness, colourful foliage and large, spreading crown, in combination with its tolerance of urban conditions [18].

Acer pseudoplatanus L. (**Sycamore maple**), belongs to the genus *Acer* which belongs to the family Sapindaceae in the order Sapidales. The sycamore maple is a large deciduous tree growing up to 35 m in height and up to 80 cm in diameter. It has a very broad domed crown whose diameter can sometimes exceed the height of the tree. Sycamore has a characteristic leafy shape similar to that of

Norway maple, but the sycamore leaves are rounded. Its leaves are large and palmate with five pointed lobes that vary considerably in shape and size depending on the age and vigour of the shoot, but which may reach 18 × 26 cm in young vigorous trees. The underside of the sycamore leaf is gray-green in color, while the top is dark green. The leaf position of this tree is opposite. It has a strong root system making it quite wind-firm despite the large crown. The bark is smooth and grey in young trees, later becoming rougher and cracked into scaly squares that curl away at the edges. Sycamore has an incredibly long life span of about 350-400 years. Its natural distribution range includes Central and Eastern Europe and the mountain systems of Southern Europe, Caucasus and North of Minor Asia. It is tolerant of a wide range of soil types and pH, except heavy clay, and is at its best on nutrient-rich, slightly calcareous soils. Sycamore is planted in parks for ornamental purposes, and sometimes as a street tree, since its tolerance of air pollution makes it suitable for use in urban plantings. Because of its tolerance to wind, it has often been planted in coastal and exposed areas as a windbreak [18].

Betula pendula Roth. (**Silver birch**) belongs to the genus *Betula* L. which belongs to the family Betulaceae in the order Fagales. Silver birch is a fast growing, medium-sized deciduous tree, growing up to 30 m. Its leaves are roughly triangular with broad, untoothed, wedge-shaped bases, slender pointed tips and coarsely double-toothed, serrated margins and, therefore, have the potential to be efficient particulate scavengers. It has golden-brown bark that later turns to white as a result of a papery tissue developing on the surface and peeling off in flakes. The bark remains smooth until the tree gets quite large, but in older trees, the bark thickens, becoming irregular, dark and rugged. Birch belongs to the Euro-Siberian floristic geographic element and grows naturally in most of Europe. Birch trees commonly live for 90-100 years, and, more rarely, up to 150 years. They are light-demanding and can grow rapidly on poor, acid soils. Its tolerance to pollution make it suitable for planting in industrial areas and exposed sites. It is also widely planted in urban parks and gardens as a ruderal ornamental tree [18].

Figure 2. *Bark of Acer platanoides* L., *Acer pseudoplatanus L. and Betula pendula Roth*

Results and discussion

The Cu concentration in the bark of the examined species showed regular spatial distribution, with the highest values measured in the bark of all three species in the park located in the municipality of Palilula, and the lowest in Topčider Park, which is isolated from direct sources of pollution. It was further determined that there is a significant difference ($p < 0.001$) in the ability of the studied species to accumulate this element. Namely, the lowest concentrations of Cu were measured in the *B. pendula* bark, while the existing results cannot determine which of the other two species accumulates Cu better (Table 1), since the accumulation depended mostly on the habitat in which they grow. These results are consistent with the findings of Parzych et al. [19] who found that the accumulation of Cu directly depends on the structure or porosity of the bark. In his study, Suzuki [20] measured 3.06-14.9 mg kg^{-1} in the bark of *Acer saccharum* March and *Prunus sargentii*, which is similar to values determined in this study, as well as some previous studies [12-14]. The average concentration of Cu in the bark of *B. pendula* was similar to its concentration in the bark of *Betula pubescens* (4.3-7.4 mg kg^{-1}, [21]). On the other hand, Kosiorek et al. [22] found significantly lower Cu concentrations in the bark of *Betula pendula* (1.532-2.238 mg kg^{-1}), and in the bark of *Acer platanoides* (1.278-2.280 mg kg^{-1}).
The results obtained in this research indicate the certain spatial distribution of Mn in the bark of the examined species. The highest Mn content was measured in the bark of *A. platanoides* and *A. pseudoplatanus* in the park in the municipality of Palilula, and in the bark of *B. pendula* in the municipality of Savski venac and the lowest in the bark of *A. platanoides* and *B. pendula* in the municipality of Obrenovac, and in the bark of *A. pseudoplatanus* in the municipality of Savski venac (Table 1). In general, there is a significant difference ($p<0.001$) in the ability of the studied species to accumulate Mn, so it is shown that the bark of *B. pendula* is characterized by the lowest ability to accumulate Mn, while the accumulation in the bark of *A. platanoides* and *A. pseudoplatanus* varies depending on habitat. The average Mn concentration in the bark of *A. platanoides* and *A. pseudoplatanus* was similar or slightly higher in relation to the bark of *Acer saccharum* and *Prunus sargentii* (30.4-93.7 mg kg^{-1}, [20]). Manganese concentration in the bark of *B. pendula* was similar or slightly higher than the same in the bark of *Pinus sylvestris* (4.7-6.5 mg kg^{-1},. [22]) and *Pinus nigra* (4.02-20.89 mg kg^{-1}, [12]). In contrast, the Mn concentration in the bark of *B. pubescens* in the study of Reimann et al. [21] was many times higher (192-2160 mg kg^{-1}) than that found in this research.
Similar to previous elements, the park next to the Pionir hall in the municipality of Palilula is characterized by a higher concentration of Pb in the bark of all examined species in relation to the other two municipalities. Lead concentration ranged from 2.42 mg kg^{-1} in the bark of *B. pendula* from the park in the municipality of Obrenovac to as much as 25.70 mg kg^{-1} in the bark of *A. pseudoplatanus* from the park in the municipality of Palilula. A similar regularity was observed for Pb as for Cu and Mn, ie *B. pendula* has the lowest potential for Pb accumulation, while Pb accumulation by both Acer species depends not only on the structure of the bark but also on the specific conditions prevailing in the habitat. Compared to the average values obtained by our research, a similar or slightly lower concentration of this element was measured in the bark of *B. pubescens* (0.21-8.6 mg mg^{-1}, [21]), and the bark of *Acer saccharum* and *Prunus sargentii* (0.12 -10.7 mg kg^{-1}, [20]). On the other hand, Kosiorek et al. [22] found significantly lower Pb concentration in the bark of *Betula pendula* (0.097-0.163 mg kg^{-1}) and *Acer platanoides* (0.131-0.194 mg kg^{-1}).
Zinc concentration in the bark of examined species varied in a wide range from a minimum of 1.33 mg kg^{-1} measured in the bark of *A. platanoides* from the park in the municipality of Palilula to a maximum of 81.23 mg kg^{-1} in the bark of *A. pseudoplatanus* growing in the same locality. Suzuki [20] also found a wide range in Zn concentration in a study conducted on the bark of *Acer saccharum* and *Prunus sargentii* (3.65-107 mg kg^{-1}). However, when comparing the accumulation ability of the examined species, a slightly different pattern in terms of Zn accumulation was found. The main characteristic that separates the bark of *B. pendula* from *A. platanoides* and *A. pseudoplatanus* is its greater potential for Zn accumulation, apart from *A. pseudoplatanus* from the park in the municipality

of Palilula. The bark of *A. platanoides* has the lowest potential for Zn accumulation. The good ability of *B. pendula* to accumulate Zn has also been described by numerous other authors [14,22-25]. Raimann et al. [21] found that the Zn concentration in the bark of *B. pubescens* varies in the range of 48-231 mg kg^{-1}, which significantly coincides with the Zn concentration in the bark of *B. pendula* measured in this research (Table 1).

Table 1. Differences in Cu, Mn, Pb and Zn concentrations in the bark of selected tree species in three Belgrade municipalities, ANOVA, n=5, *p<0,05, **p<0,01, ***p<0,001, ns-not significant

Cu [mg kg^{-1}]	**Palilula**				**Obrenovac**				**Savski venac**			
Species	**M±SD**	***Pl***	***Ps***	***B***	**M±SD**	***Pl***	***Ps***	***B***	**M±SD**	***Pl***	***Ps***	***B***
A. platanoides	11.668±0.496	/	***	***	10.341±0.499	/	***	***	10.456±0.586	/	***	***
A.pseudoplatanus	17.642±0.360	***	/	***	7.079±0.193	***	/	***	9.418±0.477	***	/	***
B. pendula	9.253±0.377	***	***	/	4.156 ±0.085	***	***	/	5.952±0.184	***	***	/
Mn [mg kg^{-1}]	**Palilula**				**Obrenovac**				**Savski venac**			
Species	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*
A. platanoides	145.623±1.797	/	***	***	48.094±1.039	/	***	***	63.183±0.681	/	***	***
A.pseudoplatanus	121.913±1.009	***	/	***	52.738±0.536	***	/	***	45.482±0.632	***	/	***
B. pendula	11.978±0.321	***	***	/	7.996±0.089	***	***	/	13.314±0.337	***	***	/
Pb [mg kg^{-1}]	**Palilula**				**Obrenovac**				**Savski venac**			
Species	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*
A. platanoides	9.751±0.472	/	***	ns	6.461±0.592	/	***	***	2.541±0.202	/	***	ns
A.pseudoplatanus	25.703±3.691	***	/	***	4.143±0.251	***	/	***	5.053±1.101	***	/	***
B. pendula	9.094±0.682	ns	***	/	2.424±0.362	***	***	/	2.924±0.222	ns	***	/
Zn [mg kg^{-1}]	**Palilula**				**Obrenovac**				**Savski venac**			
Species	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*	M±SD	*Pl*	*Ps*	*B*
A. platanoides	1.330 ±0.076	/	***	***	2.071±0.023	/	***	***	2.071±0.023	/	***	***
A.pseudoplatanus	81.533±1.208	***	/	***	28.463±0.210	***	/	***	29.683±0.888	***	/	***
B. pendula	74.417±0.541	***	***	/	53.696±0.649	***	***	/	45.783±0.824	***	***	/

When comparing the examined localities, it was noticed that the park near the Pioneer Hall in the municipality of Palilula is characterized by a higher concentration of all examined elements in the bark in relation to the parks in the municipalities of Obrenovac and Savski venac. The reason for such behavior of examined species could be atmospheric deposition, which is mainly associated with traffic. Particulate matter within the urban environment contains a range of PTEs that are attributed to a number of both natural and anthropogenic sources. The elements Cd, Cu, Fe, Ni, Pb and Zn are often associated with high traffic densities, originating from exhaust emission, tire, brake, vehicle and engine wear, or the re-suspension of road dust [26]. Furthermore, exhaust gases from cars can be a source of Mn, since methylcyclopentadienyl-manganese-tricarbonyl (MMT) is used as an additive in the production of unleaded gasoline [27]. Manganese can also originate from moving metal parts of the car given the fact it is used as the main alloying element in many aluminum alloys due to its ability to resist corrosion [28].

When comparing the accumulation potential of the examined species, it can be concluded that the bark of *A. platanoides* and *A. pseudoplatanus* retain significantly higher amounts of Cu, Mn and Pb, while *B. pendula* bark shows good potential for Zn accumulation. The results obtained for studied species are not uncommon given that tree bark with a rough surface, such as *A. platanoides* and *A. pseudoplatanus*, is a more effective trap for atmospheric particles than smooth *B. pendula* bark [29], because the surface of such tree bark is very porous and enables efficient accumulation and retention of PTEs [30]. However, the efficient accumulation of pollutants from the air is conditioned not only by the structure of the bark, but many different factors have an effect on elements collecting on the

bark surface, such as trace elements quantities in the air, physiological and chemical properties of the bark, precipitation, soil factors, climatic factors. and anthropogenic factors [12].
Based on the obtained data, it can be concluded that the bark of the examined tree species can be used as an indicator of air pollution, with the bark of *A. platanoides* and *A. pseudoplatanus* more efficient as indicators of Cu, Mn and Pb accumulation, while the bark of *B. pendula* as an indicator of Zn accumulation. The use of different parts of plants for biomonitoring purposes is generally accepted worldwide, and is especially useful in areas where there is no official network of air monitoring stations

Conclusion

Based on the analysis and measurement of PTEs concentration in the bark of *Acer platanoides*, *Acer pseudoplatanus* and *Betula pendula* in three Belgrade municipalities (Palilula, Obrenovac and Savski venac) it was noticed that the park near the Pioneer Hall in the municipality of Palilula is characterized by a higher concentration of all examined elements in the bark in relation to parks in other two municipalities. The reasons for this behavior of the examined species are traffic emissions and dust resuspension associated with road traffic.
The results obtained from this research show that the bark of the examined tree species can be used as indicators of air pollution. The bark of *A. platanoides* and *A. pseudoplatanus* was found to retain higher amounts of Cu, Pb and Mn in relation to the bark of *B. pendula*, but the accumulation potential depends not only on the characteristics of the bark but also on specific habitat conditions. The bark of *B. pendula* showed good potential for Zn accumulation.
Research related to the use of different plant parts for the purpose of biomonitoring needs to be further developed in terms of standardization of methods, which could find its greatest application in areas where there is no developed network of air monitoring stations.

Acknowledgements

This work was supported by the Ministry of Education, Science, and Technological Development of the Republic of Serbia, grant no. 451-03-68/2022-14/ 200007.

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