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Original article

Trees as natural barriers against heavy metal pollution and their role in the protection of cultural heritage

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ABSTRACT

Leaves of common deciduous trees: the horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia* spp.) from the park, near one of the most important cultural institutions, the National Library of Serbia, were studied as bioaccumulators of heavy metal (Cr, Fe, Ni, Zn, Pb, Cu, V, As and Cd) air pollution. The leaf samples were collected from the urban park exposed to the exhaust of heavy traffic. The May–September heavy metal accumulation in the leaves, and their temporal trends, were assayed in a multi-year period (2002–2006). Comparing the obtained concentration of the investigated elements from the beginning to the end of growing seasons, a significant rate of accumulation was determined for a majority of measured elements, and it was concluded that these tree species (horse chestnut and linden) can be used as bioaccumulators of the investigated heavy metals. The SEM-EDAX analysis of individual particles deposited on the leaves showed that the 50–60% belong to a class of fine particles ($D < 2\ \mu m$), mainly of anthropogenic origin. Thus, the investigated tree species could be grown as a natural barrier against urban air pollution in the vicinity of libraries, museums and other buildings for cultural heritage storage.

1. Research aims

Knowing that shelterbelts are used to modify local environmental conditions and reduce the effects of emitted pollutants (industrial zones, dumps), it could be useful to assess an ability of tree species in urban areas to be used in shelterbelts around objects of cultural heritage against the urban air pollution. Since the building of the National Library of Serbia is located in the heavy traffic area of Belgrade, the aim of this study was to evaluate the applying of common urban tree species – horse chestnut and linden – as a natural barrier against particulate/heavy metal air pollution. Thus, leaves of these tree species were tested for bioaccumulation of the selected heavy metals, present at low concentrations in air, but with high potential for human health risks and degradation of cultural heritage. Additionally, particulate capture and their physico-chemical characterization were observed on the examined tree leaves.

2. Introduction

Air pollution effects and environmental conditions are main causes of degradation of cultural heritage [1]. The process of degradation can be defined as a progressive and cumulative process of materials that respond differently to the values given by environmental variables and their changes [2].

Particulate matter (PM) and some gaseous pollutants, such as O_3, NO_x and SO_2, have been recognized as key environmental problem in many cities around the world. Particulates in the air are a mixture of solid and liquid droplets that vary in size, morphology, and chemical composition. Residence time of particles in the air depends, first of all, on their size, and mainly varies from several minutes or days for particles over 1 μm, while approximately 30–40 days for particles smaller than 0.5 μm [3]. As constituents of airborne particles, heavy metals and other trace elements are transferred to the biosphere. Nowadays, more than 40 chemical elements are measured in atmospheric particulate matter samples. About 70% of the mass of As, Pb, Zn and Cd are emitted to the atmosphere as fine particles with diameter less than 0.95 μm [4,5]. Road traffic contributes significantly to air pollution in urban areas, generating PMs and heavy metals around roads [5]. The results for the daily mass concentrations of PM_{10} ($68.4\ \mu g\ m^{-3}$) and $PM_{2.5}$ ($61.4\ \mu g\ m^{-3}$) in the Belgrade urban area during 2003–2005

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exceeded the limit (50 and 25 $\mu g\,m^{-3}$ respectively) set in the EU legislation [6].

The impact of air pollution has been studied most intensively in the context of human health problems [7], but also the accelerated degradation of cultural heritage has been reported by conservators and curators all over the world [1,8–10]. According to the literature research, the condition of collections from the libraries located in big city agglomerations have been always reported as worse than those of the collections from the rural areas [8–10]. The comparison of books from the same edition but stored in different libraries located in the areas with different air pollution levels was the subject of investigations performed by Brzozowska-Jabloñska [8]. Havermans and Porck [9,10] also emphasized the dependence of the ageing rate of paper and cellulose based materials on the level of air pollution in the storage place. Paper degradation from particulates has apparently not been well studied, but they certainly contribute to soiling of museum archives, contributing to visible damage of the paper issues. Degradation is accelerated by high amounts of sulphur and/or nitrogen oxides; furthermore, it can be also accelerated by the transition of trace elements from atmospheric particles [11]. The ions of transition metals in such micro-areas can locally change the kinetics of chemical reactions and have been shown to catalyze oxidation of sulphur dioxide, increasing its uptake rate and consequently also the rate of paper degradation [11]. A correlation has also been found between the presence of some transition metals in paper and paper degradation. Transition metals have a role in the catalytic oxidative degradation of cellulose [12].

For many centuries, paper was the main material for recording cultural achievements all over the world. Paper is mostly made from cellulose with small amounts of organic and inorganic additives, which allow its identification and characterization and may also contribute to its degradation. Paper degradation can be accelerated by the effect of aggressive chemical compounds; furthermore, it can be also accelerated by the presence of metals from air particles. So, indoor air pollution in cultural institutions, such as museums, libraries and archives, is of particular importance [13].

Polluted urban settlements are unfavourable environments, not only for the life of the people, but also for all living beings as well as for cultural heritage.

Investigations of a long-term effect of indoor air pollution on paper, which had been stored for 12 years in the storage rooms of Krasinski Palace (Warsaw, Poland) showed that sulfur and lead tended to accumulate in the indicators stored at the street side of the building, while the presence of a green area outside decreased the indoor air pollution affecting paper degradation [14].

Plants could represent some kind of natural barrier from the air pollution. Shelterbelts are vegetation systems that typically use trees and shrubs arranged in row or group configuration to redirect wind and reduce wind speeds, thereby modifying environmental conditions within the upwind and downwind sheltered zones. In urban areas, shelterbelts help to reduce the atmospheric particulate matter entering the flats, offices, schools and other objects to be protected [15]. Trees are very efficient in trapping atmospheric particles [16–20] which is especially important for urban areas since they could have a special role in reducing the level of fine, “high risk” respirable particulates with the potential to have adverse effects on human health. It also may be assumed that trees in the vicinity of museums/libraries and other cultural heritage would have a protective role against particulate air pollution.

The National Library of Serbia (NLS) was founded in 1832, and it is the oldest cultural institution in Serbia. Although complete library was burnt to the ground during the bombing of Belgrade in the II WW and a great part of the holdings, catalogues, and inventory was destroyed, NLS still possesses a rich, multiculturally and multiethnically diverse. The rich collection of the National Library of Serbia has approximately 300 ancient Cyrillic manuscripts, 100 incunables, valuable and rich collection of old printed books, followed by old photographs, maps, and other historically significant non-book materials on paper and parchment. Within the various collections in the NLS there are Cyrillic manuscripts in Russian, Vlach-Moldova and Bulgarian version of Old Church language dating from 13–19 century, old printed Cyrillic books dating from 1494–1638 period, as well as manuscripts in other languages (latin, coptic). There are also old printed books in other languages (Arabic, Latin, Bulgarian, German, Greek, Hungarian, Italian, English, etc). Also, NLS is entrusted with the collection of manuscripts and old printed books of Visoki Dečani Monastery for preservation, protection and research.

Having in mind that tree leaves may capture large amounts of atmospheric particulates and bioaccumulate heavy metals, the aim of this study was to evaluate deciduous trees next to the NLS *in situ* as a barrier against urban air pollution. Thus, we studied the accumulation of some heavy metals (Cr, Fe, Ni, Zn, Pb, Cu, V, As and Cd) in leaves of tree species common for the Belgrade urban area: horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia* spp.) during the vegetation season. In addition, physico-chemical characterization of deposited particulates, captured by the tree leaves, was also performed.

3. Materials and methods

The leaf samples of the horse chestnut (*Aesculus hippocastanum* L.) and linden (*Tilia* spp.: *Tillia tomentosa* L. being more frequently present, than *Tillia cordata* Mill.) were collected at the beginning (May) and the end (September) of the vegetation cycles from 2002 to 2006. The samples were collected from the Karadjordjev park, near the NLS, exposed to the exhausts of heavy traffic. The National Library of Serbia is located next to the park, sheltering it at one side from the busiest road (Fig. 1).

Each sampling was performed in the same area, where five subsamples (10–15 fully developed leaves) were taken from different trees of about the same age, randomly from all sides of the crown. The leaves were cut off with stainless steel scissors from a height of about 2 m. The subsamples were packed in polyethylene bags and polyethylene gloves were worn to prevent contamination. The leaf samples were washed with bidistilled water so that adhering coarse impurities, i.e. large loosely adhered particles, should be removed, which anyhow may be easily lost from the leaf surface by either wind or rain. Accordingly, the short washing procedure would diminish the large variability of the element concentration between leaf subsamples taken per tree or studied site, and thus provide more reliable information about the representative element content in leaves at each site and the area, respectively [21]. Then, leaf samples were dried in an oven at 40 °C for 24 h, pulverized by using agate mortars, packed in polyethylene bags and kept under stable laboratory conditions until the chemical analysis. Approximately 0.4 g of leaves (dry weight) was digested with 3 ml of 65% HNO_3 and 2 ml of 30% H_2O_2 in the microwave oven (SpeedwaveTM MWS-3 +, Berghof). After digestion, the solution was diluted with distilled water to a total volume of 25 ml. The concentrations ($\mu g\,g^{-1}$) of trace elements V, As and Cd in the extracts were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using an Agilent 7500ce spectrometer equipped with an Octopole Reaction System (ORS) and by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES SpectroGenesis EOP II, Spectroanalytical Instruments GmbH, Kleve, Germany). The concentration measurements ($\mu g\,g^{-1}$) of Cr, Fe, Ni, Cu, Zn and Pb in the leaves were performed by ICP-OES, while the concentration measurements of As, V and Cd were performed by ICP-MS.

For Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDAX), samples were prepared for both upper and

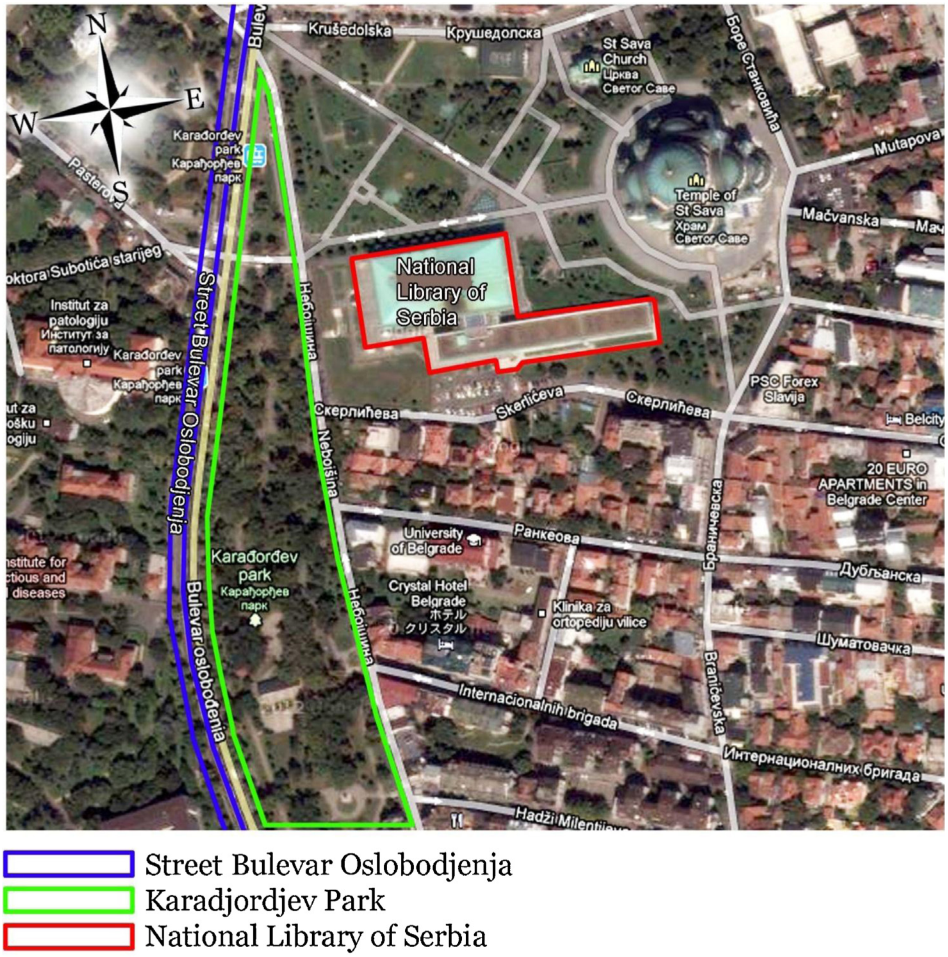

Fig. 1. Position of the Karadjordjev Park and the National Library of Serbia on the map of Belgrade.

lower leaf surfaces from at least ten leaves of different trees (3–5) sampled in 2006. Discs of 10 mm diameter were cut from unwashed leaves with a sharp device. Each leaf disc was mounted on an aluminum stub, over double-sided stick tape. The stubs were placed on a perforated round Teflon plate, cut to fit in a polycarbonate Petri dish. To minimize charge build-up on the samples from exposure to the SEM electron beam the samples were coated with 100–150 Å layer of high purity carbon using vacuum evaporator (Balzers/Union FL-9496) prior to analysis. SEM Philips XL30 apparatus equipped with a thin-window EDAX DX4 system for energy dispersive X-ray microanalysis was used for physico-chemical characterization of particles deposited on the leaf samples. Three different leaf discs of the upper and lower surfaces were examined in the same way. Ten photomicrographs were randomly taken of each 0.03 mm^2 area at 624 times magnification and the morphology of about 1800 particles were assessed (by semiautomatic system including optic microscope, CCD camera and OZARIA 2.5® software package) and about 900 for X-ray spectra analysis. About 0.025% of the original leaf surface was examined. The elements observed were: Al, Si, C, S, N, Cl, P, K, Ca, Na, Mg, Cr, Fe, Cu, Zn, Ni, Cd, As, Ti and V with detection limit >1 wt %. The relative elemental composition of the particles, were computed directly with EDAX software, using the atomic number, absorption and fluorescence (ZAF) correction.

4. Results and discussion

The National Library of Serbia is situated in a heavy traffic area of Belgrade with high total pollution load as previously reported for bulk deposition measurements [22], as well as for particulates and heavy metals [6]. Since the vegetation barrier may alleviate the pollutant impacts and consequently modify local environmental conditions, it was of interest to assess the bioaccumulation capability of the most common vegetation *in situ* – *A. hippocastanum* and *Tillia* spp. tree leaves.

Seasonal accumulation trends of element concentration in leaves, often referred to as accumulative biomonitors, have been known from the literature, and reported for some plant species [5]. In this study, starting from 2002 to 2006, the element concentrations in leaves of horse chestnut and linden, at the beginning and the end of vegetation seasons, are shown in Fig. 2. An increase of the element concentrations from May to September was evident in all leaf samples of *A. hippocastanum* and *Tillia* spp. throughout the investigated years for Cr, Fe, Ni, Zn, Pb, As and V (Fig. 2a-g), but was not so regular, i.e. absent in some years for Cu and Cd (Fig. 2h-m). Significant accumulation of Cr, Fe, Ni, Zn, Pb, As and V was evident in the leaves of *A. hippocastanum*, as well as those of *Tilia* spp., but with higher regularity of elements accumulation in leaves of horse chestnut.

It could be pointed out that during the time span (2002–2006), the temporal decrease of the Pb, highly toxic heavy metal, was observed in leaf tissue of both species (Fig. 2d). That is a consequence of decrease in the use of leaded gasoline in Belgrade during the years of investigation. However, the study of the origin of Pb in leaves [23] showed that less than 2% of the Pb content of needles and twigs of the Norway spruce comes from the root uptake, and approximately 98% is of atmospheric origin. The previous study in the Belgrade urban area also pointed to a good correlation between

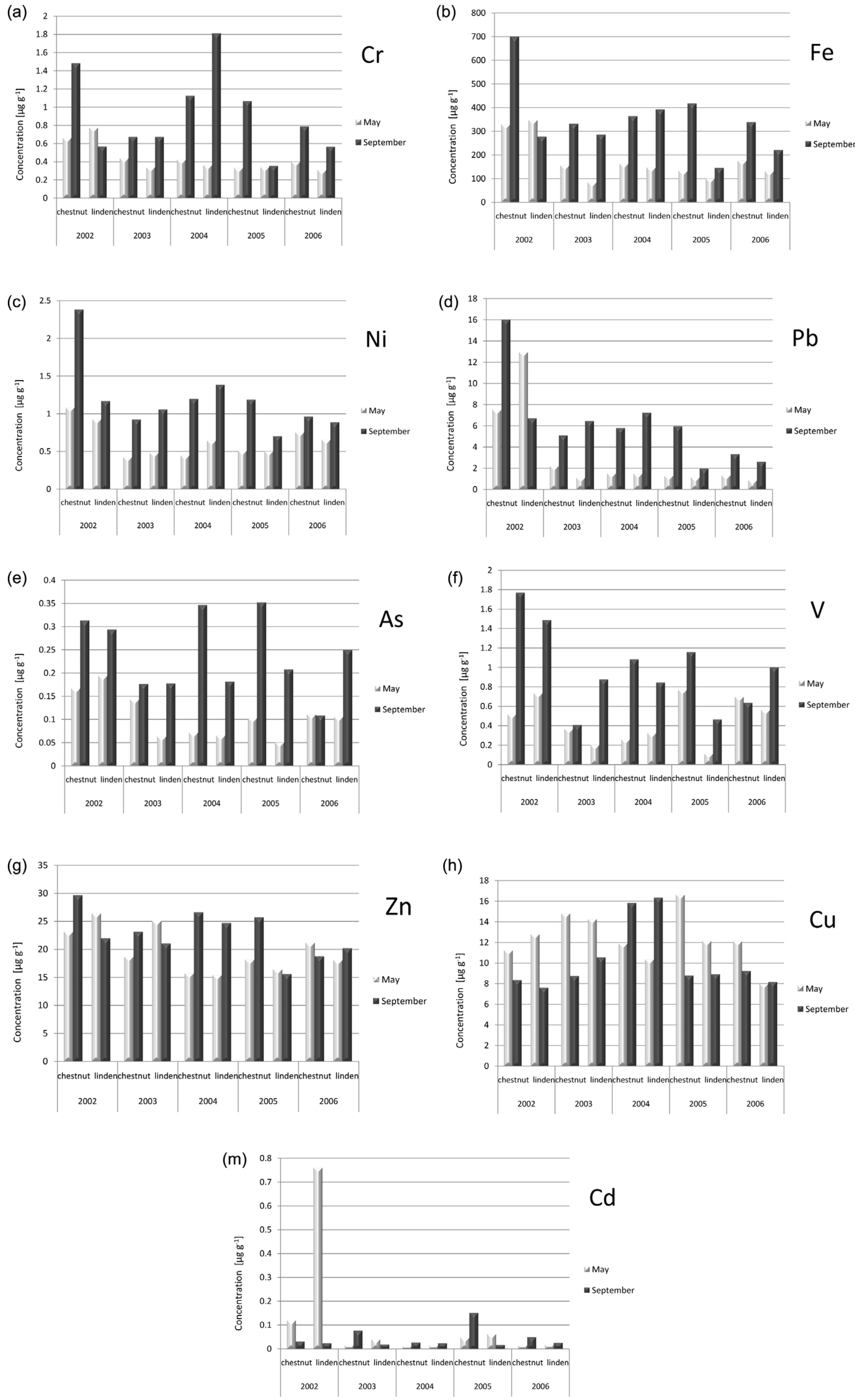

Fig. 2. Concentration of Cr (a), Fe (b), Ni (c), Pb (d), As (e), V (f), Zn (g), Cu (h) and Cd (i) in the leaves of *Tilia* spp. (linden) and *A. hippocastanum* (chestnut) at the beginning (May) and the end (September) of the vegetation seasons (2002–2006).

the Pb leaf content of *A. hippocastanum* and a significantly increased level of atmospheric Pb in suspended particles during the two successive years (1996–1997), as reported by the Health Institute in Belgrade. So, the Pb concentration in the leaves of *A. hippocastanum* certainly reflected changes in the atmospheric lead pollution [24]. For the other measured elements, it is difficult to say that the content in the leaves directly and solely reflect their atmospheric concentrations, but their accumulation in the leaves was evident during the vegetation season.

Since the total element content in digested leaf samples does not provide information about physico-chemical characteristics of the deposited particles on leaf surfaces, an additional analysis (SEM-EDAX) was conducted. This observation may also provide necessary information regarding plant physiology (leaf stomatal size, adhering and absorbing possibilities of leaf surface). Selected scanning electron photomicrographs presented in Fig. 3 (a-d) show deposited particles observed on the surface of *A. hippocastanum* leaves: lower surface, general appearance (Fig. 3a); upper surface,

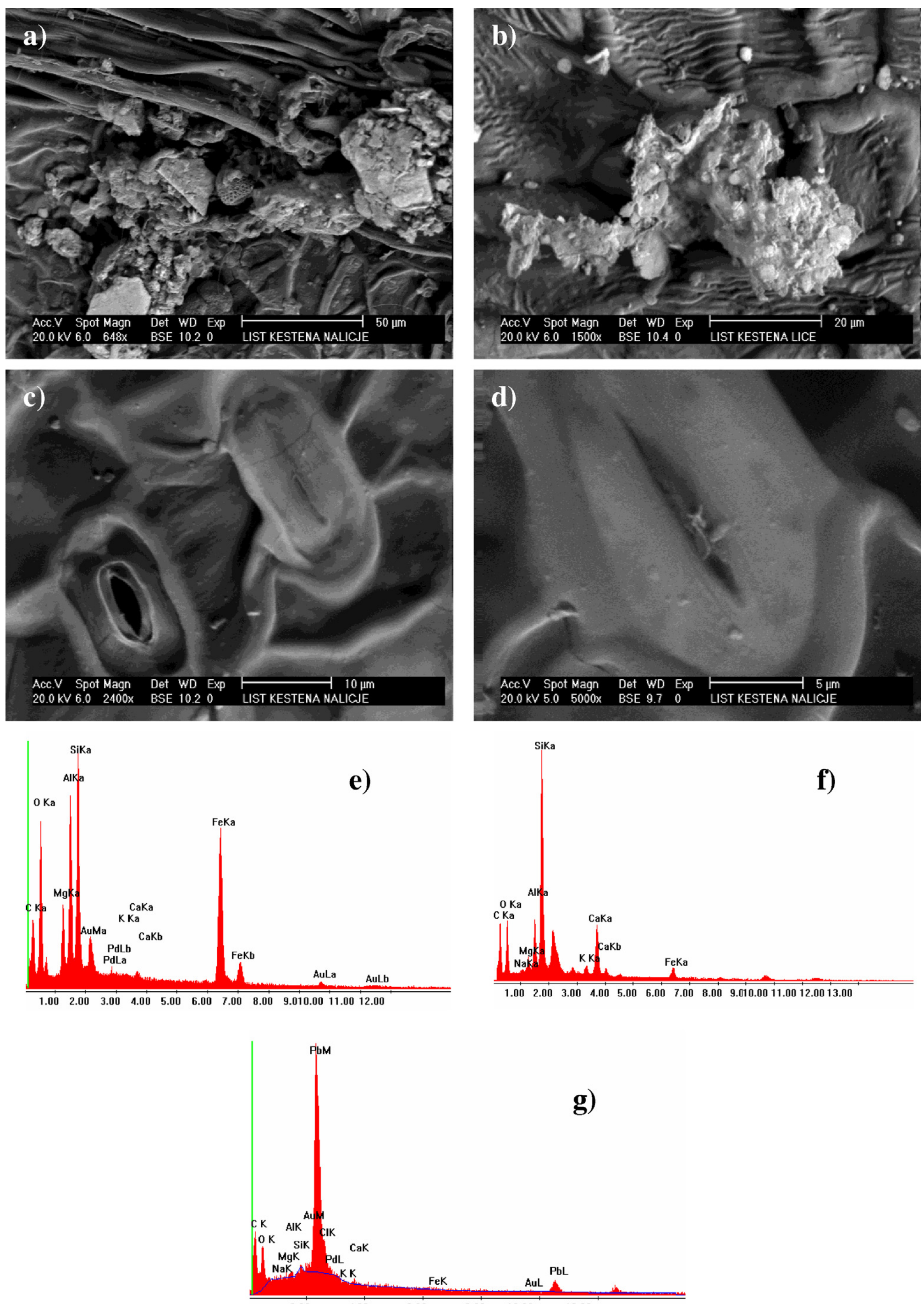

Fig. 3. SEM-EDAX photomicrographs of *A. hippocastanum* leaf surface: upper (b) and lower (a, c, d), and spectra presenting the chemical composition of the most frequently observed particles (e-g).

general appearance (Fig. 3b); stoma openings for plant transpiration as well as input of air pollutants (Fig. 3c, d); and chemical composition of most frequently observed particles (Fig. 3e-g).

The particulates were single or gathered in agglomerates of various shapes (spherical, flakes, irregular). The semiautomatic system provided information on particle size and analysis indicated the highest percentage (50–60%) of fine particles (diameter < 2 μm) on the leaf photomicrographs. The particles were distributed with higher density on the upper leaf surfaces. However, on lower leaf surface, stomata may be covered with fine particles which may easily enter the stomatal openings (~ 10 μm), (Fig. 3c, d). It was pointed out that fine particles, which are more hygroscopic [25], more firmly adhere and stay longer on the leaf surface, and also penetrate the leaf stomata more easily. Thus, it could be concluded that tree leaves may play an important role in removing predominantly fine particles from the air. Heavy metals deposited on leaves are more often present in the fine particle fractions, which are in urban areas mainly of anthropogenic origin [4].

The chemical composition of the observed particles deposited on the leaves suggested that the most abundant particles were: soot (C) and soil dust with characteristic matrix elements (Si, Al, Fe, Mg, N, S, Ca, K, Cl); fuel oil particles rich in Al, Si, Ca, Ni, Fe, V and Pb; coal ash particles containing C, Al, Si, K, Ca; and particles emitted by the local industrial processes (Fe, Zn, Ni, Cu or Pb-rich) (Fig. 3). Among the particles containing heavy metals, the most abundant were particles in aggregates form, where Pb was the major element associated with lower concentrations of S, Fe, Cd, Cu, As and Zn (Fig. 3g).

According to the particle morphology and chemical composition indicated by the SEM-EDAX procedure, it may be suggested that particles deposited on the leaves mostly originated from the traffic or from the resuspended particles, and possibly local sources. The EDAX data were just qualitative (counts), which is not directly comparable to the quantitative concentrations measured in digested leaves. The leaves were scanned for some typical types of particles most often deposited on leaf surface, indicating either crustal or anthropogenic origin. For example, the Pb-rich particles were often observed on the leaf micrographs. Also, the concentrations of lead in leaves in general followed the atmospheric Pb trend measured by bulk deposition collectors in the Belgrade urban area [22,26].

Considering the indoor air pollution, the influence of outdoor particulate concentrations appeared to be relatively large on the indoor particulate content [27,28]. Based on both theoretical calculations and experimental results, Camuffo et al. [29] estimated that the deposition flux is largest in the size range around 0.5 μm. About 70% of the mass of As, Pb, Zn and Cd are emitted to the atmosphere as fine particles with diameter less than 0.95 μm [4]. In principle, all atmospheric particles can be considered harmful for works of art because they can cause significant soiling when they are deposited onto them. Therefore, high particulate matter concentrations should be avoided in any case in museums. Fe- and/or Mn-containing particles can be dangerous because they are particles with hygroscopic properties, that can favor the formation of this “liquid phase” [30]. Organic, S-rich and Fe-rich particles in the size range around 0.5 μm can be considered most harmful with respect to the preservation of works of art [31]. Metals influence the catalytic degradation of the paper; especially iron and copper are well known as effective oxidation catalysts causing the decomposition of cellulose [32]. A recent report [12] also indicated an influence of some transition metals (Fe, Cu, Mn, Co, Cr, Ni, Zn) as paper constituents on the paper degradation. Embrittlement of the paper and the brownish discoloration can result from the oxidative decomposition of paper by copper(II)–ions, so called “copper-pigment corrosion”. Identifying the damages caused by heavy metals has great importance as it can allow the restorer to select adequate options for the elaboration of a conservation treatment.

As suggested in a recent report regarding indoor particulate pollution in the museum in the city centre, intensive traffic is one of the main reasons for the pollution levels recorded inside the museum [28]. Outdoor particulate pollution, brought indoors by visitors or entering through air leaks in the buildings, can easily move with the air and cause chemical damage or soiling onto exhibited surfaces by deposition [33,34]. The air pollutants may infiltrate into buildings from outdoors and/or they are generated from indoor sources. The National Library of Serbia is equipped with a ventilation system where the inlets are positioned on the roof and using the primary filters – class G4 for pre-filtering [35]. So there is a possibility for fine particles (< 2 μm) to pass through the filter. Consequently, the paper degradation in the NLS probably influenced by incoming outdoor particulates (heavy metals) pollution, and also on particulates from indoor emission present in the legacy indoor air, as well as the metal contained in the paper.

In some cases it was found that the same particle types were presented inside and outside; however, the proportions differ, indicating the accumulation and chemical changes of the particles. There were, however, also particles, which were not present outside; therefore there is a high probability of some chemical processes occurring inside. It should be taken into account that the particles transported inside are confronted with different microclimatic conditions. The difference in temperature and, particularly, in humidity, induces chemical changes [28]. Thus, there is a high probability of some chemical processes occurring inside depots.

Considering particulate removal from the urban air through deposition processes (dry – due to the force of gravity, and wet – due to precipitation), vegetation is a significant sink for particulates and heavy metals. In general, forest vegetation, mainly coniferous trees, has great importance for precipitation of aerosols [5]. However, this study also confirmed that deciduous trees could be efficient for trapping atmospheric particles, i.e. accumulation of atmospheric heavy metals. The SEM-EDAX analysis of deposited particles on the leaves showed that the highest percentage (50–60%) belonged to a class of fine particles. Thus, a substantial amount of fine particulates that may penetrate to indoor could be captured by deciduous trees. Between the studied species, *A. hippocastanum* could be suggested as a more appropriate bioaccumulator of the investigated elements than *Tilia* spp. probably due to specific morphology of the leaves (more pronounced leaf nervature). However, both plant species showed significant bioaccumulative capabilities during the vegetation season. The studied tree species protect the NLS against the heavy traffic street from one side only (Fig. 1). Anyhow, the forming of a tree belt around the building of the National Library of Serbia could be even more efficient natural barrier against the heavy metal pollution, especially the fine particulates due to their longer residence time in the ambient air.

5. Conclusion

Leaves of the studied deciduous trees, growing in the park next to the National Library of Serbia – the horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia* spp.) – showed seasonal heavy metal accumulation in a multi-year period (2002–2006). Significant accumulation of Cr, Fe, Ni, Zn, Pb, As and V was evident in the leaves of *A. hippocastanum*, as well as those of *Tilia* spp., but with higher regularity of elements accumulation in leaves of horse chestnut. The SEM-EDAX analysis of individual particles deposited on both, upper and lower, sides of the leaves showed that the 50-60% belong to a class of fine particles (D < 2 μm). The most abundant were particles in aggregates form, where Pb is the major element what was in agreement with the total Pb content measured in the leaf samples.

It may be suggested that the particles deposited on leaves mostly originated from the traffic (especially those Pb-enriched).

According to the results of this study both plant species showed significant bioaccumulative capabilities during the vegetation season. However, *A. hippocastanum* could be suggested as a more efficient bioaccumulator of the studied heavy metals than *Tilia* spp. probably due to specific morphology of the leaves. Since it is considered that the indoor particulate content greatly depends on the outdoor particulate concentrations, it may be assumed that some transition metals (Fe, Cu, Mn, Co, Cr, Ni, Zn) may influence the paper degradation. Hence, the investigated tree species could be grown as a shelterbelt for reducing atmospheric level of fine particles/heavy metals in vicinity of libraries, museums and other cultural legacy buildings object. However, due to the slow realization of the importance of a controlled environment inside cultural legacy buildings, many problems still remain unsolved. Ideally, in such studies, it would be useful to obtain outdoor and indoor air concentrations of heavy metals regarding the significance of element absorption by leaves, and this needs to be subject of further research.

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