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Urban deciduous tree leaves as biomonitors of trace element (As, V and Cd) atmospheric pollution in Belgrade, Serbia

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Abstract: Leaves of common deciduous trees: horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia spp.*) from three parks within the urban area of Belgrade were studied as biomonitors of trace element (As, V, and Cd) atmospheric pollution. The May–September trace element accumulation in the leaves, and their temporal trends, were assayed in a multi-year period (2002––2006). Significant accumulation in the leaves was evident for As and V, but not so regularly for Cd. Slightly decreasing temporal trends of V and As accumulated in the leaf tissues were observed over the years. During the time span, the concentrations of Cd remained approximately on the same level, except in May 2002 and September 2005, when a rapid increase was observed. The May–September accumulations of As and V were higher in horse chestnut than in linden, although both may be used as biomonitors for these elements, and optionally for Cd in conditions of its high atmospheric loadings.

Keywords: trace elements; tree leaves; biomonitoring; *Aesculus hippocastanum*; *Tilia spp.*; ICP-MS.

INTRODUCTION

Increasing industrialization and human activities intensify the emission of various pollutants, including trace elements, into the atmosphere and introduce harmful substances into the environment.[1,2] Particulate pollution is a matter of great concern due to its adverse effects on human and living plant populations. Road traffic contributes significantly to air pollution in urban areas, generating particulate matter, aerosols and trace elements around roads.[3,4]

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Trees are very efficient at trapping atmospheric particles, and they have a special role in reducing the level of fine, "high risk" respirable particulates, which have the potential to cause serious human health problems.[5] Therefore, tree leaves have been used for biomonitoring of particulate pollutants, which are often associated with trace elements, in air quality studies.[3,6] Leaves of different evergreen and deciduous tree species and their validity for the biomonitoring of trace elements have been assessed in urban and industrial areas.[7–9]

Previous investigation showed that common tree species in the Belgrade urban area had distinguishable seasonal accumulations of some elements, especially horse chestnut, for which the Pb accumulation in the leaves reflected changes of atmospheric Pb concentrations.[10]

The purpose of this study was to extend these investigations by applying horse chestnut (*Aesculus hippocastanum*) and linden (*Tilia spp*.) leaves for the biomonitoring of atmospheric contamination with V, As and Cd, present at low concentrations in air but with high health risk potentials.[11] Vanadium is required for the activity of enzymes, while As and Cd do not have any known physiological function in plants and can be toxic. The aim was to evaluate the accumulation during the growing season (May–September) and the temporal accumulation of the elements in a multi-year period (2002–2006).

EXPERIMENTAL

The study was conducted in Belgrade, the capital of Serbia, which is located in south-eastern Europe, on the Balkan Peninsula (φ = 44° 49' N, λ = 20° 27' E, H_s = 117 m). Belgrade has a moderate continental climate, with four seasons (cold winters and hot, humid summers, with well-distributed rainfall). By the end of 2004, Belgrade had about 1.6 million urban inhabitants, which is 20 % of the total population of Serbia. The samples were collected from three urban parks exposed to the exhaust of heavy traffic: Karadjordjev Park (KP), Botanička bašta – Botanical Garden (BG) and Studentski Park (SP). Tree species with broad leaves *Aesculus hippocastanum* L. and *Tilia sp*. L. were chosen since they are common in Belgrade city parks. The leaf samples were collected at the beginning (May) and the end (September) of the vegetation cycles from 2002–2006. The leaves were cut off with stainless steel scissors from a height of about 2 m (polyethylene gloves were worn to prevent contamination). Five subsamples (10 to 15 fully developed leaves) were taken randomly from all sides of a crown. The subsamples were packed in polyethylene bags. The leaf samples were carefully washed with bidistilled, deionized water to remove adhering coarse particles, dried in an oven at 40 °C for 24 h, pulverized using agate mortars, packed in polyethylene bags and kept under stable laboratory conditions until chemical analyses. Approximately 0.4 g leaf (dry weight) was digested with 3 ml of 65 % HNO_3 and 2 ml of 30 % H_2O_2 using a microwave oven (Speedwave™ MWS-3$^+$, Berghof). After digestion, the solution was diluted with distilled water to a total volume of 25 ml. Trace elements 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). With this method, low detection limits can be obtained for elements present in low concentration and for metalloid elements, such as As, with high ionization energies. Prior to the ICP-MS analysis, all the samples were filtered through a 0.45 μm pore diameter membrane filter. Calibration was performed with external standards obtained by appropriate dilution of a Fluka multi-element standard solution IV. The blank and calibration standards were prepared in 2 % nitric acid for all the measurements except for those used to determine the detection limits. A tuning solution containing 1 μg L^{-1} Li, Mg, Co, Y, Ce and Tl (Agilent) was used for all instrument optimizations. Details of the ICP MS operating conditions are summarized in Table I.

TABLE I. Optimal instrument (Agilent 7500ce) operating conditions

Parameter	Value
RF frequency, MHz	27
RF power, W	1500
Plasma gas flow, L min^{-1}	15
Nebulizer gas flow, L min^{-1}	0.9
Sample uptake rate, rps	0.3
Data acquisition	
Acquisition mode	Peak hopping
Dwell time, ms	100
Integration time, s/point	0.1–0.3
Repetition	3 (FullQ)

The determination of the method detection limit (MDL) was based on seven replicate measurements of a series of spiked calibration blanks. Each blank solution was spiked with analytes at concentrations between 2 and 5 times the calculated IDL (instrument detection limit). The MDL was calculated by multiplying the standard deviation of the seven replicate measurements by the appropriate Student's test value based on a 99 % confidence level (t = = 3.14 for six degrees of freedom).

The analytical quality control included daily analyses of standards and triplicate analysis of samples and blanks. The accuracy and precision of the analytical procedures were verified through analysis of the standard reference material lichen-336 (IAEA). The recovery range was 90–95 %. All results were calculated on a dry weight basis.

RESULTS AND DISCUSSION

The concentrations (μg g^{-1}) of As, Cd, and V in the leaves of horse chestnut (*A. hippocastanum*) and linden (*Tilia spp.*) from three parks (KP, BG and SP), representative for the urban area of Belgrade, are presented in Table II (mean concentration of triplicate analysis, *RSD* less than 3 %). The leaves were sampled at the beginning (May) and at the end (September) of the vegetation periods from 2002 to 2006. For the investigated species, the concentrations of V and As in the leaves increased at a significant level $p < 0.05$ from May to September. In case of Cd, the May–September increase of this element in the leaves was not significant (except for 2005). This is in agreement with a previous study on *A. hippocastanum* leaves, in which no clear Cd accumulation in leaves was found within a single season.[12]

In general, the ratio of the September/May concentrations of the elements in the leaves were higher in horse chestnut than in linden, over the multi-year period, suggesting a better accumulative ability of the former species.

TABLE II. Concentration (μg g^{-1}) of V, As and Cd in *Tilia spp*. (linden) and *A. hippocastanum* (chestnut) leaves from the Belgrade urban area during the vegetation periods from 2002–2006

Year	KP				BG				SP			
	Linden		Chestnut		Linden		Chestnut		Linden		Chestnut	
	Month											
	May	Sept.	May	Sept.	May	Sept.	May	Sept.	May	Sept.	May	Sept.
	V											
2002	0.728	1.483	0.515	1.764	0.269	0.324	0.448	0.881	0.405	0.745	0.286	1.104
2003	0.200	0.873	0.364	0.405	0.044	0.381	0.158	0.332	0.089	0.408	0.123	0.858
2004	0.322	0.841	0.258	1.080	0.235	0.480	0.378	0.664	0.118	0.661	0.277	0.416
2005	0.110	0.463	0.765	1.154	0.080	0.460	0.336	0.298	0.082	0.372	0.179	0.494
2006	0.556	0.999	0.694	0.633	0.162	0.235	0.339	0.518	0.135	0.229	0.141	0.493
	As											
2002	0.193	0.293	0.166	0.313	0.121	0.274	0.252	0.530	0.281	0.754	0.313	0.913
2003	0.063	0.177	0.142	0.176	0.054	0.294	0.098	0.296	0.169	0.360	0.223	0.704
2004	0.065	0.181	0.071	0.346	0.077	0.213	0.133	0.265	0.100	0.388	0.289	1.217
2005	0.050	0.207	0.102	0.352	0.060	0.233	0.146	0.201	0.106	1.144	0.189	0.691
2006	0.105	0.249	0.110	0.108	0.078	0.193	0.216	0.244	0.138	0.486	0.544	0.670
	Cd											
2002	0.758	0.023	0.119	0.031	0.074	0.019	0.302	0.032	1.963	0.054	0.614	0.096
2003	0.040	0.018	0.015	0.076	0.025	0.029	0.014	0.035	0.012	0.056	0.007	0.075
2004	0.014	0.023	0.011	0.027	0.035	0.052	0.024	0.026	0.011	0.118	0.020	0.030
2005	0.062	0.016	0.046	0.150	0.038	0.554	0.297	1.577	0.013	2.777	0.066	0.271
2006	0.017	0.025	0.014	0.049	0.016	0.014	0.020	0.018	0.010	0.020	0.006	0.033

Considering a physiological significance of the studied elements, only V is beneficial for higher plants, *i.e.*, it may be involved in lipid metabolism and nitrogen fixation. Cadmium and arsenic may interfere with protein synthesis, and thus exhibit toxic effects.[13,14] Although, according to some authors, these elements are regarded as beneficial for some plants (algae and fungi) at low concentration, but toxic at higher concentrations.[3]

It is widely accepted that higher plants, including trees, take up elements mostly *via* the roots, although some uptake is considered possible through the leaves from atmospheric deposition. The foliar uptake and atmospheric origin has been clearly proven only for Pb.[15] However, topsoil analyses showed no serious contamination with the examined elements at the studied sites during the investigated period, *i.e.*, the values were: As ,7.2,[16] V, 1.4,[10] and Cd, 1.8[17] and 8.9 mg kg^{-1}.[18]

Moreover, the soil pH at the studied sites was mostly alkaline (> 8.0),[10,17] causing a decrease in the solubility of the trace elements. Trace element availability depends on several factors, such as, organic matter content, redox potential and pH. In the literature, it is emphasized that as a rule, the axial transport of elements from the roots (or other assimilation organ) to the bark can be assumed to be negligible. In fact, leaves are the main sink for many pollutants.[3] According to the previous assumption, the V, As, and Cd contents in the leaves of horse chestnut and linden are most likely of atmospheric origin. Furthermore, trace elements deposited on leaves are often present in the fine particle fraction, as was also shown previously for horse chestnut in Belgrade, with the majority of the particles observed on leaves belonging to the class of fine particles ($d < 2$ μm).[19] Most of elements in fine particles are considered as water soluble, as was also recently confirmed for Cd.[20]

The concentrations of the elements in the leaves of the investigated species, obtained for the Belgrade urban areas (2002–2006) (Table II) were compared to the values of the "reference plant" (*RP*) given by Markert (V: 0.5, As: 0.1, and Cd: 0.05 μg g^{-1}).[21]

In all the leaf samples from Botanical Garden and Studentski Park, and most of the samples from Karadjordjev Park, the concentration of V in May was even below the reference plant value (*RP* = 0.5 μg g^{-1}) and in most samples had increased to about this level by September. The highest *c*(measured)/*c*(RP) ratio was obtained for September 2002 (Fig. 1a), indicating vanadium accumulation in the leaves, probably as a consequence of atmospheric pollution. Considering the temporal accumulation trend, a decreasing V content in the leaves of the investigated species (September 2002/September 2006) was observed and its content at two locations (Botanical Garden and Studentski Park) decreased from a level about two times higher in 2002 to the level of the "reference plant"; even below this value in 2006. Examining the site dependence, the highest concentration of V was evident in both horse chestnut and linden leaves sampled from the KP site (Fig. 1a). This sampling site is located in an area with a high traffic density with a highway in the vicinity.

The arsenic concentration in most samples was higher than the reference plant value (*RP* = 0.1 μg g^{-1}), indicating a continuous source of emission at all locations in all the examined years (Fig. 1b). The accumulation of this element during the vegetation period was evident in the leaves of both tree species, linden and horse chestnut, which can be related to increasing deposits from aerosol arsenic and the increase was enough to offset the dilution effect by leaf material which increase during the growing period. The highest As concentration, about twelve times the RP value were found in the leaves from Studentski Park, a small park with a bus terminal and surrounded by many high buildings.

During the investigated time span, the Cd concentrations at all sites were mostly at about the same level, except for a few extremely high values in 2002 and 2005 registered for both horse chestnut and linden, (Fig. 1c). It should be em-

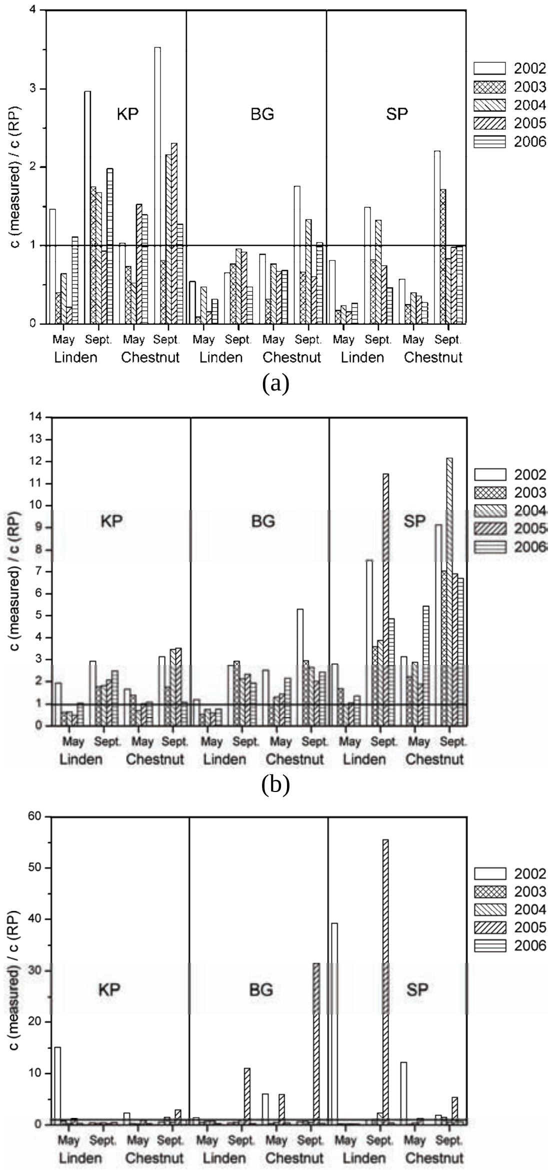

Fig. 1. The ratio of measured concentration of V (a), As (b), and Cd (c) in the leaves of *Tilia spp.* (linden) and *A. hippocastanum* (chestnut) and the relevant concentration in the "reference plant".

phasized that at all locations in May 2002, the cadmium concentration was higher than the background level proposed by Markert.[21] However, no accumulation of Cd was observed until September in these samples from 2002, which probably indicates a decreasing cadmium concentration in the air and dilution by leaf material. An accumulation of cadmium in the leaves was observed from September 2005 for all samples, except in linden from Karadjordjev Park. Five times higher level than the RP value was determined in samples from the Botanical Garden from May 2005, and even more than 30 times in samples from the same location taken in September 2005. At all locations, it seems that higher concentrations of cadmium compared with other years resulted in increased accumulation of this element. Cadmium is emitted into the atmosphere by several sources and it is highly volatile, thus undergoing long-range transport.

As suggested in a previous investigation of element concentrations in $PM_{2.5}$ (particles smaller than 2.5 μm in diameter) in central Belgrade, vanadium and cadmium had a common source, traffic, with a considerable portion of resuspended road dust, and products of other fossil fuel combustion processes.[4] The relatively low concentrations of vanadium and cadmium found in leaves in the present study could be explained by a lack of heating sources during the vegetation period because the dominant source of PM in Belgrade is stationary combustion.[22] In addition, most of the coarse particulates were removed by the procedure of washing the leaves before chemical analyses, which diminished the contribution of road dust resuspension on the surface of the leaves. Consequently, the V, As and Cd found in the leaves originated mainly from traffic, motor exhaust and also metallic parts of cars.

CONCLUSIONS

This study gives evidence for the accumulation of As and V during the growing season (May–September) in the leaves of horse chestnut and linden sampled in the Belgrade urban area. During the studied time span (2002–2006), the concentrations of As and V in the leaves showed slightly decreasing trends. In general, Cd showed no significant May–September accumulation over the years, except in 2005 when higher concentration around the parks resulted in increased accumulations. The highest vanadium and cadmium contents were found in the leaves sampled from Karadjordjev Park, while the highest As concentration was detected in the leaves sampled in Studentski Park. The contents of As and V in September were mostly higher than those May, especially in horse chestnut, although both studied trees may be used as biomonitors for these elements, and optionally for Cd under conditions of its high atmospheric loading.

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ИЗВОД

ИСПИТИВАЊЕ ЗАГАЂЕНОСТИ ВАЗДУХА У БЕОГРАДУ ЕЛЕМЕНТИМА У ТРАГОВИМА (As, V, Cd) ИЗ ЛИСТОВА ЛИСТОПАДНОГ ДРВЕЋА

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Једна од последица интензивног економског и индустријског развоја је повећана емисија загађујућих супстанција у атмосферу. Дрвеће, посебно у урбаним срединама, веома је значајно са аспекта пречишћавања ваздуха; поред тога, уочено је да постоји корелација између концентрације појединих загађујућих материја у ваздуху и у лишћу дрвећа, што је искоришћено за биомониторинг квалитета ваздуха. У овом раду је испитивана могућност биомониторинга елемената у траговима у ваздуху помоћу две врсте листопадног дрвећа, дивљег кестена (*Aesculus hippocastanum*) и липе (*Tilia spp.*), које су веома заступљене у Београду. Узорци су сакупљани на почетку вегетационог периода, у мају, као и на крају вегетационог периода, у септембру, током пет година, од 2002. до 2006. године. У експерименталном делу извршена је анализа садржаја елемената у траговима (арсен, ванадијум, кадмијум) у листовима наведених врста дрвећа сакупљеним са три локације у Београду (Карађорђев парк, Студентски парк и Ботаничка башта), које су одабране због интензивног саобраћаја. Поређењем добијених вредности са концентрацијама испитиваних елемената у суспендованим честицама у ваздуху одређен је степен акумулације и закључено је да се испитиване врсте могу користити за биомониторинг квалитета ваздуха, односно његове загађености испитиваним елементима у траговима, при чему је дивљи кестен имао боље акумулативне способности.

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