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INFLUENCE OF AIRBORNE SULPHUR DIOXIDE ON TOTALS CONCENTRATIONS IN LINDEN AND PINE

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ABSTRACT
Bor and the surroundings (Eastern Serbia) have a poor air quality, due to emissions from the mining-metallurgical complex for copper production. Considering the processing and smelting of sulphide ores, one of the dominant air pollutant is SO_2, which causes acidification of waters and soil, affecting vegetation. Biomonitoring of air pollution was conducted in order to examine the effect of the increased SO_2 concentrations in the air on the total S concentrations in linden and pine. Roots, branches and leaves/needles were sampled in the urban-industrial, rural and background zone. The obtained S concentrations showed that in the condition of increased air pollution pine roots and branches are better for biomonitoring of total S than same parts of linden. Nevertheless, linden leaves contained higher S concentrations than pine needles. According to the Enrichment factors, the most endangered zone in Bor is urban-industrial (at sampling sites 0.5 km and 1 km away from the copper smelter).
Keywords: linden, pine, biomonitoring

1. INTRODUCTION
One of the most important environmental impacts of anthropogenic activity in the urban ecosystem is the atmospheric pollution [1]. Gaseous and particulate atmospheric emissions react under the influence of sunlight and diverse meteorological conditions creating a variety of products which are toxic to animals, humans and vegetation [2]. Trees can serve as a good tool for biomonitoring in case of possible air pollution, as they develop large canopies that extend high into the air, offering a large surface area for deposition and potential assimilation of airborne substances [3]. Higher plants show detectable alterations in presence of the pollutants such as SO_2 at concentration levels lower than those that are toxic for humans. The assimilation of SO_2 by the plants and the produced harm depend on both the atmospheric SO_2 concentration and the time of the exposure to the pollutant [2]. It has been shown that plants are sensitive to SO_2 during the sunny days, high humidity of the air, during the late spring and early summer [4].
Bor and the surroundings (Eastern Serbia) are well known for pyrometallurgical production of copper from sulphide ores. From the environmental standpoint, the most dangerous unit of the mining–metallurgical complex is the copper smelter. Daily and annual SO_2 concentrations in the urban-industrial area (the town core) from 1994 to 2008, greatly exceeded thecurrent air quality standards [5]. The critical SO_2 concentration (30 $\mu g/m^3$)for forests and vegetation on annual level according to WHO [6] also exceeded up to ten times. Additional, annual concentrations of total atmospheric deposition (which contains sulfates) in the urban-industrial and rural zone of Bor, also exceeded maximum allowable concentration[7]. The aim of this study was to determine the influence of high

polluted environment with SO_2 on concentrations of total sulphur in parts of linden and pine at different distances from the pollution sources.

2. RESULTS AND DISCUSSION

2.1. Sampling of biomaterial and sample preparation

The sampling sites were located in the directions where the prevailing winds bring the pollution from the smelter, open pits and tailing ponds. Plant parts of linden and pine were sampled from three zones:

1. Urban-industrial, which includes the sampling sites Town Park (0.5 km away from the copper smelter) and Hospital (1 km away from the copper smelter).
2. Rural, which includes the sampling sites Ostrelj (4.5 km away from copper smelter) and Slatina (6.5 km away from copper smelter). These sampling sites represent the rural settlements endangered by air pollution.
3. Background (sampling site Zlot-rural area), which is located 15 km away from the copper smelter. This sampling site is located in the Lazar's Canyon, which is a significant centre of floral diversity in the Balkans.

It should be noted that linden was sampled from each sampling site, while pine was not available at the sampling sites Town Park and Hospital.

Branches and leaves/needles were sampled 2–3 m above ground level. The roots were sampled from topsoil, at a sampling depth of about 10–20 cm. Leaves/needles were detached from perennial branches in the laboratory. Individual samples (roots, branches, leaves/needles), from the particular site, were homogenized into one sample. Plant samples were thoroughly washed with running tap water and rinsed with distilled water to remove soil particles, surface dust and airborne depositions attached to the plant surfaces. All the samples were dried at room temperature for 10 days, and then in a dryer for 24 h at 50°C. The dried plant material was ground in a laboratory mill into fine powder (average particle diameter 100 µm) [7].

All the plant samples (0.1000 g of dry weight) were digested in a mixture of nitric acid (HNO_3, 65%, *p.a.)* and hydrogen peroxide (H_2O_2, 30%) in a volume ratio 4:1 as in the papers Serbula et al. [7] and Piczak et al. [8].Concentration of total S (µg/g of dry weight) in the plant material were determined by ICP-AES (Model „Spectro Ciros Vision“), at the Mining and Metallurgy Institute Bor (Serbia). Limit of detection for S was 25 µg/g.

2.2. Total S concentrations in the parts of linden and pine

Total S concentrations in parts of linden and pine depending on the sampling site are given on the Fig. 1.

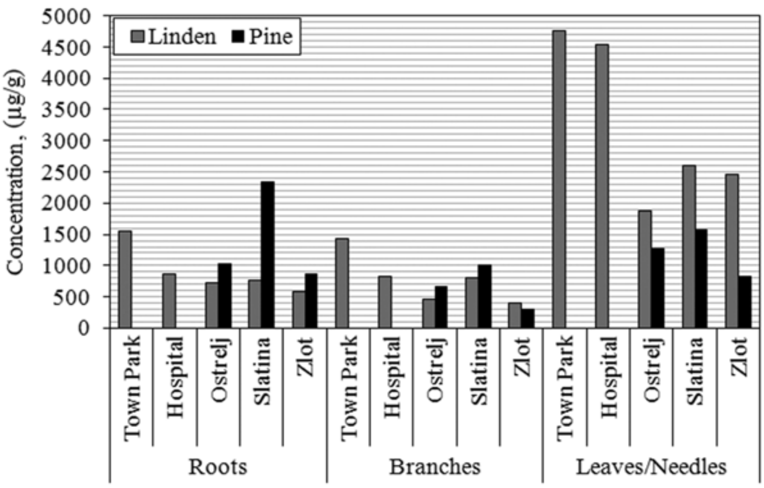

Figure 1. Total S concentration (µg/g) in roots, branches and leaves/needles of linden and pine, depending on the sampling site

Concentrations of total S in the roots of linden and pine decrease from the urban-industrial towards background zone. Within the rural zone, S concentrations are higher at the sampling site Slatina (6.5

km) than at the sampling site Ostrelj (4.5 km), just like in our previous study, in the case of heavy metal concentrations in the samples of linden and pine. Between the sampling site Ostrelj and the dominant source of pollution there is a physical barrier (a hill) which prevents transfer of the pollutants. In the conditions of lower wind velocities, the topography of the terrain has a crucial influence on the lower pollution at the site Ostrelj compared to the site Slatina [7]. Pine roots have higher S concentrations, compared to linden roots at the sampling sites where both plants were sampled. Total S concentrations in linden and pine branches decrease with the increasing distance from the copper smelter, with the exception of the sampling sites Ostrelj and Slatina. Pine branches contain higher S concentrations than linden branches in the rural zone. When S concentrations are compared at the sampling sites at which foliar parts of linden and pine were sampled, linden leaves are observed to contain more S than pine needles. Leaves of linden sampled in the urban-industrial zone have the highest S concentrations compared to parts of linden and pine at all the sampling sites. From the Fig. 1. it can be seen that linden leaves at the sampling site Zlot (background zone) have a greater content of total S than leaves at the sampling site Ostrelj, and similar content as leaves at the sampling site Slatina. According to Mingorance et al. [9] differences in plant behavior at sites with different concentrations of air pollutants could be a result of spatial variability in the soil chemical properties, as well as different organic compounds released by the roots of each species. Both of these factors and many others are responsible for the bioavailability of the elements. Except for the sampling site Slatina (6.5 km), linden leaves have the highest S concentrations compared to linden roots and branches. At the sampling sites Slatina and Zlot pine roots have higher S concentrations than pine branches and needles. At the sampling site Ostrelj pine parts with the highest S concentrations are needles.
The natural concentration of S in pine needles exceeds 600 μg/g[10] at each sampling site. Critical foliar S level for pine of about 900 μg/g [11]does not exceed only at the sampling site Zlot within the background zone, which indicates the direct impact of SO_2 from the copper smelter.

2.3. Enrichment factor

The plant Enrichment factor (EF) has been calculated in order to derive the degree of element accumulation in plants growing at the contaminated sites with respect to plants growing at the background site. EF was calculated as $EF=C_{plant}/C_{backgound}$, where C_{plant} and $C_{backgound}$ represent element concentrations (μg/g) in plant parts (leaves, branches and roots) from the polluted sampling site and the background site, respectively. According to Singh et al. [12]EF>1 is a measure of environmental pollution. According to the EFs (Table 1), it can be concluded that the largest sulphur enrichment in the parts of linden is at the sampling sites in the urban-industrial zone, compared to the rural zone.

Table 1. EFs for total S in parts of linden and pine

	Sampling site	Plant part	Linden	Pine
Urban-industrial zone	Town Park	Roots	**2.67**	n.s.
		Branches	**3.46**	n.s.
		Leaves	**1.93**	n.s.
	Hospital	Roots	**1.49**	n.s.
		Branches	**2.03**	n.s.
		Leaves	**1.84**	n.s.
Rural zone	Ostrelj	Roots	**1.25**	**1.17**
		Branches	**1.13**	**2.14**
		Leaves/Needles	*0.75*	**1.53**
	Slatina	Roots	**1.34**	**2.65**
		Branches	**1.98**	**3.25**
		Leaves/Needles	*1.05*	**1.89**

n.s. – not sampled

At the sampling sites Town Park, Hospital and Slatina branches are distinguished as parts of linden in which the degree of S enrichment is the highest. Pine branches sampled in the rural zone are distinguished as parts with the highest enrichment, too. This could be a consequence of long-term absorption of S by perennial branches in the condition of the increased air pollution [7]. EFs for aerial parts of pine were higher compared to the same parts of linden.

3. CONCLUSION

According to the obtained results, it could be concluded that pine and linden are suitable for biomonitoring of the environmental pollution with SO_2 and other sulphur compounds. Pine roots and branches contain higher total S concentrations than the same parts of linden. Linden leaves are better plant parts for biomonitoring of environmental pollution, than pine needles. Nevertheless, total S concentrations in pine needles at the sampling sites in the rural zone are above the critical concentration. Enrichment factors for linden parts indicate that the urban-industrial zone of Bor is the most polluted (at the sites 0.5 km and 1 km away from the copper smelter, in the very town core and in prevailing wind direction). Pine parts at the sampling sites in the rural zone (pine was not available in the urban-industrial zone) are enriched with total sulphur, too. This is a confirmation that the rural zone is also affected with SO_2 pollution, regardless of the absence of the data on SO_2 imission in this area.

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