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Heavy metals accumulation in tree leaves from urban areas

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Abstract Higher plants may be used as biomonitors for the assessment of atmospheric heavy metal pollution by means of their bioaccumulative properties. We evaluated the reliability of biomonitoring heavy metal pollution by horse chestnut and linden leaves, common species found in Belgrade city parks. The results show that the highest concentrations of heavy metals were found in horse chestnut leaves at Studentski Park site, amounting to 110.2, 20.3 and 4.9 μg g^{-1} dry weight for Cu, Pb and Cd, respectively, which are considered above toxic levels for plants.

Keywords Urban pollution · Atmospheric deposition · Heavy metals · Biomonitoring · Tree leaves

Introduction

Several studies have pointed out the importance of atmospheric input in the biogeochemical cycling of heavy metals, as reviewed by Bargagli (1998). The responses of plants to elevated concentrations of air contaminants are modified by environmental factors and by plant physiological status. Positive relations have been found between atmospheric heavy metals deposition and heavy metal concentrations in grasses (Tjell et al. 1979). The contribution of atmospheric deposition to heavy metal accumulation has also been evidenced for forest and other types of vegetation (Berthelsen et al. 1995).

Plant leaves are used as indicators of heavy metal pollution. Although higher plants are usually not as suitable biomonitors as lichens and mosses, in industrial and in urban areas, where lichens and mosses are often missing, higher plants can act as biomonitors. Also, in industrial and urban areas higher plants can give better quantifications for pollutant concentrations and atmospheric deposition than non-biological samples. Therefore, using plant leaves primarily as accumulative biomonitors of heavy metals pollution has a great ecological importance (Markert 1993; Bargagli 1998; WHO 2000).

The accumulation of heavy metals by higher plants depends on the binding and solubility of particles deposited on leaf surfaces, as well as on concentrations and bioavailability of elements in the soil. Considering that metal uptake in higher plants takes place through roots and leaves, it is difficult to distinguish whether the accumulated elements originate from the soil or from the air. In spite of difficulties in interpretation of the data, the use of the leaves of higher plants has been increasingly investigated for the purpose of heavy metals accumulation monitoring. Hence, studies are in progress in search for suitable tree species and approval of a validity of using their leaves as biomonitors. Various reports to a certain extent either support or deny such possibilities. The presence of heavy metals on foliar surfaces has recently been confirmed as an indication for environmental pollution using some key tree species in Carpathian Mountains (Mankovska et al. 2004).

The research in heavy metals contamination of vegetation requires the use of standard methodological procedures (Markert 1993; Bargagli 1998). The representative sampling of plant material is necessary, otherwise may contribute to serious experimental errors (Markert 1995). As also pointed out by some authors (e.g. Wyttenbach and Tobler 1998), there has been a significant difference between the concentrations in washed and unwashed leaves.

In this work, we evaluated the reliability of biomonitoring by tree leaves in Belgrade urban areas. Two tree

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species with broad leaves, *Aesculus hippocastanum* L. and *Tilia sp.* L., common for Belgrade city parks, were used for the measurements of heavy metal concentrations.

Direct collection of atmospheric deposition, using bulk sampling devices, offers a practical approach to monitor atmospheric heavy metal deposition, providing valuable information on the influences of atmospheric inputs of heavy metals on the surface environment.

Experimental

Three representative locations, in heavy traffic areas, Studentski Park, Karadjordjev Park and Botanic Garden in Belgrade, were chosen for an investigation of heavy metals accumulation in leaves. Sampling was conducted in May 2002. Fully developed leaves of about the same age were sampled at 2 m height above the ground. Each leaf was picked on the side of the crowns facing heavy traffic streets at about 5 m from the street, except for linden in Botanic Garden, which was about 10 m. Two tree species, horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia* sp.) were chosen. The samples were prepared in a clean laboratory, class 100. The leaves were first washed with tap water, then rinsed with bidistilled, deionized water, dried at 60 °C, powdered and dried again at 105 °C to constant weight. After wet digestion with 65% w/w HNO_3, then 30% w/w H_2O_2, concentrations of Pb, Zn, Cu, Cd, Fe, Mn, Hg, Cr, and Ni were determined by atomic absorption spectroscopy using the Spectra AA 55 Varian, equipped with hydride vapour system.

Heavy metal concentrations were also determined in soil samples. Composite topsoil samples at 0–15 cm of depth were taken at the same parks, simultaneously with leaves. Soil samples were air dried, powdered, and dried at 105 °C to constant weight. Heavy metal concentrations in soil were analysed by flame atomic absorption, using a Perkin-Elmer 5000, after wet digestion with strong acids.

Sampling of the total (bulk) atmospheric deposition (the sum of dry and wet deposition) was conducted for a 1-year period, using open cylindrical deposit bottles with standardized dimensions made of high-density polyethylene. After 1 month of collection, the contents of the jars were carefully evaporated to dryness. The dry residues were digested with 50 ml 0.1 M HNO_3 in an ultrasonic bath, then the samples were filtered with 0.45-μm porosity filters. The analytical technique for heavy metal contents was atomic absorption spectrometer using the Spectra AA 55 Varian.

The physical and chemical characteristics of particles deposited on the leaves were analysed by scanning electron microscopy and X-ray energy dispersive spectrometer, type XL30 DX4i Philips, for defined leaf surfaces. The leaves for electron microscopy analysis were placed in clean Petri dishes using polyethylene gloves and clean scissors and then transferred in horizontal position to the laboratory. Leaf discs were punched out from the leaves, aside from the main veins, mounted on aluminum holders by double-sticky tape and dried in air, all performed in a clean laboratory. The samples were coated with carbon prior to analysis by SEM-EDAX system.

Results and discussion

Total atmospheric heavy metal deposition

In this study, the concentrations of heavy metals were measured in the monthly total atmospheric depositions in the Belgrade urban area.

From the obtained data, the average monthly depositions were calculated in order to provide an indication on the extent of the contribution of anthropogenic emissions to atmospheric elemental levels. The enrichment factor (*EF*) has been calculated for each element, using Fe as reference element and the crustal composition given by Mason (1966). By convention, the average elemental concentration of the natural crust is used instead of the continental crust composition of the specific area, as detailed data for different areas are not easily available. The enrichment factor *EF* of an element *E* in total deposition (TD) relative to crustal reference material *R* is defined as:

$$EF = \frac{[E]_{\mathrm{TD}}/[R]_{\mathrm{TD}}}{[E]_{\mathrm{crust}}/[R]_{\mathrm{crust}}}$$

If the *EF* approaches unity, the crustal material is likely the predominant source for element; if the *EF* is higher than 10, the element has a significant fraction contributed by non-crustal sources (anthropogenic).

Figure 1 shows that Pb, Cu, Cd and Zn were the most enriched elements in the total atmospheric depositions. These findings suggest that the dominant sources for these elements at all three locations were anthropogenic and a variety of pollution emissions might contribute to their loading in the ambient air. Results for Mn, V, and Ni denote that anthropogenic influence was not prominent. The *EF* values for Al and Cr were close to 1 in all

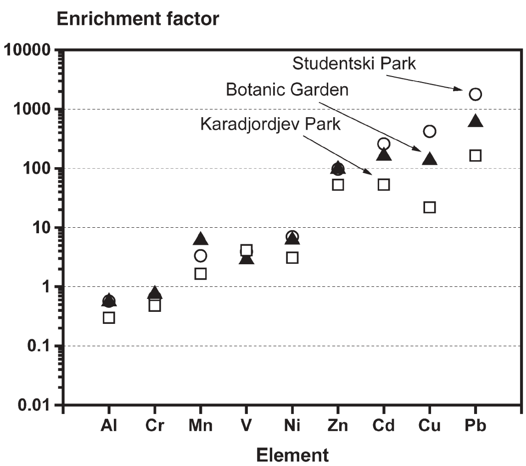

Fig. 1 Enrichment factors of heavy metals in the total atmospheric depositions sampled at three sites. EF for Pb, Cu, Cd and Zn, being >10, indicate their anthropogenic origin

samples, indicating that almost all parts of aluminum and chromium in total deposition collected in this study were presumed to be soil in origin. The highest enrichment factors for Pb, Cu, Cd and Zn were calculated at Studentski Park, a small city park and square with bus terminal and a very high traffic density, so traffic emission is the predominant source of air pollution. The park is surrounded by buildings, which results in poor ventilation and dilution of atmospheric constituents, and most airborne particles are trapped between the buildings.

Physical and chemical characterization of deposited particles

We analysed atmospheric particles on leaf surfaces using the scanning electron microscopy coupled with the energy-dispersive X-ray analysis (SEM-EDAX). Widely accepted, scanning electron microscopy provides direct proof for the presence of atmospheric particles on leaf surfaces. In comparison to smooth surfaces, which have been routinely investigated by the SEM-EDAX, an investigation of deposited particles on leaves appeared to be a difficult task. In this study, the shape, size and chemical composition of the particles deposited on leaves were analysed by SEM-EDAX (Fig. 2A,B). The results show that the observed particles were of spherical and non-spherical shape; single or in agglomerates; fine and coarse. Three size classes: 1–2 μm, 10–20 μm and >20 μm were examined both on adaxial and abaxial leaf surfaces (Fig. 2A). Fine particles were often found in areas around and over the stomata as is presented in Fig. 2A. The morphological and chemical composition suggested that the most abundant particles were carbonaceous soot and coal ash. Other matrix being quartz, iron, soil and mixed aggregates with Mg, Ca, S, K, P, Pb, Cu, Zn, W and Cd as minor constituents were identified.

The chemical characterization was performed on a semi-quantitative level. The X-ray spectrum corresponding to the typical heavy metal particle from the city's aerosol is presented in Fig. 2B The results indicate that the traffic emission is a major source of urban particulate matter as leaded gasoline is still widely used in the country.

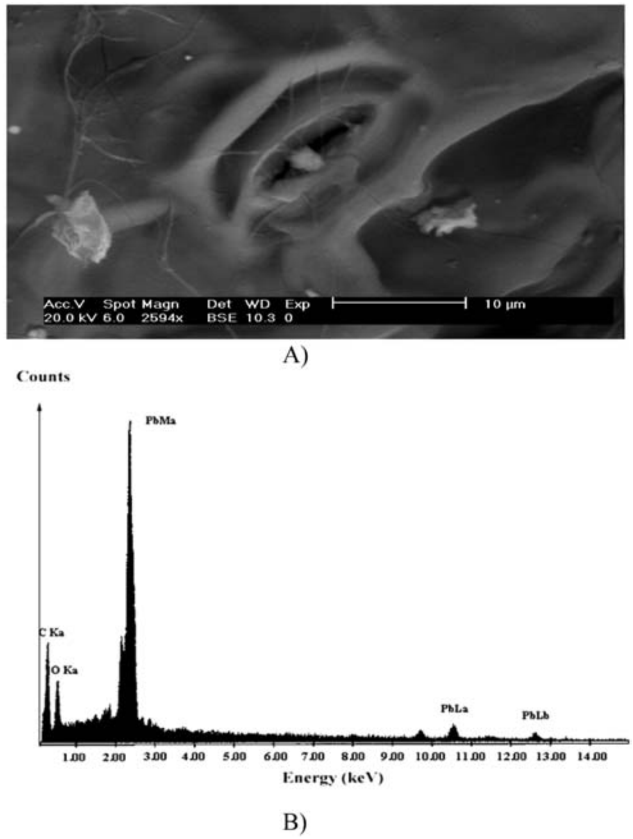

Fig. 2 Deposited particles on horse chestnut leaf, abaxial surface, area around the stomata (**A**), and the X-ray spectrum (**B**) of the particle over the stomata, obtained by the scanning electron microscopy coupled with the energy-dispersive X-ray analysis

Heavy metal accumulation in leaves and in soil

Table 1 presents the average values of heavy metal concentrations in linden and horse chestnut leaves. Heavy metal concentrations in most of the leaf samples were above the “reference plant” values, the system that has been widely used to compare different plant species and different environments (Markert 1992). In horse chestnut leaves sampled at Studentski Park, the concentrations of heavy metals were much higher than the “reference plant” values: Fe being 3-fold, Cu 10-fold; Pb 20-fold and Cd several hundred times higher than the reference values (Table 1). Pb content was the lowest in the linden leaves that were the most distant from the street at the Botanic Garden site.

Pb, Cd and Cu concentrations in the leaves at Studentski Park were at toxic levels, especially the horse chestnut tree, which was positioned at the edge of the park and very close to the bus station. In general, the following concentration levels in leaves are considered to be toxic (Markert 1993): 3–20 $\mu g\ g^{-1}$ dry weight for Pb; >200 $\mu g\ g^{-1}$ for Zn; >20 $\mu g\ g^{-1}$ for Cu and >10 $\mu g\ g^{-1}$ for Cd. However, it should be noted that in natural conditions it has been difficult to estimate toxic concentrations and heavy metal effects due to the complexity of the environmental conditions. Also, the results of such investigations depend on plant species, physiological status, metal availability for plants and heavy metal concentrations in air and in soil. The time of exposition also influences the level of plant damage, as low concentrations at longer durations may cause chronic damage, in principle more serious than the acute ones. The concentrations of heavy metals in leaves increase along a vegetation period. This was clearly shown in our previous experiments (Tomašević PhD Thesis). Concentrations of Zn, Cu and Pb in horse chestnut leaves were higher in September: for Pb over 7–fold, Zn over 4-fold, and for Cu more than double when compared to the beginning of the vegetation

Table 1 Heavy metal concentrations (μg g^{-1} dry weight) in linden and horse chestnut leaves and in soil at three Belgrade parks

Site	Fe	Mn	Cd	Pb	Hg	Cr	Zn	Cu	Ni
Botanic Garden, (linden)	105.9	72.0	<dl	1.88	0.2	<dl	15.2	10.3	/
Botanic Garden, (horse chestnut)	183.8	112.3	0.4	5.35	0.1	<dl	17.2	13.1	/
Botanic Garden, (soil)	256.5	/	1.49	54.0	/	97.2	122.7	30.4	72.5
Studentski Park, (linden)	246.3	77.7	1.4	9.3	0.8	<dl	21.8	41.4	/
Studentski Park, (horse chestnut)	439.6	110.8	4.9	20.3	0.2	0.33	47.1	110.2	/
Studentski Park, (soil)	215.4	/	1.73	237.0	/	118.0	215.6	98.4	73.6
Karadjordjev Park, (linden)	324.5	46.5	0.9	11.4	<dl	0.02	28.6	12.9	/
Karadjordjev Park, (horse chestnut)	353.0	66.9	0.2	9.3	<dl	<dl	25.2	13.3	/
Karadjordjev Park, (soil)	284.9	/	1.34	114.8	/	83.5	151.3	94.2	62.4
"Reference plant"	150	200	0.05	1	0.1	1.5	50	10	1.5

Average values of five samples are presented
Relative standard deviations were 30–50%
dl detection limit

period (May). Therefore, horse chestnut showed good bioaccumulative properties.

The concentration values for heavy metal contents of urban soils in parks of Belgrade are also presented in Table 1. Soil concentrations of Pb, Cu and Zn were the highest at the Studentski Park site and are similar to the data for Seville parks, and in particular for the Madrid parks (Madrid et al. 2002). It was concluded that a significant degree of metal pollution existed in soils within the urban area of Belgrade. The levels did not exceed the maximum acceptable limits for residential sites, as compared to the reference values given by the Quebec Ministry of Environment: 100, 500 and 500 μg g^{-1} for Cu, Pb and Zn, respectively (Madrid et al. 2002).

Conclusion

The results of the measurements of heavy metal concentrations in tree leaves from city parks showed the accumulation of Cu, Pb, Zn and Cd, reflecting atmospheric concentrations and soil contamination. The influence of atmospheric deposition, wet and dry, was significant, and the soil contamination was mostly the result of it. Horse chestnut and linden could be a good choice for Belgrade urban areas, where they are very abundant species. Especially high heavy metal contents were measured in horse chestnut leaves, indicating a better response to atmospheric heavy metal pollution.

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