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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 $1\ \mu m$, while approximately 30–40 days for particles smaller than $0.5\ \mu m$ [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 $0.95\ \mu m$ [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