Assessment of Airborne Heavy Metal Pollution Using *Pinus spp.* and *Tilia spp.*

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ABSTRACT

The influences of airborne pollution originating from the Mining–Metallurgical Complex Bor (Serbia) on the concentrations of Cu, Pb, Zn and Mn in the samples of *Tilia spp.* and *Pinus spp.* were examined. The roots, branches, leaves/needles and soil were sampled in urban-industrial, rural and background zone at different distances from the copper smelter and at prevailing wind directions. According to the results of the enrichment factors, branches were the plant parts most enriched with Cu and Pb. The results of cluster analysis indicate that the most endangered zone in Bor is urban-industrial (at sites 0.5 km and 1 km away from the copper smelter). Aerial parts of both plant species can be used for biomonitoring of air pollution, although pine needles showed a higher level of response to pollution. According to the bioconcentration factor, translocation factor and translocation index, high concentrations of Cu and Pb in aerial parts of pine and linden are mostly a consequence of airborne pollution.

Keywords: Linden; Pine; Air pollution; Copper smelter; Copper; Lead.

INTRODUCTION

Air pollution is a serious problem in urban and industrial areas. Heavy metal deposition near smelters may affect vegetation growth and may lead to the damage and alteration of animal, including human, physiological functions through the food chains (Al-Alawi and Mandiwana, 2007; Nouri et al., 2009; Fowler et al., 2009). The threat that heavy metals pose to human and animal health is aggravated by their long-term persistence in the environment (Yoon et al., 2006).

Trace metals accumulation in plants from anthropogenic sources has drawn greater attention to inorganic pollution, and established plants as passive biomonitor, since plants respond directly to the state of soil and air (Divan et al., 2009; Fowler et al., 2009). Higher plants which are most often used for biomonitoring in industrial and urban areas, are coniferous and deciduous trees (Rademacher, 2001; Piczak et al., 2003). The results of many researches show that metal accumulation in plants varies, depending on the species, tissues and metals (Rossini Oliva and Mingorance, 2006; Memon and Schröder, 2009; Rucandio et al., 2011; Sawidis et al., 2011; Serbula et al., 2012a). Pine (*Pinus spp.*) and linden (*Tilia spp.*) meet many of the requirements of good bioindicators. Pine has needles with a thick epicuticular wax layer which made pine species the best suited biomonitor, particularly sensitive to environmental pollution (Mingorance et al., 2007). The morphology, canopy structure and epicuticular wax on the leaf surface make linden trees suitable for biomonitoring of air pollution (Braun et al., 2007). Pine needles are most frequently used for biomonitoring of airborne pollution, because of the possibility of passive and active uptake of needles tissue from the atmosphere (Mingorance et al., 2007; Sun et al., 2009; Sun et al., 2010; Kuang et al., 2011). The most frequently identified elements which cause biological/ecological harmful effects are Pb, Cs, As, Cr, Zn, Ni, and Cu. Heavy metals have different patterns of behaviour and mobility within a tree, whereas Cd, Ni and Zn are more easily translocated to the aerial parts (Kabata-Pendias and Pendias, 2001). The uptake of hazardous materials, directly from wet and dry deposition by aerial parts of plants, has often been reported in the conditions of high air pollution level (Divan et al., 2009).

Determination of heavy metal content in the plant and soil samples is of great importance for the assessment of the effects of hazardous airborne materials originating from the mining-metallurgical complex. The paper focuses on the concentrations and correlation of Cu, Pb, Zn and Mn, in roots, branches and leaves/needles of *Tilia spp.* and *Pinus spp.* Considering that both plant species easily accumulate heavy metals, our aim was also to evaluate their air pollution biomonitoring ability in the vicinity of the mining-
metallurgical complex.

METHODS

Study Area

The town of Bor is situated in a mountainous and forested area in Eastern Serbia, close to the Bulgarian and Romanian borders and approximately 210 kilometers away from Belgrade (Fig. 1). The climate on the territory of the Bor area is moderately continental. Dominant winds in the examined area are in the W, WNW and NW direction. Winds less frequent are in the direction of E, ENE and ESE, whereas the least frequent winds are in the direction of S and SSW (Serbula et al., 2012a). Bor and its surroundings are known for the largest copper ore deposits in Serbia, and they are among the largest ones in Europe. The main industrial activities in the study area are mining and metallurgy. The dominant source of pollution is copper smelter in which sulphide copper concentrate (with the accompanying elements Fe, Pb, As, Cd, Ni, Zn, Mn and precious metals) is processed (Serbula et al., 2010). Emissions from copper smelter are principally particulate matter (PM) and sulfur oxides (SO\textsubscript{x}). Every year the copper smelter emits 5–8 kg of Zn, 6–25 kg of Pb and 5–20 kg of As per inhabitant of the Bor region (Serbula et al., 2010). For the purpose of reducing air pollution, around 40% of SO\textsubscript{2} (from the smelter) is utilized in the sulphuric acid plant, while the rest of waste gases are emitted into the atmosphere (Serbula et al., 2010). Open pits and flotation tailing ponds are also big sources of dust, which endangers the surrounding villages and agricultural soil, leading to reduced agricultural production and health threat for people who live there.

The concentrations of PM\textsubscript{10} in the air of Bor and the surroundings, for years have considerably been exceeding the daily limit value (LV) according to: EC Directive 2008/50/EC (50 μg/m\textsuperscript{3}) (EC, 2008), U.S. EPA (150 μg/m\textsuperscript{3}) (U.S. EPA, 2010), and Serbian Regulation (50 μg/m\textsuperscript{3}) (“Off. Gazette of the RS”, No. 75/10). More detailed discussions about concentrations of heavy metals in PM are given in Serbula et al. (2010, 2011, 2012b). The annual concentrations of total atmospheric deposition at the four measuring sites in the urban-industrial and rural zone of Bor (MMI Bor, 1994–2008) and annual anode copper production in the period from 1994 to 2008 (nine months) are given in Fig. 2. The measuring site “Šumska sekcija” is closest to the Site 1 (Town Park) where plant material was sampled. These data represents a historical pollution with significant exceedance of maximum allowed concentration of total atmospheric deposition for one year (200 mg/m\textsuperscript{2}/day) according to the Serbian Regulation (“Off. Gazette of the RS”, No. 75/10).

Sampling and Sample Preparation

Leaves/needles, branches, roots and soil samples of Tilia spp. and Pinus spp. were collected from the three zones (Table 1): urban-industrial (Site 1 and 2), rural (Site 3 and 4) and background (Site 5). The sampling sites were located in the directions where the prevailing winds bring the pollution from the smelter, open pits and tailing ponds.

Fig. 1. The study area: location of Bor, industrial area and sampling sites.
Table 1. Description of sampling sites (the dominant wind directions at each site from the pollution source, the distance of the sites from the source of pollution) and the availability of the plant species.

| Site                  | Wind direction | Distance (km) | Pinus spp. | Tilia spp. |
|-----------------------|----------------|---------------|------------|------------|
| (1) Town Park         | ENE            | 0.5           | No         | Yes        |
| (2) Hospital          | ESE            | 1.0           | No         | Yes        |
| (3) Oštrelj           | WNW            | 4.5           | Yes        | Yes        |
| (4) Slatina           | NW             | 6.5           | Yes        | Yes        |
| (5) Zlot (Lazar’s Canyon) | NE          | 13.0          | Yes        | Yes        |

* No available plant.

Among the rural settlements within the Bor region, the sampling sites 3 and 4 are the most endangered by air pollution (Serbula et al., 2011). The background site 5 (Zlot) was located in Lazar’s Canyon, which is a significant centre of floral diversity in the Balkans.

About 200 g of leaves/needles of pine and linden trees were collected 2–3 m above ground level from each direction (W, E, S and N). Branches (perennial) and roots were cut off with stainless steel knife from two counter sides. The coarse roots were sampled from topsoil, at a sampling depth of about 10–20 cm. Each sample was taken from three plants for each species (depending on the availability). Leaves/needles were detached from perennial branches in the laboratory. Afterwards, individual samples (roots, branches, leaves/needles), from the particular site, were homogenised into one sample. Plant samples were thoroughly washed with running tap water and rinsed with distilled water to remove any soil particles, surface dust and airborne depositions attached to the plant surfaces. Otherwise, a large experimental error can be made because of the unknown amount of surface deposition (Yilmaz and Zengin, 2004). All plant samples were air dried first for 10 days at room temperature. In order to obtain concentrations on a dry matter basis, the samples were further dried in an 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). To avoid contamination, the mill was thoroughly cleaned and dried after each grinding. Soil samples from the rooting zone (10–20 cm) were collected around each plant at four directions, and stored in clean polyethylene bags. Each soil sample was air dried first, and then in a dryer at 50°C. The samples of soil were sieved through a 0.883 mm mesh stainless steel sieve, and then ground in the same way as the plant material.

The samples of the plant material and the soil were digested according to the U.S. EPA method 3050B (U.S. EPA, 1996), as in the paper Piczak et al. (2003). The total concentrations of copper (Cu), lead (Pb), zinc (Zn) and manganese (Mn) in plant and soil samples were determined by ICP-AES (Model „Spectro Ciros Vision“), at the Institute of Mining and Metallurgy Bor (Serbia). Three replicates were done for each sample. The concentrations of all the measured elements are expressed as μg/g of dry weight. Limits of detection for Cu, Pb, Zn, Mn were: 1 ppm, 10 ppm, 1 ppm, 0.05 ppm, respectively. The pH value of the soil was determined according to the ISO standard 10390:2005 (ISO, 2005).

Data Analysis

A statistical processing of the data was carried out using the SPSS 17.0 for Windows Version. Pearson’s correlation coefficients were calculated in order to study the relationship between the elements concentrations in all the samples of linden and pine at all the sampling sites. The research of
the existing similarities (or differences) among the sampling sites was performed by cluster analysis (CA). CA was applied for the concentration data using linkage between groups, with Euclidean distances. In general, this form of CA is regarded as very efficient, although it tends to create small clusters (Aničić et al., 2009).

The plant Enrichment factor (EF) has been calculated in order to derive the degree of heavy metal accumulation in plant parts growing at the contaminated sites with respect to plant parts growing at the background site. EF was calculated as EF = Cplant/Cbackground, where Cplant and Cbackground are metal concentrations (μg/g) in plant parts (leaves, branches and roots) from the polluted sampling sites and the background site, respectively (Serbula et al., 2012a).

Accumulation and translocation of the elements in the parts of linden and pine were determined by the Bioconcentration factor (BCF), Translocation factor (TF) and Translocation index (Rl/b). Bioconcentration factor was determined by the equation BCF = Cplant/Croot. BCF > 1 indicates that a particular element is accumulated in plant roots from the soil (Yoon et al., 2006). Translocation factor can be expressed by the equation TF = Cplant/Cleaf. TF > 1 indicates that a certain element is effectively translocated from the roots to a branches (Yoon et al., 2006). Rl/b represents a ratio of concentrations of a certain element in leaf/needles and concentrations in a branches, according to the equation Rl/b = Cleaf/Cbranch. Rl/b > 1 means a successful translocation from a branches to a leaves (Rossini Oliva and Mingorance, 2006). According to Rossini Oliva and Mingorance (2006), this index is a significant indicator of direct accumulation by atmospheric deposition. In those equations Cleaf, Cplant, Croot, Cbranch represents concentrations (μg/g) of certain element in soil, roots, branches and leaves/needles, respectively.

RESULTS AND DISCUSSION

Soil Element Content

Concentrations of Cu, Pb, Zn and Mn in the topsoil samples collected around both linden and pine trees, as well as pH of the soil, at all the sampling sites, are shown in Table 2. The table also shows the maximum allowable concentration (MAC) of heavy metals in soils according to the Regulation of the Republic of Serbia (RS) (“Off. Gazette of the RS”, No. 23/94).

Concentrations of Cu in linden surrounding soil are not within the MAC at any of the sampling sites. On the other hand, Cu concentrations in the pine surrounding soil are within the MAC only at the sampling site 5. According to the Regulation of the RS, Pb concentrations in linden surrounding soil are increased only in the urban-industrial zone (sites 1 and 2). At the sampling site 4, Pb concentration in soil around pine is close to the MAC. Zn concentrations in linden and pine surrounding soils, at all the sampling sites are in the range of MAC. Mn concentrations in soil collected around linden and pine are in the range of normal values from 170 μg/g to 1200 μg/g, given by Tian et al. (2009). Regarding the average concentrations of the studied heavy metals in soils collected around linden and pine at all the sampling sites, Pb concentration is the lowest, followed by Zn, Cu and Mn. Concentrations of the studied elements indicate that pollution of soil is greatly influenced by the emission from the copper smelter at the closest sampling sites. The reported results on the concentrations of Cu, Pb and Zn in the soil in 1997 (EIA Study, 2010), were from the same sampling sites as the ones in this study (located within urban-industrial and rural zone in Bor and its surroundings). It can be stated that soil pollution for the period of more than ten years has considerably increased up to several times. This indicates the cumulative pollution due to atmospheric deposition of heavy metals in Bor and its surroundings. In the study area, soil pH ranges from 5.16 to 8.13 (Table 2).

Levels of Heavy Metals in Plant Parts

Copper

Copper is a microelement, essential for all organisms (Yadav, 2010). Plants absorb Cu from the soil most often through the roots, but the intensive absorption also occurs

Table 2. Concentrations of the studied elements in topsoil (μg/g) and soil pH in the Bor region at five sampling sites, compared to the current soil quality standard.

| Sampling site | Plant species | Cu   | Pb   | Zn   | Mn   | pH  |
|---------------|---------------|------|------|------|------|-----|
| Site 1        | linden        | 421  | 166  | 124  | 920  | 5.16|
| Site 2        | linden        | 1333 | 151  | 118  | 832  | 6.28|
| Site 3        | pine          | 268  | 82   | 161  | 644  | 7.91|
| Site 4        | linden        | 267  | 55   | 62   | 798  | 7.70|
| Site 5        | pine          | 123.8| 94   | 58   | 908  | 6.77|

Average      427.12 96.50 104.87 781 7.13
Minimum      24.23  49   41   465 5.16
Maximum      1333 166 178  920 8.13
MAC RSa 100 100 300 / /

a “Off. Gazette of the RS”, No. 23/94

EIA Study (2010): Urban-industrial zone: Cu (100 μg/g), Pb (32 μg/g), Zn (29 μg/g)
Site 3: Cu (130 μg/g), Pb (11 μg/g), Zn (22 μg/g); Site 4: Cu (138 μg/g), Pb (24 μg/g), Zn (25 μg/g)
Lead

Although Pb occurs naturally in all plants, it has not shown to play any essential role in their metabolism. The translocation of Pb from roots to aerial parts is greatly limited. Airborne Pb, a major source of Pb pollution, is also readily taken up by plants through foliage (Kabata-Pendias and Pendias, 2001). Pb concentrations in linden and pine roots range from 27 μg/g to 82 μg/g, and from 45 μg/g to 178 μg/g, respectively (Fig. 3(b)), which is above the critical value of 20–35 μg/g (Rademacher, 2001). At the sampling sites where both plant species are sampled and in the conditions of the increased pollution (the sites 3 and 4) the pine roots are observed to contain more Pb than the linden roots. Concerning the distance from the source of pollution and its influence on the Pb concentrations in the roots of linden and pine, it can be concluded that there is no clear decreasing trend and the difference in pollution regarding different zones. Therefore, no conclusion can be drawn about the direct effect of the distance from the copper smelter on Pb root concentrations in either plant species. Pb concentrations in the samples of linden branches vary considerably within the zones. Pb concentrations are about 35 times higher at the sampling site 1 compared to the background zone. At the sampling sites 3 and 4, Pb concentrations are approximately the same, whereas in the background zone the level is much lower (Fig. 3(b)). When Pb concentrations are compared at the sampling sites at which branches of linden and pine were sampled, pine is observed to contain more Pb than linden. Pb concentrations (12–33 μg/g) in the samples of linden leaves are below critical value (Rademacher, 2001). Pb, as well as Cu concentrations, in aerial parts of both plant species (depending on the availability) decrease with the distance from the copper smelter. It can be determined that branches and leaves/needles of linden and pine, at the sites where both plants were sampled, are better bioindicators of airborne Pb than the roots. Pine branches and needles, contain more Pb than the same parts of linden. Having in mind the low mobility of Pb (low translocation to the aerial parts), and concerning the observed pattern of their content in leaf/needle and branch, it can be concluded that Pb arises from airborne emissions. Compared to the mean values reported in the literature (Yılmaz and Zengin, 2004; Al-Alawi and Mandiwana, 2007; Sun et al., 2009; Kord et al., 2010; Sun et al., 2010; Dmuchowski et al., 2011), concentrations of Pb in pine needles from our study area are higher. Similar or slightly lower Pb concentrations in linden leaves predominantly from traffic related sites were also reported by Piczak et al. (2003), Tomašević et al. (2004) and Anićić et al. (2011).

Zinc

Zinc is an essential element in all the organisms having an important role in biosynthesis. The roots often contain much more Zn than the tops, particularly if the plants are grown in Zn-rich soils (Kabata-Pendias and Pendias, 2001). Zn levels in the linden roots at all the sampling sites except for the sampling site 1, do not vary considerably (Fig. 3(c)). In the pine roots at the site 3, Zn concentration of 350 μg/g is the highest, compared to the other Zn concentrations. Zn concentrations in linden and pine branches range between 17 μg/g and 194 μg/g, and from 12 μg/g to 43 μg/g, respectively. The threshold of Zn phytotoxicity of 230 μg/g (Nouri et al., 2009) for aerial parts was not exceeded in the linden
Fig. 3. Levels of a) Cu, b) Pb, c) Zn and d) Mn in belowground (roots) and aboveground (branches, leaves/needles) parts of linden and pine, depending on the distance of the sampling sites from the copper smelter (1, 2, 3, 4 and 5 are the sampling sites).

and pine branches at any of the sampling sites. Zn levels in the linden branches, generally, decrease from the urban-industrial towards the background zone, except at the sites 3 and 4 (the influence of the terrain topography). A decreasing trend is observed in Zn concentrations in the pine branches with the distance from the pollution source. Zn levels in the
leaves of linden (10–52 μg/g) do not exceed the threshold of Zn phytotoxicity for aerial parts (Nouri et al., 2009). Zn concentrations in the pine needles (30–58 μg/g), are lower than the regarded excessive values according to Rademacher (2001). In other words, contamination of the environment with Zn does not seem to have had negative effects on pine and linden in Bor and the surroundings. Pine needles have been determined to have higher Zn concentrations than the linden leaves, at the sampling sites where both plant species were sampled. Zn concentrations in pine needles have shown to be lower in our research than the concentrations in the studies of Yilmaz and Zengin (2004), Al-Alawi and Mandiwana (2007), Yang et al. (2008), and Sun et al. (2009). The content of Zn in linden leaves is similar to Zn concentrations in the research of Piczak et al. (2003). However, Zn concentration is higher than the one detected in the urban area of Belgrade (Serbia) (Tomašević et al., 2004; Aničić et al., 2011).

Manganese
Due to the ability to be transported fast through the plant, Mn accumulates most in aerial parts but hardly in roots (Kabata-Pendias and Pendias, 2001). The highest Mn concentration in the linden roots is at the sampling site 1. The tendency of decrease of Mn concentrations in linden and pine roots was not observed with the distance from the copper smelter (Fig. 3(d)). The highest Mn concentrations in branches of linden were observed in the urban-industrial zone (sites 1 and 2), whereas at the other sampling sites the detected concentrations are much lower. The level of Mn in the pine branches was rather low (8–18 μg/g). At the sampling sites where both plant species were sampled, it was found that the branches of linden and pine contain approximately the same Mn concentrations. Mn concentrations in linden leaves decreased from the site 1 to the site 4 (Fig. 3(d)). Mn concentrations in the pine needles are about the value (≤ 40 μg/g), thus being below the suggested minimum amounts (Rademacher, 2001). Literature data show that the increased SO₂ concentrations in the air can lead to the Mn deficit in the plants (Kozlov et al., 1995), which also may be the case for pine in this research, considering the long-term pollution by SO₂ in Bor and the surroundings (Serbula et al., 2011, 2012b). The contents of Mn in pine needles in this study are lower compared to the concentrations in the study of Yang et al. (2008). Mn concentrations in linden leaves in Piczak et al. (2003) and Tomašević et al. (2004), were lower than the concentrations in the urban-industrial zone of Bor.

Correlations between the Studied Elements
Dendrograms for the concentrations of Cu, Pb, Zn and Mn in the roots, branches and leaves of linden at four sampling sites, affected by air pollution, which are situated in the urban-industrial and rural zone are shown in Fig. 4. In Fig. 4(a) two clusters can be observed. Two sampling sites, 1 and 2, form the first cluster and this is where the highest Cu concentrations in the parts of linden are detected, which is a consequence of the pollution from the mining-metallurgical complex. The sampling sites 3 and 4 in the rural zone, which is less polluted, form the second cluster. In dendrograms for Pb, Zn and Mn (Figs. 4(b–d)), the sampling sites in the rural zone are closely related to the site 2, whereas the sampling site 1 is at a considerable Euclidean distance. The obtained clusters confirm that the urban-industrial zone (site 1) in Bor is the most polluted.

Interactions of chemical elements are of similar importance to deficiency and toxicity in the physiology of plants. Table 3 shows Pearson’s correlation coefficients for Pb, Cu, Zn and Mn concentrations in all the samples of linden and pine at all the sampling sites. The strongest correlations were observed for the paired elements Cu–Pb, Zn–Pb, Zn–Cu. The Zn–Cu antagonistic interactions, in which the uptake of one element is competitively inhibited by the other, were also observed. The Zn–Pb antagonism adversely affects the translocation of each element from roots to aerial parts. According to Kabata-Pendas and Pendias (2001), Pb inhibits uptake of Zn in plants. The close correlation between Cu and Pb indicates that these metals have the same origin.

Enrichment Factors
Figs. 5(a) and 5(b) shows EFs for roots, branches, leaves/needles of linden (4 sites) and pine (2 sites), respectively, at the sampling sites in the urban-industrial and rural zone. According to Mingorance et al. (2007), the EF value > 2 is a measure of environmental pollution.
Table 3. Pearson correlations between heavy metals in leaves, branches and roots of linden and pine

|       | Pb   | Cu     | Zn     | Mn   |
|-------|------|--------|--------|------|
| Pb    | 1    |        |        |      |
| Cu    | 0.639** | 1      |        |      |
| Zn    | 0.654** | -0.822** | 1      |      |
| Mn    | 0.147 | 0.024  | 0.051  | 1    |

** significance level p < 0.01.

According to the EFs (Fig. 5(a)), it can be concluded that the largest metal enrichment in the parts of linden is at the sampling sites 1 and 2 in the urban-industrial zone, compared to the rural zone (sites 3 and 4). At all the sampling sites, even in the rural zone, branches are distinguished as parts of linden in which the highest degree of enrichment with all the elements is observed. In the parts of pine at the sampling sites in the rural zone, the EFs are similar for all the elements, except for more enrichment appearing in branches (Fig. 5(b)). The highest concentrations in the branch samples of linden and pine are, most likely, a consequence of long-term absorption of metals in the condition of the increased air pollution. The EFs for foliar parts, at the sampling sites where both plant species were sampled, have confirmed that pine needles indicate pollution, compared to the linden leaves whose EF < 2 (no pollution) for all the elements.

The EFs show that both plant species are the most enriched with Cu and Pb, due to anthropogenic (industrial) activities in the study area. It can be concluded that pine samples have higher EFs than linden samples at the sampling sites 3 and 4, for all the studied elements, probably due to different needle, branch and root physical and physiological characteristics (Mingorance et al., 2007).

Accumulation and Translocation of Metals in Plants

The mean values of BCF, TF and R_l/w for Cu, Pb, Zn and Mn are given in Table 4. The accumulation pattern of the studied elements according to the BCF values for linden and pine is the same: Cu > Zn > Pb > Mn. According to this pattern, Cu is accumulated most effectively from soil to the roots of the examined plants, which can be a cause of the highest Cu concentrations in the roots compared to the other parts of linden and pine. In the study area, only linden has accumulated Cu from the soil into roots (BCF > 1), whereas pine roots have accumulated all the studied elements, except Mn. The sequence of increasing TFs values for linden and pine, is the same: Pb > Mn > Cu > Zn. Only Pb is successfully translocated from roots into branches of linden, and not a single element is translocated
The only translocation of Mn which takes place in linden is from branches to leaves. Pb concentrations exceed the MAC only in linden surrounding soil in the urban-industrial zone, which is the closest to the copper smelter, and where traffic density is greatest during the day. For Zn and Mn there are no exceedances of the MAC.

Cu concentrations in aerial parts of linden and pine above the toxic limit, at all the sampling sites, indicate a high level of environmental pollution with Cu. For biomonitoring of environmental pollution with Cu, pine needles are better bioindicators than linden leaves. According to the accumulation and translocation factors, Cu in aerial parts of linden and pine greatly originates from the air.

Branches and leaves/needles of linden and pine are better biomonitors of airborne pollution with Pb than the roots of these plant species. Although Pb concentrations in the samples of the roots of linden and pine exceeds the critical value, translocation to the aerial parts is limited. Therefore, atmospheric deposition is the most important source of this element in aerial parts. Zn concentrations in aerial parts of linden and pine are not above threshold of Zn phytotoxicity, so it can be said that Zn does not belong to the major pollutants in the study area. Mn concentrations in pine needles were below the suggested minimum amounts, which could be attributed to the effect of long-term air pollution with SO2 in Bor and the surroundings.

The results of cluster analysis indicate that the urban-industrial zone in Bor is the most polluted area. According to the EFs, linden and pine branches compared to the root and leaves/needles have the highest enrichment with the studied elements, which is a consequence of long-term uptake of the airborne pollution. Enrichment was the greatest for Cu and Pb in both plant species. Pine needles show more enrichment compared to linden leaves.

According to the obtained concentrations of heavy metals in plant material from the sampling sites where both plant species were sampled, and in the conditions of increased air pollution, it can be concluded that pine is more suitable for biomonitoring than linden. This is also indicated by the EFs for pine parts, which are higher compared to the EFs for linden parts. However, concentrations of heavy metals in some linden samples, which were higher than normal, suggest that linden parts could be used for bioindication of environmental pollution.

Since linden and pine are used as medical plants, it is necessary to be careful about the sources of pollution which are situated in the vicinity of the exploitation sites of these plant species. Linden and pine survive in the conditions of increased pollution, so that Cu, Pb and possibly many other metals can enter food chain through ether oils and teas.

### Table 4. Accumulation and translocation of Cu, Pb, Zn and Mn between soil and the parts of linden and pine.

| Element | Plant species | BCF  | TF   | Rl/b  |
|---------|---------------|------|------|-------|
|         | Soil to root  | Root to branch | Branch to leaf |
| Cu      | linden        | 1.05 | 0.90 | 0.62  |
|         | pine          | 5.32 | 0.33 | 1.16  |
| Pb      | linden        | 0.64 | 1.87 | 0.38  |
|         | pine          | 1.44 | 0.85 | 0.84  |
| Zn      | linden        | 0.9  | 0.80 | 0.67  |
|         | pine          | 1.9  | 0.3  | 1.57  |
| Mn      | linden        | 0.06 | 0.96 | 4.38  |
|         | pine          | 0.05 | 0.45 | 1.92  |

from the pine roots (TF < 1 for all the studied elements). The sequence of increasing Rl/b values for linden and pine is the same: Mn > Zn > Cu > Pb. Only Mn is successfully translocated (Rl/b > 1) into linden leaves, and all the elements, except Pb, are translocated into the needles of pine.

By comparing the BCFs and TFs, we can compare the ability of different plants to take up metals from soils and translocate them to the aerial parts (Yoon et al., 2006). The roots of linden accumulate Cu from the soil, with no further translocation (TF, Rl/b < 1). Cu concentrations in the leaves and branches are far above critical ones, which indicates that the exceedances are a consequence of Cu uptake through the aerial parts from the air. It is the same with linden, BCF > 1, and TF < 1 for pine, which indicates that Cu is held in the pine roots. Roots holds Cu against the transport to aerial parts under conditions of Cu excess (Kabata-Pendias and Pendias, 2003) (TF > 1), and Cu concentrations in aerial parts are far above the critical values. Cu is assumed to generate mainly from the air in the aerial parts of linden and pine (Maistro et al., 2004).

Pb is not accumulated into the roots of linden. However TF > 1, and Rl/b < 1, which means that translocation to aerial parts is limited, and therefore deposition from the atmosphere is the most important source of this element (Rossini Oliva and Mingorance, 2004). Kabata-Pendias and Pendias (2001), state that 95% Pb can reach plants by foliar absorption. According to the BCFs, Pb is accumulated into the root of pine and there is no further translocation into branches. The content of Pb in the needles above critical values indicates the uptake of Pb through aerial parts (Sawidis et al., 2011).

For Zn BCFs, TFs and Rl/b are lower than 1, which indicates that there is neither accumulation nor translocation in linden. Zn is held by the pine roots (BCF > 1), where translocation from branches to leaves takes place, whereas the only translocation of Mn which takes place in linden and pine is from branches to leaves.

### CONCLUSION

Linden and pine surrounding soil shows the exceedances of Cu concentrations, compared to the MAC. Heavy metal contamination cannot be attributed only to air pollution produced by the smelter, but also to general composition of the topsoil of the examined area. Pb concentrations exceed the MAC only in linden surrounding soil in the urban-industrial zone, which is the closest to the copper smelter.
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