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Trace elements and radionuclides in urban air monitored by moss and tree leaves

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1. Introduction

In urban areas, air quality is strongly influenced by numerous anthropogenic activities. High population density, heavy traffic and domestic heating in winters in the centre, and various industrial activities at the outskirts, influence atmospheric concentrations of trace elements and radionuclides. Consequently, large population is exposed to possible adverse effects arising from the altered urban air composition. Therefore, air quality monitoring has become one of the standard quality control procedures in urban areas.

1.1 Trace elements and radionuclides in air

Due to changed atmospheric concentrations of trace elements, their availability and cycling has changed, too. Numerous studies showed that trace metals as persistent, widely dispersed and interacting with different natural components, cause threat to human health and environment (Seinfeld & Pandis, 1998). Trace elements in urban areas (such as Cu, Zn, and Pb) are mainly emitted by traffic, including exhaust emissions and vehicle wear products (Harrison et al., 2003). Even though the use of leaded gasoline has been drastically reduced, our understanding of the effects of whole lead emission to air is far from sufficient (Van der Gon & Appelman, 2009). As reported recently, though atmospheric Pb had declined by a factor of 7 from 1980 to 2007, atmospheric deposition is still recognised as a major pathway of Pb to vegetation and topsoil (Hovmand et al., 2009). Since it offers a practical approach for monitoring deposition of atmospheric trace elements on the surface environment (Azimi et al., 2003; Tasić et al., 2008), collection of atmospheric deposition using bulk sampling devices has been extensively used. However, instrumental studies on atmospheric contamination are often limited by high cost and difficulties in carrying out extensive monitoring surveys in time and space, and do not offer reliable information about an impact of atmospheric pollutants on the living systems.

Among the naturally occurring radionuclides in air, beryllium-7, radon and its short lived progenies are most significant, while caesium-137 is of major interest among the fission products. Long-lived radionuclides, potassium-40, uranium and thorium, found in significant quantities in soils, are usually not detectable in air, thus, if found on leaves, they are mainly resuspended from soils (Vandenhove et al., 2009). The soil-to-plant transfer factor above 1.0 is reported for ^{40}K, while values for uranium and thorium are much lower (10^{-4}) (Uchida et al., 2007). In higher plants, the distribution of the radionuclides is uneven. In tropical forest plants, for example, the highest ^{40}K concentrations are found in stem, and the lowest in root, while ^{137}Cs is mostly accumulated in root (Somashekarappa et al., 1996).

Beryllium-7 (half-life 53.28 days) is produced by cosmic rays in spallation processes with light elements (nitrogen, oxygen, carbon) in the upper troposphere and lower stratosphere. Its production depends on the Earth's magnetic field, and the variations in its annual mean concentrations are a good indicator of changes in the atmospheric production rate caused by cosmic ray intensity. The ^{7}Be seasonal patterns are correlated to the stratosphere–to–troposphere exchange processes. The ^{7}Be concentration in ground level air in the midlatitudes has the maximum during spring and summer (e.g., Ajtić et al., 2008), caused by a seasonal thinning of the tropopause which allows the ^{7}Be rich stratospheric masses to enter the troposphere (Gerasopoulos et al., 2003).

Lead-210 (half-life 22.3 years) is an effective tracer of continental surface air masses history and often used to identify soil aerosols sources. It mostly originates from the decay of uranium-238 in the Earth's crust, but anthropogenic sources (uranium ores sintering, coal combustion, production or use of phosphate fertilizers) also contribute to the total ^{210}Pb in air (UNCEAR, 1988). Deposition of ^{210}Pb varies with season and geographical position. The ^{210}Pb concentration maxima in fall could be attributed to an enriched emanation of radon. Radon emanation, and therefore concentration of ^{210}Pb in air, is affected by atmospheric pressure, temperature inversions, covering vegetation, snow and ice ground coverage, etc. Furthermore, important factors influencing the ^{210}Pb concentrations in air are soil geology, continental and areas masses distribution, conditions of surface air layers, etc. (Delfanti et al., 1999).

Due to its half-life of 30 years, ^{137}Cs is a good indicator of nuclear weapon atmospheric tests and nuclear power plant accidents on global scale. Since 1986, ^{137}Cs in ground level air has mainly originated from the Chernobyl nuclear accident, with concentrations of the order of μBq/m^{3}, and with one or two maxima in summer and winter. The ^{137}Cs winter maxima are attributed to the inversion weather conditions and to soil dust air resuspension from the Chernobyl fallout (Todorovic et al., 1999).

1.2 Moss and tree leaves as biomonitors

For several decades, air quality biomonitoring has been widely applied to detect and monitor the effects of trace elements pollution (Bargagli, 1998; Markert et al., 2003). Mosses and lichens are recognised as the most appropriate biomonitors of atmospheric trace elements and radionuclides contamination. Many studies have demonstrated the ability of moss to absorb and accumulate trace elements in their tissue. Due to the absence of root and cuticle, mosses uptake their nutritive elements from wet and dry atmospheric deposition (Rühling & Tyler, 1968). Mosses have also been recognised as valuable biomonitors in the assessment of temporal trends in trace metal accumulation (Harmens et al., 2008), and in spatial variations across national boundaries (Schröder et al., 2008).

Mosses are also highly efficient in accumulating radionuclides and have been widely used as reliable bioindicators of radioactive contamination of the environment since the late 1960's (Sumering, 1984; Steinnes, 2008; Frontaseyeva et al., 2009; Aničić et al., 2007; Barandovski et al., 2008; Guillén et al., 2009). Due to their continuous accumulation of elements, mosses offer information about the sources of pollution long after the pollution episode itself took place (Golubev et al., 2005). Being globally spread, mosses are an important tool in mapping global distribution of radionuclides following nuclear weapon atmospheric tests and in radioactivity monitoring in the vicinity of nuclear and coal power plants (Delfanti et al., 1999; Uğur et al., 2003). In 1986, mosses and lichens proved to be reliable indicators of environmental contamination after the nuclear plant accident in Chernobyl (Papastefanou et al., 1989; Hofmann et al., 1993). In the late 1990's, mosses and lichen were used to estimate the level of contamination caused by the military use of depleted uranium (DU) in the Balkans (UNEP, 2002; Loppi et al., 2003; Frontasyeva et al., 2004; Popovic et al., 2008a).

Since naturally growing mosses are often rare or absent in urban areas, the "moss bags technique'' (*active biomonitoring*) has been developed in order to spatially and/or temporally assess deposition of trace elements in highly polluted areas (Goodman & Roberts, 1971; Vasconcelos & Tavares, 1998; Fernandez et al., 2004; Culicov & Yurukova, 2006). The technique offers several advantages compared to naturally growing mosses: one can precisely limit the time of exposure, acquire data on the concentrations of different elements in the sample prior to the exposure, and choose a most suitable site for moss transplantation. The *Sphagnum* moss species are especially recommended for active biomonitoring for their large surface area and a number of protonated anionic functional groups (ion exchange sites) in the form of uronic acids. However, moss bags tend to dry out and thus their efficiency in retaining elements varies with the environmental conditions, especially humidity (Al-Radady et al., 1993). Until now, only a few quantitative comparisons of biomonitoring methods with the standard measurements of atmospheric deposition have been published (Berg & Steinnes, 1997; Thöni et al., 1996; Aničić et al., 2009a,b). Moreover, the exact relationship between the element content in moss and the actual atmospheric deposition is not yet well understood, though some studies have given evidence of possible quantitative conversion with unsedimentable dry deposited particles (<0.8 µm) (Vasconcelos & Tavares, 1998).

In urban and industrial areas, however, where lichens and mosses are often not found, higher plants could replace them. In areas with high atmospheric pollutant loads, plants may provide information, not only about quality/quantity of air pollutants, but also about effects on ecosystems. Leaves of both evergreen and deciduous tree species have been recognised as valuable accumulative biomonitors of atmospheric elements and radionuclides in urban areas. Tree leaves are also very efficient in trapping atmospheric particles (Freer-Smith et al., 2005; Peachey et al., 2009; Qiu et al., 2009), and they have a special role in reducing the level of "high risk" respirable particulates possibly harmful to the environment and human health (Beckett et al., 2000). There are numerous studies searching for sensitive tree species, and their validity for urban air quality biomonitoring (Alfani et al., 1996; Monaci et al., 2000; Piczak et al., 2004; Mingorance & Oliva, 2006; De Nicola et al., 2008). Some species show a good response to atmospheric trace elements pollution, e.g. *Q. ilex* may be appropriate for biomonitoring in urban areas where it is naturally present and widely distributed (Gratani et al., 2008). A significant correlation was reported between the Cu and Fe contents in inhalable atmospheric particles (PM_{10}) and in leaves of *Nerium oleander* (Espinosa & Oliva, 2006). According to Bargagli (1998), the species of *Tilia* genus could be used as biomonitors of trace elements in urban and industrial environments, while Baycu et al. (2006) reported that, compared to other urban tree species, *A. hippocastanum* accumulated the highest Pb concentrations in leaves.

Plants are also an important link in the transport and distribution of radionuclides from the source of pollution to man and can be used as biomonitors of atmospheric pollution by radionuclides (Djuric and Popovic, 1994). Radionuclides can be deposited on plants from air (foliar deposition) where they appear from fallouts or by natural sources, or can be taken through soil root system. Most of the air borne radionuclides are quickly attached to aerosols, and their concentration in air is manly due to behaviour of aerosols in the atmosphere. Thus, the rate of their removal from the atmosphere and deposition on ground and vegetation depends on the size of particles they are attached on (Djuric and Popovic, 1994). Foliar deposition and absorption of radionuclides from air to leaves are closely associated not only with morphological characteristics of leaves, but also with local climate (moisture, concentrations of dust particles, wind velocity and direction, amount of precipitation, etc). Thus, some authors found radionuclides concentrations in leaves to be of an order of magnitude or two less than those in stem or roots (Somashekarappa et al., 1996). Accumulation of radionuclides by plants, e.g. estimation of soil-to-plant transfer factors, foliar deposition rate and root uptake, has been in focus of investigations of many authors, but mainly for agricultural plants, cereals and vegetables, in laboratory and/or in field conditions (Djuric et al., 1996; Djuric & Popovic, 1994; Golmakani et al., 2008; Koranda & Robison, 1978). The main problem in assessing the contribution of air pollution compared to root uptake is the fact that soil-to-plant/leaves transfer factors are found in the large range of values (10^{-3}–10^{-1}) due to numerous factors, mainly characteristics of soils and leaves/plant morphology (IAEA, 1994). Solubility, pH, acidity, organic matter content, etc., play a vital role to radionuclides availability by plants (Golmakani et al., 2008). Still, some studies found similar seasonal variation pattern of ^{7}Be and ^{210}Pb between leaves and aerosol samples, high in spring and low in summer (Sugihara et al., 2008).

Trace elements in Belgrade air are mostly bound to the particulates of the mixed road origin (Rajšić et al., 2008). As reported previously for the area, the leaves of *A. hippocastamum* and *Corulys colurna* showed a distinguished seasonal accumulation of some elements (Cu, Zn and Pb). Among the two, *A. hippocastanum* seems a more suitable biomonitor, not only by the leaf content, but also because it was found that a level of the Pb accumulation reflected marked changes in the atmospheric Pb concentrations (Tomašević et al., 2008).

Active biomonitoring with the moss bag (MB, *Sphagnum girgensohnii* Russow, Russia) and bulk deposition (BD) measurements were performed for trace elements (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb) atmospheric deposition in the urban area of Belgrade in 2005 – 2006. The aim of the research was to evaluate trace element accumulation in the moss bags, and to examine its relationship to the atmospheric bulk deposition measurements. In order to assess the actual responses of moss to trace element concentrations in air, and to investigate the role of water supply on the moss accumulation ability, experiments with dry and irrigated (wet) moss bags were carried out. The content of natural and fallout radionuclides (^{7}Be, ^{210}Pb, ^{40}K and ^{137}Cs) in moss bags was also determined, with an aim to assess the validity of the method for radioactivity monitoring and control in ground level air.

The trace elements (Cr, Fe, Ni, Zn, Pb V, As, and Cd) accumulation and the temporal trends were also assessed in leaves of the trees common for the city of Belgrade: *Aesculus hippocastanum* (horse chestnut) and *Tilia spp.* (linden), over a period of five years (2002 – 2006). The relationship between the trace elements concentration in the leaves and the instrumental measurements of atmospheric bulk deposition was also examined. The contents of radionuclides in leaves in comparison with their activities in ground level were determined, too.

2. Experimental

2.1 Study area

The study was conducted in Belgrade (44˚ 49′ N, 20˚ 27′ E; 117 m a.s.l.), the capital of Serbia, with about 2 million inhabitants, situated at the confluence of the rivers Sava and Danube. The climate is moderate continental with fairly cold winters and warm summers. In winter, severe air pollution as aerosol smog occurs frequently in the central city area, particularly during meteorologically calm and stable conditions. The number of vehicles is around 500,000, including heavy-duty trucks and over 1,000 city buses run on diesel. The average age of passenger cars is more than 15 years, and leaded gasoline is still widely used. There are many old buses and trucks in the city traffic, which could be the major source of ambient particulates. The city is heated with a number of heating plants run on natural gas or crude oil, but there are still individual houses heated with coal (Todorović et al., 2005; Todorovic et al., 2007). Natural gas has only been introduced in the last few years.

The moss bags measurements were carried out at three representative sites in heavy traffic areas: the Faculty of Veterinary Medicine (VF), the Rector's Office Building of the Belgrade University (RB), and the Public Health Institute (HI). The tree leaves samples were collected in the parks adjacent to those three locations. Trace elements and radionuclides accumulation was investigated in dry and wet moss bags and tree leaves (in May and September), while bulk deposition and aerosols were collected on a monthly basis at the same places and time. The map of Belgrade central area, with the sampling sites, is presented in Fig.1.

Fig. 1. Map of Belgrade central city area with the sampling sites: A) the Rector's Office building of the Belgrade University RB, B) the Public Health Institute HI, and C) the Faculty of Veterinary Medicine VF.

2.2 Moss sampling, bag preparation and analysis

2.2.1 Trace elements

Moss (*Sphagnum girgensohnii* Russow) was collected in June 2005 from a pristine wetland area near Dubna, Russia (56˚ 44' N, 37˚ 09' E; 120 m a.s.l.), and cleaned from soil particles and other matter. About 3 g of moss was packed in (10 x 10) cm^2 nylon net bags (1 mm mesh size). The bags, with and without irrigation (WET and DRY MB) were exposed at the same time at the three sampling sites (Fig.1). Wet moss bags were placed on the top of cellulose sponge with the bottom immersed in distilled water, and the setup was put in a polyethylene box. Distilled water was added every several days, depending on meteorological conditions (precipitation and temperature) (Aničić et al., 2009a). Using specially constructed holders (1.5 m high) on platforms 5–10 m above the street level, two dry (hung freely in the air) and two wet moss bags were exposed for five 3-month periods, between July 2005 and October 2006. After the exposure, the moss was removed from the net, homogenised and dried to a constant weight at 40 ºC for 24 h.

The concentrations of Al, V, Cr, Mn, Fe, Ni, Zn, and As were determined by instrumental neutron activation analysis (detection limit 0.01–10 µg/g). Short-term irradiation (2 min) was applied for short-lived radionuclides (Al, V, and Mn). The long irradiation (100 h) was applied to determine elements associated with long-lived radionuclides (Na, Cr, Fe, Ni, Zn, and As). The concentrations of Cu, Cd, and Pb in moss were analysed by flame atomic absorption spectrometry. Quality control was performed using the standard reference material: Lichen (IAEA–336), Tomato Leaves (SRM–1573a) and Coal Fly Ash (SRM–1633b).

2.2.2 Radionuclides

Moss (*S. girgensohnii*) was packed in nylon net bag (total mass 255 g), and exposed on the VF site (Fig. 1) for one year (May 2006 – May 2007). The site is in the vicinity of a highway, and is one of the pollution “black spots” in the city. It is also the sampling site for air radioactivity monitoring by filter paper method (Todorovic et al., 2007).

Prior to exposure, the moss was dried and cleared of soil and other material. After the exposure, the sample was divided into eight subsamples of 25–36 grams to examine the uniformity of radionuclides’ distribution within the sample (Popović et al., 2009b).

The activities of ^{7}Be, ^{210}Pb, ^{40}K and ^{137}Cs were determined on an HPGe detector (Canberra, relative efficiency 23%) by standard gamma spectrometry. Geometric calibration was performed using the standard reference radioactive material IAEA-373 (grass, with ^{134}Cs, ^{137}Cs, ^{40}K and ^{90}Sr, total activity of 15 kBq d.w. on 31.12. 1991). Counting time was 58,000 s, with the total standard error of 16% for ^{40}K, 20% for ^{210}Pb, and 10% for ^{137}Cs (Popović et al., 2009b).

2.3 Tree leaves sampling and analysis

Leaves were sampled from *Aesculus hippocastanum* L. (horse chestnut), and *Tilia spp.* (linden: *Tilia tomentosa* L. and *Tilia cordata* Mill.), at the beginning (May) and the end (September) of the vegetation seasons from 2002 to 2006. Five subsamples (10 to 15 fully developed leaves) were taken randomly from several crowns 2 m above the ground (Tomašević et al., 2008). Leaves were washed with bidistilled deionised water, dried at 40 ºC for 24 h, and pulverised with agate mortars prior to analyses. About 0.4 g of leaves were digested for 2 h in a microwave digester with 3 ml of 65% HNO_3 (Suprapure, Merck) and 2 ml of 30% H_2O_2, and then diluted with distilled water to a total volume of 25 ml. The content of Cr, Fe, Ni, Cu, Zn, and Pb was determined by inductively coupled plasma optical emission spectrometry, and V, As, and Cd by inductively coupled plasma mass spectrometry. Quality control was performed using the standard reference material Lichen-336 (IAEA).

For radionuclide analysis, the samples of leaves were collected in the identical fashion (Tomašević et al., 2008). In addition, samples of soils were also collected in the three sites. Soils and leaves were measured in native state, leaves were dried up to 105 ºC. Aerosols were also sampled and analysed for the contents of radionuclides by standard procedures (Todorović et al., 2005; Todorovic et al., 2007).

2.4 Sampling and analysis of bulk deposition

Bulk depositions were collected monthly, in open polyethylene cylinders (29 cm x 40 cm) fixed in baskets at the measuring sites, from the beginning of 2002 to the end of 2006. The samples were evaporated to dryness and digested with 50 ml of 0.1 N HNO_3 on an ultrasonic bath. The content of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb was determined by flame atomic absorption spectrometry (Perkin Elmer AA 200) and graphite furnace atomic absorption spectrometry (Tasić et al., 2009). For calibration, standard solutions containing all metals of interest were prepared using Merck certified atomic absorption stock standard solutions.

2.5 Trace elements data analysis

Data analysis included the basic statistics (mean/average, correlation, and t-test) for Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb concentrations measured in DRY and WET MB, the tree leaves and the monthly BD samples. To assess the element accumulation in moss, the relative accumulation factors (RAF) were calculated as the ratio of the moss content of element after and before the exposure ($C_{exposed}$ - $C_{initial}$), and before the exposure ($C_{initial}$):

$$RAF = (C_{exposed} - C_{initial}) / C_{initial} \qquad (1)$$

3. Results and Discussion

3.1 Trace elements in moss bags

The initial (background) content of elements plays a crucial role in obtaining the relative accumulation level in biomonitoring studies. For most of the examined elements, the initial values in *S. girgensohnii*, used for active biomonitoring in Belgrade (Aničić et al., 2009a,b), were significantly lower than those from other sites (Adamo et al., 2003; Djingova et al., 2004; Culicov & Yurukova, 2006) or in other *Sphagnum spp*. (Djingova et al., 2004). The initial element concentrations in *S. girgensohnii* were even lower than the values proposed by Markert (1992) as "reference plant values" used to compare elements accumulation among the different species. This points to the variation in natural *Sphagnum* element content from different areas and, consequently, to a necessity to determine the background (control) levels prior to each biomonitoring study. The advantage of low background levels is the higher method sensitivity in areas with low atmospheric deposition (Culicov et al., 2005).

Significant accumulation of the majority of examined elements in the *S. girgensohnii* moss bags were observed over the 3-month exposure periods (Table 1) indicating that this species is an efficient trace element accumulator (Aničić et al., 2009a). Higher element content was measured in the WET MB (except for Mn) which is in agreement with other studies (Al-Radady et al., 1993). One of the differences between the WET and DRY MB is that deposited particles are trapped in higher quantities on wet surfaces. Furthermore, WET MB could incorporate the elements in its tissues, whereby being less susceptible to rinsing and thus better reflecting the atmospheric conditions (Astel et al., 2008). This is in agreement with findings of Berg & Steinnes (1997) that atmospheric humidity and precipitation are important factors for moss accumulation.

To compare the element accumulation in DRY and WET moss bags, relative accumulation factors RAF (Eq. 1) were calculated. The RAF values, which are inherently insensitive to the influence of the initial element content, have been used to compare accumulation between different monitoring species (Adamo et al., 2003; Culicov & Yurukova, 2006). The most accumulated elements in DRY MB, according to the RAF value were V (22), followed by Cr (11) > Cu (9) > Pb (8) > As (5) > Al (4) > Fe (3) > Ni (3) ≈ Zn (2.5) > Mn (0.9) > Cd (0.5). In WET MB, the order for the most accumulated elements was somewhat different: Cu (68) > V (26) > Cr (21) > Pb (13) > Al (6.5) > As (6) > Fe (5) > Zn (4.5) > Ni (4) > Cd (1) > Mn (0.2) (Aničić et al., 2009b). The accumulation of Cu in WET MB was about eight times higher than for DRY MB. Likewise, the content of Cr was about twice as high in WET MB. Other elements, such as Pb, Al, Fe, and Zn, were slightly more accumulated in WET MB than in DRY MB. In some moss bags, both dry and wet, a loss of Mn, compared to the initial material, was evident (10% and 80%, respectively). The loss of Mn caused by washing out and leaching from moss, was described in Couto et al. (2004). The RAF values, obtained in this study, are significantly higher than the literature data (Adamo et al., 2003; Culicov & Yurukova, 2006). This is most likely related to higher atmospheric pollution in Belgrade urban area, and to lower initial concentration of the elements in used *S. girgensohnii* moss.

	S. g.	*S. girgensohnii* (DRY MB)			*S. girgensohnii* (WET MB)		
Element	Initial	Min	Max	Median	Min	Max	Median
Al	254	659	1960	1363	802	3523	1870
V	0.54	2.9	112	13	2.9	69	14
Cr	0.25	2.0	6.8	3.1	3.7	8.3	5.8
Mn	113	92	322	215	77	212	134
Fe	297	732	2496	1219	1026	4810	1682
Ni	2.4	1.9	41	8.7	4.5	30	12
Cu	2.1	10	49	20	42	476	144
Zn	20	44	105	71	85	264	113
As	0.11	0.38	2.2	0.67	0.53	5.4	0.80
Cd	0.18	0.19	0.36	0.27	0.25	0.50	0.36
Pb	2.2	7.0	38	20	14	63	31

Table 1. Trace elements (μg g^{-1} of dry weight) in DRY and WET MB of *S. girgensohnii* exposed in Belgrade urban area.

3.1.1 Trace elements accumulation in moss bags *vs.* bulk deposition

To compare the element accumulation in moss bags with the bulk deposition data, the moss element concentrations (µg g^{-1}) were expressed as the deposition fluxes (µg m^{-2} day^{-1}) and the Spearman rank correlation coefficients (r) were calculated to estimate a relationship between the element deposition flux in DRY MB/WET MB and BD. The correlation between the element BD and the element deposition flux in WET MB was high for V (r=0.87), As (r=0.74), Fe (r=0.73), Al (r=0.71), and Ni (r=0.68). No correlation was found for Cd, Mn, and Zn. The DRY MB *vs.* BD highest correlation was found for Cu (r=0.85). Lower, but still significant correlation ($r > 0.50$), was obtained for Pb, Cr, and Zn (Aničić et al., 2009a).

In general, trace elements may be deposited onto the moss surface either as dry particulates or dissolved and/or suspended in precipitation. The elements may be retained by particulate entrapment, physicochemical processes such as ion exchange or by passive and active intracellular uptake (Tyler, 1990). Therefore, moss is not a mere passive filter. Poor correlation for some element deposition fluxes in moss samples and BD probably indicates more complex mechanisms of element accumulation in moss. Furthermore, due to splash effect and irregular surfaces, it is difficult to estimate the exact atmospheric deposition fluxes in moss bags. Nevertheless, the concentrations of some elements (e.g., V, Fe, Co, As, Mo, Cd, Sb, and Pb) were found to be significantly correlated in moss and wet deposition (Couto et al., 1994; Berg & Steinnes, 1997). The rate of element uptake by moss increased markedly, but not regularly, with atmospheric humidity and precipitation, whereas their atmospheric level decreased (wet deposition), preventing the possibility of establishing a conversion factor for wet weather conditions (Vasconcelos & Tavares, 1998).

Studies on the capture of atmospheric particles by moss have demonstrated that standardised active biomonitoring with moss bags provides a better capture efficiency of particles over 20 µm in diameter (sedimentable particles) less influenced by abiotic conditions like wind speed. Therefore, it was suggested that particles trapped by bryophytes may be a major source of poorly water-soluble elements, and that moss content can reflect recent environmental conditions for dry and coarse depositions, especially for active biomonitoring experiments in highly polluted areas (Amblard-Gross et al., 2002).

3.1.2 Seasonal variations of trace elements in moss

Trace elements content in moss bags was also analysed for the summer (May – October) and winter (November – April) seasons. Seasonal variations in both DRY and WET MB samples were observed for all of the elements except Pb, Al, and Mn. At all three sites, the highest variations were noticed for V and Ni, whose content was two and three times higher in winter than in summer, respectively (Fig. 2).

The content of As and Fe in moss bags were 1.5 times higher in winter than in summer. This was not unexpected as these elements are markers for oil and coal combustion. However, concentrations of Cu were increased in summer, especially in WET MB. Moreover, the concentrations of Zn and Cd in WET and DRY MB were slightly higher in summer than in winter period. These elements are markers for traffic sources, but our results point to some other local sources, more expressed during the warm period (Aničić et al., 2009a).

Seasonal variations were also found for the elements in the bulk deposition, being higher in winter season (except for Pb, which was increased during summer time). In winter, much higher contents of V, Ni, As, and Fe were found in the bulk deposits.

3.2 Radionuclides in moss bags

Fission product ^{137}Cs and naturally occurring ^{40}K and ^{210}Pb were detected in all of the eight subsamples of moss bags, while ^{7}Be was detected only in one, with the activity of 60 Bq/kg.

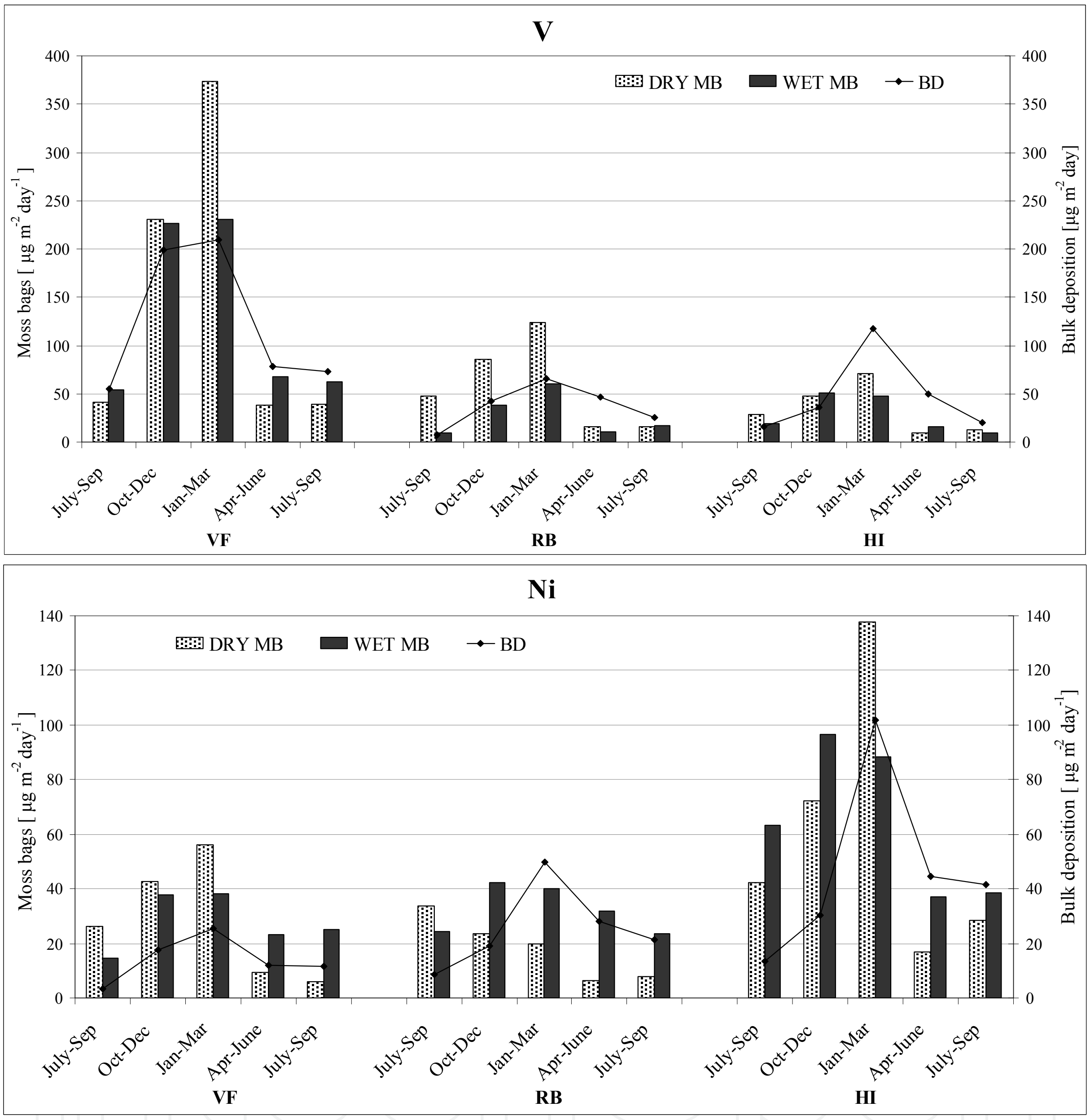

Fig. 2. Seasonal variation of V and Ni daily fluxes (mg m^{-2} day^{-1}) for DRY MB and WET MB, and BD for 3-month periods in 2005/2006 at the study sites (VF, RB, and HI).

The absence of ^{7}Be in the subsamples could be explained by its decay, since the period between the sample arrival in the laboratory and the analysis was nearly 60 days. Taking into account the standard uncertainty of the method and the volume of the composite sample, the distribution of the activities of the detected radionuclides in the eight subsamples was rather uniform with the differences not exceeding 30% (Popović et al., 2009b). The level of the annual activities of the radionuclides implied that the exposure time could be reduced to a month, and that would enable monitoring seasonal variations in the content of radionuclides in air. The mean activities with standard deviations of ^{40}K, ^{210}Pb, and ^{137}Cs in moss bags (*S. girgensohnii*), are given in Table 2. For comparison, the content of these radionuclides in naturally growing mosses (*Hypnum cupressiforme*) in Southern Serbia (Borovac) are also presented in the table.

Location	Activity (Bq/kg)			
	^{40}K	^{210}Pb	^{137}Cs	^{7}Be
Belgrade	245 ± 34	315 ± 25	28 ± 4	/
Borovac	298 ± 42	210 ± 52	226 ± 22	228 ± 34

Table 2. Activities of the radionuclides in moss bags (*S. girgensohnii)* exposed in Belgrade (Popović et al., 2009b) and in *H. cupressiforme*, Borovac (Popovic et al., 2008b).

The activity ratio ^{210}Pb/^{40}K of 1.30 was calculated. The ratio could provide a sound basis for the ^{210}Pb activity estimation by solely measuring the activity of ^{40}K, which is more easily detected, and with a lesser uncertainty than ^{210}Pb (Popović et al., 2009b). The mean activities of the detected radionuclides in moss bags were in the range of the values reported for the local moss (*H. cupressiforme*) in the region (Krmar et al., 2007; Popovic et al., 2008b), with differences arising from the species, the method, local climate and soil characteristics. Krmar et al. (2007) found measurable, even significant concentrations of ^{7}Be in *H. cupressiforme*, with an increase in summer and autumn (up to 920 Bq/kg), but the sampling in the study took place over a 14-month period. Beryllium-7 was also found in naturally growing moss (*H. cupressiforme)* in the rural area of Southern Serbia (Popovic et al., 2008b) (Table 2).

As can be seen from Table 2, there are no significant differences in the content of ^{40}K in naturally growing mosses in Southern Serbia and in the urban area of Belgrade. On the other hand, higher concentrations of ^{210}Pb in Belgrade indicate a contribution of anthropogenic air pollution sources. Significantly higher activities of ^{137}Cs, as well as the detectable amount of ^{7}Be, in mosses sampled in Southern Serbia are due to a longer, undefined exposure period (in the Belgrade study, the exposure period of one year was precisely defined). Hence, the observed differences mirror the differences in the accumulation period.

Before the Chernobyl nuclear plant accident in 1986, the concentrations of ^{137}Cs in moss and lichen in Serbia were under 1 Bq/kg (Djuric & Popovic, 1994). Immediately after the accident and later, the contents of ^{137}Cs in mosses and lichens, sampled in a mountainous region, was in the range of 8–18 kBq per kg of dry weight (Djuric et al., 1992, 1996; Popović et al., 1996). In 1997, the activities of ^{137}Cs in the naturally growing mosses in a region in Serbia were up to 3 kBq/kg, while the soil-to-moss transfer factors calculated for the same region in 2000 were in the range of 3.0–10.0 (Popović et al., 2009a). High transfer factors for ^{137}Cs and ^{210}Pb from soil to mosses were also found in Southern Serbia, in the range of 1–10 and 4–10, respectively (Popovic et al., 2008a).

Still, as already mentioned, naturally growing mosses are unlikely to be found in urban areas, and the active moss monitoring is therefore a suitable alternative technique for monitoring contents of radionuclides in urban air. Furthermore, this method solves some of the problems in monitoring using naturally growing mosses, such as intercalibration of different species of mosses and transformation of concentrations in moss to absolute deposition rate (Steinnes, 2008).

Frontasyeva et al. (2009) proposed a linear correlation between the concentrations of ^{137}Cs in mosses A_{moss} and in air A_{air}:

$$A_{air}\ (\mathrm{Bq/m^3}) = 3.3 \times 10^{-8}\ (\mathrm{kg/m^3}) \times A_{moss}\ (\mathrm{Bq/kg}) \qquad (2)$$

When applying this relationship to the activity of ^{137}Cs in moss obtained in our study, the calculated ^{137}Cs activity in air is 0.924×10^{-6} Bq/m^3, which is under the lower limit of detection in our measurements (1×10^{-6} Bq/m^3).

To conclude, since the Belgrade study showed that the exposure time for the moss bags technique could be reduced to a month, the technique could be used to monitor the level of radionuclides' contents in air, as well as to follow their seasonal variations.

3.3 Trace elements in tree leaves

Seasonal accumulation trends of elements' concentration in leaves have been well known and reported for many plant species (Kim & Fergusson, 1994; Bargagli, 1998; Piczak et al., 2003). In Belgrade urban area, the elements' concentration were determined in leaves of *A. hippocastanum* and *Tilia spp.* at the beginning (May) and the end (September) of the vegetation seasons over a period of 2002 – 2006. An increase of the element concentrations ($p<0.001$) from May to September, i.e. seasonal element accumulation, was evident in all of the *A. hippocastanum* samples throughout the investigated years for V, Cr, Fe, As, Ni, Zn, and Pb (Fig. 3). However, in *Tilia spp*. leaves the elements' increase was not regular (Fig. 4).

On the other hand, in *A. hippocastanum* leaves there was no regularity in the seasonal accumulation of Cu ($p<0.15$) and in *Tilia spp*. leaves for Cu ($p<0.2$) and Zn ($p<0.09$). For *A. hippocastanum,* such seasonal discrepancy in the Cu and Zn concentrations was previously noted by Kim & Fergusson (1994), who pointed out that these elements concentrations were the highest in new leaves, and decreased over the vegetation season. Thus, variations in seasonal accumulation of Cu and Zn in some samples of *A. hippocastanum* and *Tillia spp.* may be a result of the fact that these elements are essential constituents of plant tissue. It is considered that the Cu remobilisation to non-senescent parts occurs before the senescence, and leaf fall takes place. In walnut trees, the concentration of Cu in old leaves was just 8 % of the maximum Cu value in younger mature leaves (Drossopoulos et al., 1996). Moreover, some recent data for the black spruce needles supported the previous hypothesis and confirmed that an active translocation of essential metals, particularly Cu, takes place from senescent to non-senescent parts of a plant. However, the results for Pb, as a nonessential metal, were in accordance with a hypothesis that the passive sequestration of toxic metals was attained in the senescing foliage as a detoxification process (Aznar et al., 2009).

3.3.1 Spatial and temporal trace elements' variation in leaves *vs.* bulk deposition

Evaluation of biomonitoring validity is a complex process and, apart from the accumulation level, requires other data, such as temporal trend consistency in accumulation capability. Moreover, the biomonitor should be in correspondence with instrumental monitoring data. Following the previous assumptions, the obtained elements concentration in leaves was compared to the bulk deposition data. From 2002 to 2006, the Pb concentrations in leaves of *A. hippocastanum* at the beginning and the end of vegetation seasons showed a decreasing trend at all sites (Figs. 3 and 4). Temporal decrease of the Pb concentrations in leaf tissue of both species, observed in Belgrade urban area, might be a consequence of a diminishing use of leaded gasoline over the period. This is in accordance with the data reported for other European countries (Dmuchowski & Bytnerowicz, 2009). Furthermore, as shown by a long-term study of Hovmand et al. (2009), though atmospheric Pb declined by a factor of 7 from 1980 to 2007, airborne Pb is still considered a major pathway to vegetation and topsoil.

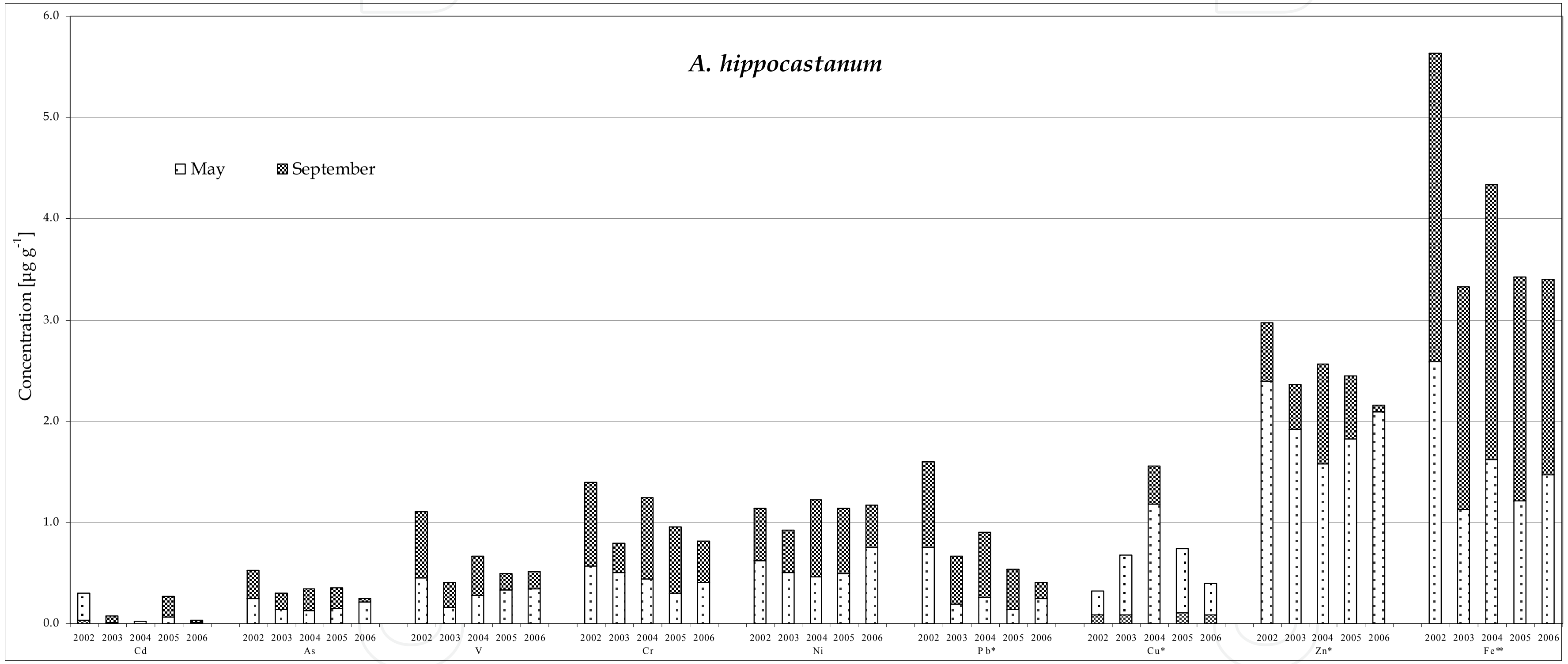

Fig. 3. Median concentrations (µg g^{-1}) of Cd, As, V, Cr, Ni, Pb*, Cu*, Zn*, and Fe** in the leaves of *A. hipposactanum*, sampled from the urban area of Belgrade in May and September from 2002 to 2006.
Note: Concentrations of Pb*, Cu* and Zn* are divided by 10 and Fe** by 100 to clearly present the results on the graph

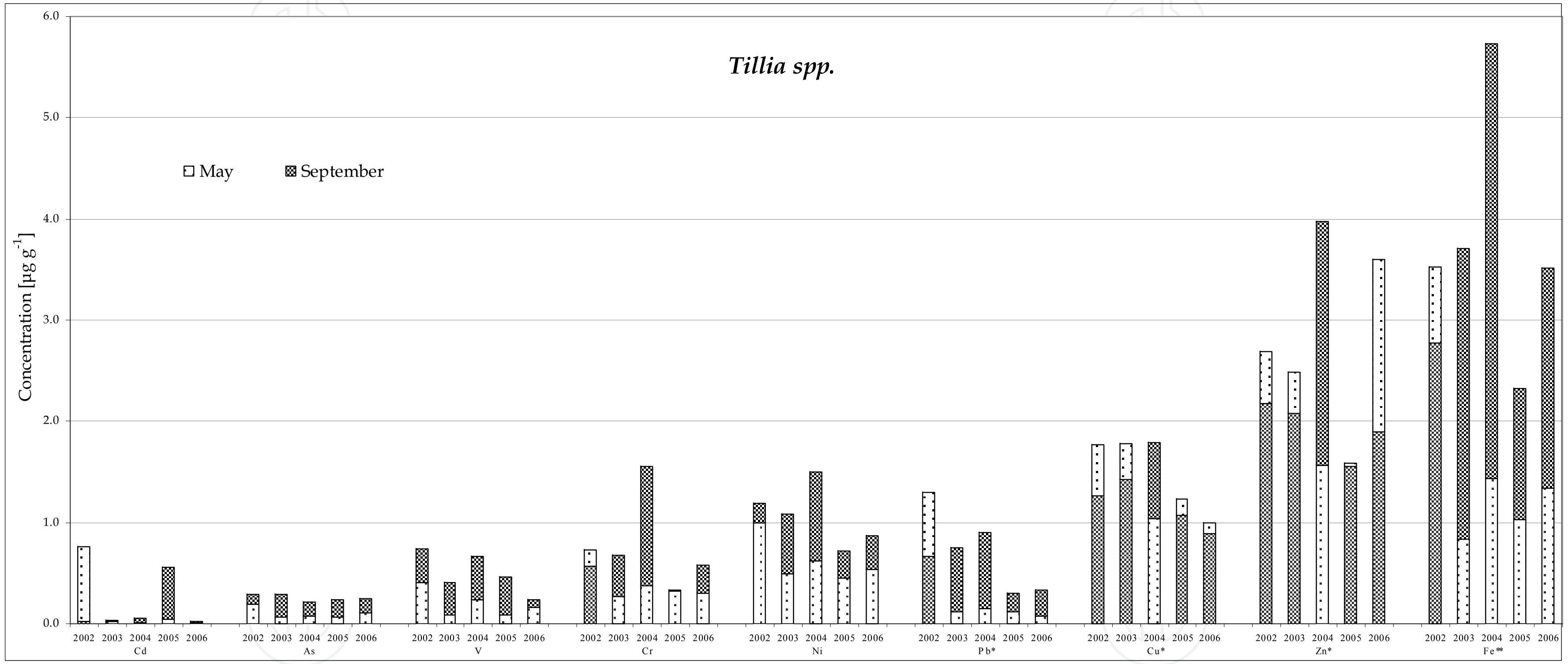

Fig. 4. Median concentrations (µg g^{-1}) of Cd, As, V, Cr, Ni, Pb*, Cu*, Zn*, and Fe** in the leaves of *Tilia spp.*, sampled from the urban area of Belgrade in May and September from 2002 to 2006.

Note: Concentrations of Pb*, Cu* and Zn* are divided by 10 and Fe** by 100 to clearly present the results on the graph

Uncertainty in element uptake pathways has generally been seen as a disadvantage for the use of the vascular plant leaves as biomonitors of trace element atmospheric pollution. However, Hovmand et al. (2009) investigated the origin of Pb in leaves and showed that less than 2 % of the Pb content of needles and twigs of Norway spruce comes from root uptake, i.e. approximately 98 % is of atmospheric origin. Tomašević et al. (2008) showed that in the Belgrade urban area there was a good correlation between the Pb leaf content of *A. hippocastanum* with a significantly increased level of atmospheric Pb in suspended particles during two successive years (1996 and 1997). Therefore, the Pb concentration in the leaves of *A. hippocastanum* reflected changes in atmospheric Pb pollution.

Among the sites, Cu concentrations were obtained at significantly higher level at the RB site, which was also shown by some instrumental monitoring techniques: BD, PMs (Rajšić et al., 2008) and active moss biomonitoring (Aničić et al., 2009a,b) pointing to an additional local source. Through the investigated years, the observed Cu concentration at this site showed a decreasing trend, a more regular one for *A. hippocastanum* (Fig. 5) than for *Tilia spp*. Presumably, a local Cu emitter (metal arts and crafts manufacturing) contributed to a much higher atmospheric Cu levels in 2002, 2003 and 2004 at the RB site, tending to decrease throughout the years until it closed down. Namely, at this site the Cu concentration was the highest in September 2002, and the accumulation level was about nine times higher in *A. hippocastanum* leaves (88 μg g^{-1}) than in the "reference plant" (10 μg g^{-1}, given by Markert, 1992). At the same time, Cu concentrations in bulk deposition were 3–4 time higher in the first than in the final year of the study (Fig. 5). Thus, the temporal trend for Cu accumulation in *A. hippocastanum* leaves follows the Cu contents in the BD for the RB site. The Cu content in *Tilia spp*. leaves did not show a clear seasonal nor temporal dependence.

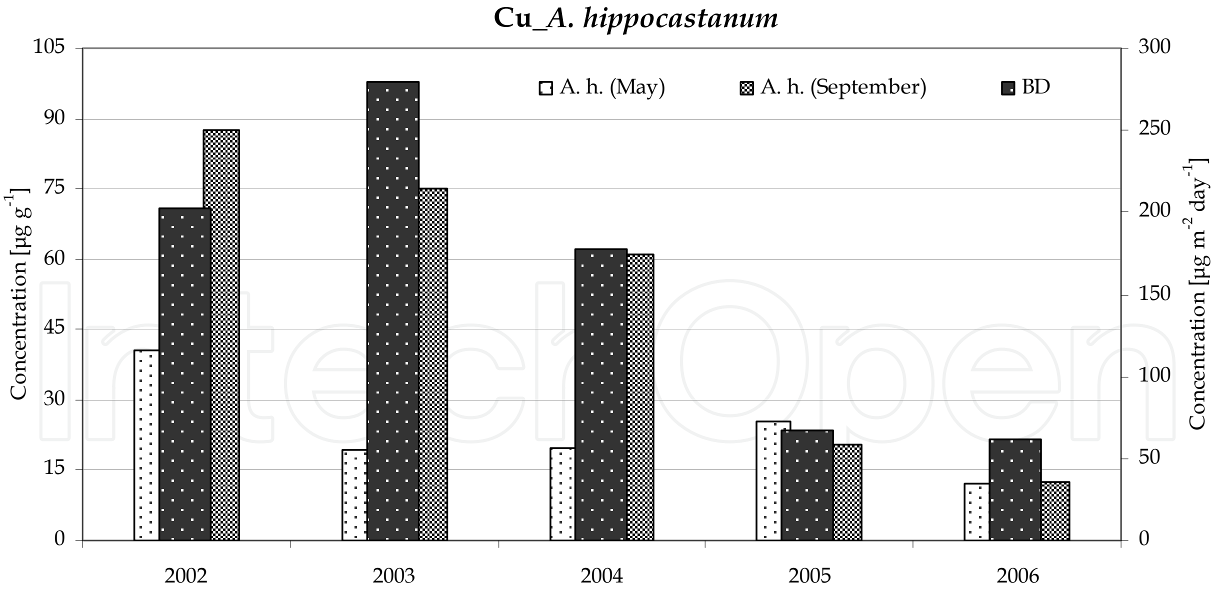

Fig. 5. The Cu concentrations in *A. hipposactanum* leaves in May and September (2002 – 2006), and bulk deposition (BD) at the RB site.

The soil Cu concentration at the RB site also decreased from 98 μg g^{-1} in 2002 (Tomašević et al., 2004) to 50 μg g^{-1} in 2008 (Marjanović et al., 2009). However, the presence of the elements in soil does not imply that they are available to plants, as plant-to-soil concentration ratio is far from a linear one (Bargagli, 1998). The results of Chojnacka et al. (2005) showed that there is a low correlation between the transfer factors of metals from polluted soils to plants. Moreover, the pH of the soil samples at the RB site was 8.8, and it is not likely that the element availability for the root uptake would be considerable. Consequently, it may be concluded that in our study the Cu content in leaves was mainly of atmospheric origin.

Temporal trends of V and As in the investigated years were slightly decreasing (Figs. 3 and 4), but no correlation with the bulk deposition was observed. However, there was no substantial variation in the accumulated content of Cr, Fe, Ni, Zn, and Cd thought the years, and no agreement in temporal trends with the bulk deposition measurements.

3.4 Radionuclides in tree leaves

The mean activities and standard deviations for the radionuclide contents in soils in Belgrade urban area are given in Table 3. The measured activities are within the range reported for the region and elsewhere (Djuric et al., 1992; RA Report, 2002; Todorovic et al., 2005) with no significant differences among the sites.

Site	Activity (Bq/kg)						
	^{226}Ra	^{232}Th	^{40}K	^{137}Cs	^{238}U	^{235}U	^{210}Pb
VF	39 ± 5	33 ± 5	402 ± 40	21 ± 2	15 ± 5	2.9 ± 0.3	/
HI	33 ± 3	34 ± 4	395 ± 35	31 ± 3	27 ± 9	1.6 ± 0.3	/
RB	26 ± 3	27 ± 4	378 ± 30	35 ± 2	16 ± 10	/	/
Mean ± SD	32 ± 4	32 ± 4	392 ± 35	29 ± 2	16 ± 8	1.7 ± 0.3	51 ± 10

Table 3. Radionuclides in soils in Belgrade urban area. Lead-210 in soils was estimated using two measuring episodes (4 samples).

Soil-to-leaves transfer factors (TF) were calculated as a ratio of an element's activity in leaves and its activity in soil (IAEA, 1994). The results for ^{40}K, ^{210}Pb and ^{137}Cs are presented in Table 4. The high TFs for ^{40}K show that its predominant route of accumulation in *Tilia spp.* and *A. hippocastanum* leaves is by root uptake, which could also be concluded for Pb, although, considering the scarcity of the Pb data in soils (Table 3), this result should be taken with caution.

The activities of radionuclides in leaves of *Tilia spp.* and *A. hippocastanum* (in Bq/kg) and aerosols (in Bq/m^3) in Belgrade parks, over the period 2002 – 2008 are presented in Table 5. The presented results include the mean, standard deviation and the coefficient of variation (in %) (Todorović et al., 2009).

Species	Transfer factor		
	^{40}K	^{210}Pb	^{137}Cs
Tilia spp.	1.29	0.90	0.09
A.hippocastanum	1.26	0.90	0.03
Tilia spp. & *A.hippocastanum*	1.27	0.90	0.06

Table 4. Transfer factors soil–to–leaves for *Tilia spp.* and *A. hippocastanum* in Belgrade.

The coefficient of variation, calculated as a ratio of standard deviation and the mean, shows dispersion of the mean activity for a detected radionuclide. The dispersion is the lowest for ^{40}K, the radionuclide generally uptaken from soil through roots. The seasonal variations, therefore, are not expected to be pronounced. The seasonal variations for ^{210}Pb are higher than for ^{7}Be, which can be explained by an additional input, resulting from coal burning and traffic, in winters. The variations in the ^{137}Cs activity, on the other hand, are very high. They are mainly influenced by low measurable quantities of this radionuclide, a very limited data set, and a large standard error. The concentrations of ^{137}Cs in Belgrade air before the Chernobyl nuclear plant accident were of an order 10^{-5} Bq/m^3, increased to 0.39 Bq/m^3 immediately after the accident, and decreased to $9.5\text{x}10^{-5}$ Bq/m^3 in 1988 (Popović et al., 2009a).

Activity variations in leaves of *Tilia spp.* and *A. hippocastanum* show a very similar behaviour (Table 5). In turn, these variations resemble those in air, thus confirming that ^{7}Be and ^{137}Cs are mainly deposited in leaves by foliar deposition. Since the ^{210}Pb variations are higher in plants than in air, Pb accumulation is influenced by root uptake and by foliar deposition.

Species	Activity in leaves (Bq/kg) and in aerosols (Bq/m^3)			
	^{40}K	^{210}Pb	^{137}Cs	^{7}Be
Tilia spp.	504 ± 196 (39)	46 ± 29 (63)	2.6 ± 2.2 (85)	131 ± 56 (43)
A. hippocastanum	494 ± 184 (37)	46 ± 34 (74)	1.0 ± 0.8 (80)	121 ± 60 (49)
Tilia spp. & *A. hippocast.*	499 ±191 (38)	46 ± 31 (67)	1.7 ± 1.6 (94)	126 ± 57 (45)
Aerosols	/	$(5.6 \pm 2.7)\text{x}10^{-4}$ (48)	$(2.5 \pm 1.8)\text{x}10^{-6}$ (94)	$(2.9 \pm 1.2)\text{x}10^{-3}$ (41)

Table 5. Activity of radionuclides in leaves of *Tilia spp.* and *A. hippocastanum* and aerosols in Belgrade, 2002 – 2008 (the mean and standard deviation, and the coefficient of variation (in %) in the parenthesis).

To estimate the concentrations of radionuclides in air due to resuspension, we applied the following equation (SRS, 2006):

$$C_{air/res}\ (\text{Bq/m}^3) = \text{RF}(\text{m}^{-1})\ \text{x}\ C_{soil}\ (\text{Bq/m}^2) \tag{3}$$

where $C_{air/res}$ is concentration of radionuclides in air due to resuspension (Bq/m^3), RF is the resuspension factor (estimated to 10^{-7} for urban and non-agricultural soils, and to 10^{-5} for agricultural soils), and C_{soil} is the surface concentrations. It was calculated using (SRS, 2006):

$$C_{soil}\ (\text{Bq/m}^2) = C_s\ \text{x}\ \rho_s\ \text{x}\ d_s \tag{4}$$

where d_s is the mean depth (15 cm), ρ_s is the density of soils (global average 1.6 g/cm^3), and C_s is the average annual concentration in soils (in Bq/kg). Thus, the calculated global average for $\rho_s\text{x}d_s$ is 240 kg/m^2. The results for the calculated concentrations of radionuclides in air caused by resuspension, together with the annual mean concentrations measured in air (C_{air}), are presented in Table 6.

The correlation coefficients for the content of radionuclides in aerosols and leaves of *Tilia spp.* and *A. hippocastanum* were calculated (Table 7). The lack of linear correlation between ^{7}Be in air and leaves could be explained mainly by leaching (rainfalls) effects and short half-life of ^{7}Be. There is a low correlation for ^{210}Pb, for both *Tilia spp.* and *A. hippocastanum*, but the uptake of lead by plants is due to many factors and is more complex than for ^{7}Be.

	Concentration (Bq/m^{3})		
	^{40}K	^{210}Pb	^{137}Cs
$C_{air/res}$	94.08x10^{-4}	12.24x10^{-4}	6.96x10^{-4}
C_{air}	(0.9-1.5)x10^{-4}	5.6x10^{-4}	2.5x10^{-5}

Table 6. Concentrations of radionuclides in air caused by resuspension from soil in Belgrade, 2002 – 2008. The activity of ^{40}K in air was estimated from the measurements with a new pump, with higher air flow capacity (average flow 30–50 m^{3}/h and volume up to 40,000 m^{3}).

Species	Correlation coefficient	
	^{7}Be	^{210}Pb
Tilia spp.	-0.266	0.302
A.hippocastanum	-0.241	0.347
Tilia spp. and *A. hippocastanum*	-0.139	0.311

Table 7. Correlations coefficients for the ^{7}Be and ^{210}Pb activities in leaves and in aerosols.

3.4.1 Seasonal variations of radionuclides in tree leaves

The seasonal variations of the radionuclides' activities in leaves of *Tilia spp.* and *A. hippocastanum* in Belgrade urban area, from 2002 – 2008, are presented in Fig. 6. The concentrations of ^{40}K and ^{137}Cs are the highest over the spring–summer periods, probably caused by a higher accumulation in young leaves. For ^{137}Cs, this conclusion should be taken with caution since there were only a few measurable episodes in the data set (up to 2005), and very low concentrations of this radionuclide were detected both in leaves and air. Concentrations of ^{210}Pb were the highest in autumn, and concentrations of ^{7}Be in summer, and both follow the pattern of seasonal variations of those radionuclides in air (Popovic et al., 2008b; Todorovic et al., 1999, 2000, 2005, 2007; Todorović et al., 2005; Sugihara et al., 2008). Thus, for these two radionuclides, leaves of higher plants could be used to monitor their concentrations and seasonal variations in air in urban areas.

4. Conclusion

Moss biomonitoring study in the urban area of Belgrade showed that most of the analysed trace elements (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb) were significantly accumulated in *Sphagnum girgensohnii* bags exposed in five consecutive 3-month periods. The highest relative accumulation factors were obtained for V, Cr, Cu, and Pb in both wet and dry moss bags. However, in general, higher element contents were noticed in the wet moss bags. Significant correlations were found between the element bulk deposition fluxes and elements concentration in dry (Cu, V, Zn, Fe, Pb, As, Cr) and wet (V, As, Fe, Al, Ni, Cu) moss bags. It may be concluded that active moss biomonitoring with *S. girgensohnii* could be used for screening monitoring of atmospheric trace element pollution in urban areas.

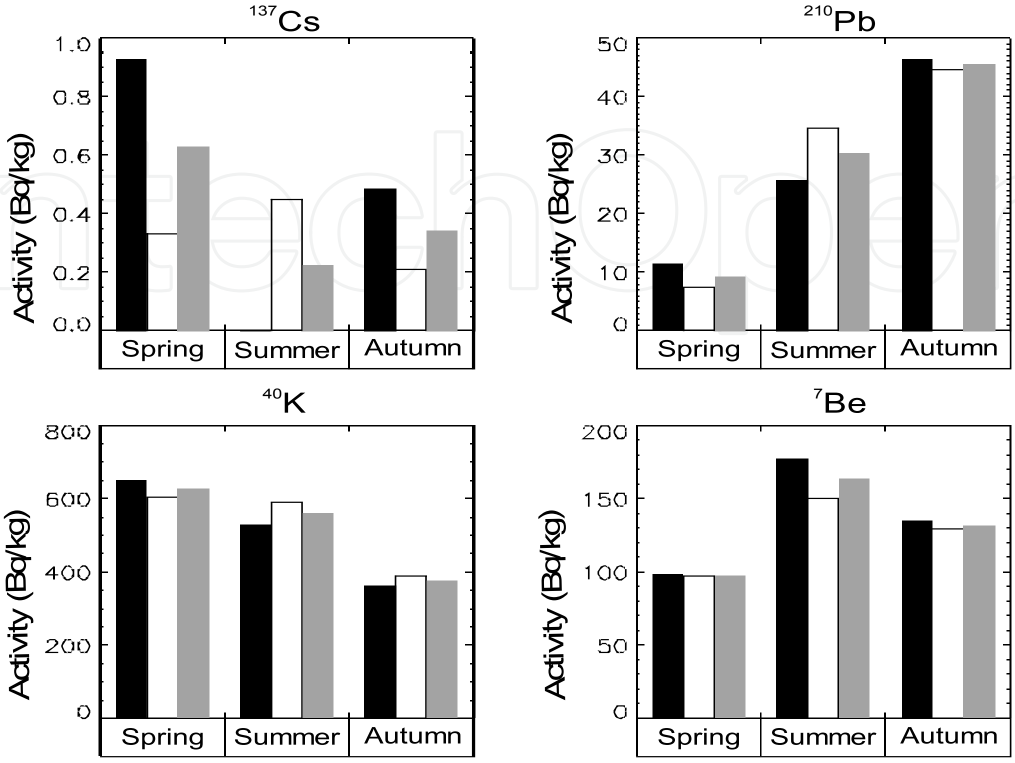

Fig. 6. Seasonal variations of radionuclides' activities in leaves of *Tilia spp.* and *A. hippocastanum* in Belgrade, 2002 – 2008 (the mean value for *Tilia spp.* is given in black, for *A. hippocastanum* in white, and the mean for *Tilia spp.* and *A. hippocastanum* in grey).

The mean activities of the detected radionuclides in *S. girgensohnii* were in the range of the values reported for other local naturally growing moss species in the region, with differences arising from the species, the method, local climate and soil characteristics. For the long lived ^{40}K there were no significant differences in its content in naturally growing mosses in a rural region of Southern Serbia and in the urban area of Belgrade. On the other hand, higher concentrations of ^{210}Pb in Belgrade indicate a contribution of anthropogenic air pollution sources. Significantly higher activities of ^{137}Cs, as well as the detectable amount of ^{7}Be, in mosses sampled in Southern Serbia are a consequence of a longer, unknown exposure period, while in the Belgrade study, the exposure period was limited to exactly one year. Hence, the observed differences mirror the differences in the accumulation period. Since naturally growing mosses are unlikely to be found in urban areas, the active moss monitoring proved to be a suitable alternative technique for monitoring contents of radionuclides in urban air. Furthermore, the exposure period in the moss bags technique could be reduced to one month, thus nominating the technique as an efficient means to monitor the level of radionuclides' contents in air, as well as to follow their seasonal variations.

Seasonal accumulation of the examined trace elements in leaves of *Aesculus hippocastanum* L. and *Tilia spp.* (*Tilia tomentosa* L. and *Tilia cordata* Mill.) was evident for V, Cr, Fe, Ni, As, and Pb, and it was more regular for *A. hippocastanum*. Considering the temporal trends of the trace elements content in leaves, some elements displayed a variation throughout the investigated years. The most obvious was the Pb variation, showing a decreasing trend from 2002 to 2006, in accordance with the lead trend in bulk atmospheric deposition measurements. Likewise, the temporal concentration trend for Cu in *A. hippocastanum* was decreasing, similarly to the Cu trends seen in the bulk atmospheric deposition at the site with the high atmospheric Cu loading. No agreement was observed between the accumulation trend of V and As in leaves and bulk deposition, although they exhibited decreasing temporal trends, as well as Cr, Fe, Ni, and Zn. The results implied that those elements' content in leaves could not reflect atmospheric deposition directly. Therefore, due to its higher accumulation capability, temporal trend consistency, and better agreement with the bulk deposition measurements, *A. hippocastanum* may be suggested as a more appropriate biomonitor of the trace elements atmospheric deposition than *Tilia spp*. The lead leaf content clearly reflected the atmospheric Pb contamination, and it may as well be assumed for Cu in highly polluted areas.

As for the examined radionuclides, the study showed that the predominant route of ^{40}K accumulation in *Tilia spp.* and *A. hippocastanum* leaves is by root uptake. The accumulation pathways for lead seem more complex, although, according to Hovmand et al. (2009), less than 2 % of Pb content comes from root uptake and 98 % is of atmospheric origin. The dispersions of the mean activities of the radionuclides in leaves were the lowest for ^{40}K, which is generally uptaken from soil by roots. Its seasonal variations, therefore, were not expected to be pronounced. The seasonal variations for ^{210}Pb were higher than for ^{7}Be. This could be explained by an additional ^{210}Pb input, e.g., coal burning and more traffic, in winter. The ^{137}Cs variations, on the other hand, were very high. They were influenced by low measurable quantities of ^{137}Cs, a limited data set, and a large standard error. Variations of ^{7}Be and ^{137}Cs in air and in leaves of *Tilia spp.* and *A. hippocastanum* showed similar behaviour, confirming that these radionuclides are mainly deposited on leaves by foliar deposition. Since the ^{210}Pb variations are higher in plants than in air, lead accumulation is influenced both by root uptake and by foliar deposition. The comparison of the radionuclides' content in aerosols and leaves of *Tilia spp.* and *A. hippocastanum* showed no linear correlation for ^{7}Be, which could be explained mainly by leaching effects and short half-life of ^{7}Be. There was a low correlation for ^{210}Pb, for both *Tilia spp.* and *A. hippocastanum*, but the uptake of lead by plants is influenced by many factors and is more complex than for beryllium-7.

The seasonal variations of the radionuclides' activities in leaves of *Tilia spp.* and *A. hippocastanum* in Belgrade urban area, from 2002 – 2008, showed that the concentrations of ^{40}K and ^{137}Cs were the highest over the spring–summer periods, probably caused by a higher accumulation of young leaves. For ^{137}Cs, this conclusion should be taken with caution as there were only a few measurable episodes in the data set (up to 2005), and the content of ^{137}Cs was generally very low in leaves and air. The concentrations of ^{210}Pb were the highest in autumn, those of ^{7}Be in summer. Both ^{210}Pb and ^{7}Be in leaves follow the pattern of their seasonal variations in air. Thus, leaves of *Tilia spp.* and *A. hippocastanum* could be used to monitor concentrations and seasonal variations of these radionuclides in air in urban areas.

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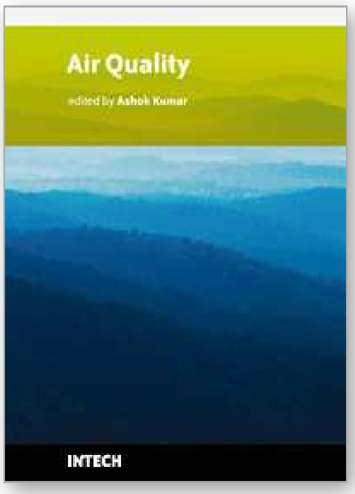

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Air pollution is about five decades or so old field and continues to be a global concern. Therefore, the governments around the world are involved in managing air quality in their countries for the welfare of their citizens. The management of air pollution involves understanding air pollution sources, monitoring of contaminants, modeling air quality, performing laboratory experiments, the use of satellite images for quantifying air quality levels, indoor air pollution, and elimination of contaminants through control. Research activities are being performed on every aspect of air pollution throughout the world, in order to respond to public concerns. The book is grouped in five different sections. Some topics are more detailed than others. The readers should be aware that multi-authored books have difficulty maintaining consistency. A reader will find, however, that each chapter is intellectually stimulating. Our goal was to provide current information and present a reasonable analysis of air quality data compiled by knowledgeable professionals in the field of air pollution.

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