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## Original article

# Assessment of vertical element distribution in street canyons using the moss *Sphagnum girgensohnii*: A case study in Belgrade and Moscow cities



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## ABSTRACT

*Sphagnum girgensohnii* moss bags were used to study the small-scale vertical distribution of some major and trace elements in different types of street canyons (regular, deep and avenue types) in Belgrade and Moscow urban area. The exposure time was 10 weeks during the summer of 2011. The exposure of moss bags was at three different levels to test differences in deposition patterns according to height. The differences between the street and off-street side in the vertical element distribution in Moscow were tested too. The concentration of 25 major and trace elements in moss was determined by instrumental neutron activation analysis. The results showed that the accumulation of elements in the exposed moss bags were higher in deep and regular street canyons in comparison to that of the avenue type, the latter even with a higher traffic flow. The element concentrations were the highest at the lowest heights compared to those of the upper floors. For most determined elements the concentrations were lower on the off-street avenue side compared to the on-street side for all heights of moss exposure. The results obtained indicate that *S. girgensohnii* is sensitive to small-scale variations of the total concentrations of elements.

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## 1. Introduction

One of the key problems of modern civilization is the increasing level of urbanisation. Urban areas with high traffic burden are susceptible to air contamination with some major and trace elements. Most of the elements are present in all aerosol fractions, including the high-risk breathable particulate matter ( $<PM_{2.5}$ ) (De Kok et al., 2006). Some elements could be used as a tracer of traffic air pollution (Pacyna and Pacyna, 2001).

Urban microenvironments such as street canyons, city tunnels, bus stations, parking garage, etc. are potential contamination hot-spots due to specific environmental conditions and heavy burden of

traffic emissions. A street canyon is a term frequently used for narrow streets flanked by buildings on both sides. Vardoulakis et al. (2003) reported a classification of street canyons according to the aspect ratio – the ratio of the height to the width ( $H/W$ ). A canyon is considered to be *regular* if it has an aspect ratio approximately equal to 1. An *avenue* canyon has an aspect ratio below 0.5 while a value of 2 is typical for a *deep* canyon. It is expected that a street canyon has no major openings on the walls.

In legislation of many countries, a permissible content of some elements in the air from the viewpoint of health risk is allowed. The quantification of major and trace element deposition implies technically complex and costly measurements, i.e. monitoring of suitable tracer element and further identification of source apportionment. In the last several decades, biomonitoring has been developed as a cost-effective method complementary to the instrumental monitoring of pollutants.

Biomonitoring, in general, involves measurements of living organisms' responses to changes in their environment (Bargagli, 1998; Markert et al., 2003). Bryophytes have proved to be

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suitable biomonitors for trace element air pollution based on their morphological and physiological characteristics (Brown and Bates, 1990, Harmens et al., 2012). However, in urban and industrial areas, where mosses are often scarce or even absent, active biomonitoring i.e., the “moss bag technique” as the most common type, has been developed for spatial and/or temporal assessment of contaminant deposition (Anićić et al., 2009a; Ares et al., 2012). The *Sphagnum* species are especially recommended as the most suitable moss for active biomonitoring of trace and other elements due to several features including a large surface area and a number of proton-binding sites on the surface (González and Pokrovsky, 2014).

Active moss biomonitoring research using *Sphagnum girgensohnii* moss bags was carried out in the street canyons of Belgrade (Serbia) and Moscow (Russia). The overall goal of this study was to compare the enrichment capacity of moss *S. girgensohnii* for 26 major and trace elements in specific urban microenvironments such as three different types of street canyons: *deep*, *regular* and *avenue*. The specific objectives were to test whether 1) there is a difference in the small-scale vertical distribution of the enriched elements and 2) the enriched elements could be banded according to their origin or its uptake by the moss. Additionally, in the Moscow case study, the difference between the on-street and off-street side in the vertical element distribution was tested. Finally, the element concentrations for both capitals were compared.

## 2. Materials and methods

### 2.1. Moss bag preparation

Moss *S. girgensohnii* Russow was collected at the end of May 2011 from a pristine area (vicinity of Dubna, Russia) chosen on the basis of results obtained previously (Anićić et al., 2009b, 2009c). In the laboratory, green upper parts of the sampled moss were separated and carefully cleaned from foreign matter. Concerning the study period (summer-autumn) characterized by high air temperatures and low relative air humidity, any devitalising treatment was not applied to the moss material. In addition, in the previous survey (Anićić et al., 2009c), a poor vitality of moss was evident after exposure, because of dry continental climate conditions in the study area. Notwithstanding, oven drying devitalising pre-treatment of moss is recommended for prior exposure to minimize the influence of possible moss growth on element uptake during the experimental period (Giordano, 2013), but the moss enrichment in elements could solely be related to passive uptake (Tretiach et al., 2007). Then, about 3 g of the moss was packed loosely in  $10 \times 10$  cm flat nylon net bags with 2-mm mesh size. Several moss bags were stored at room temperature in the laboratory conditions as a control sample for the determination of the initial pollutant concentrations. Sampling and preparation of moss bags were carried out wearing polyethylene gloves.

### 2.2. Experimental setup

The experiment was performed in the street canyons of Belgrade and Moscow (Fig. 1). In the downtown of Belgrade ( $\phi = 44^\circ 49' \text{ N}$ ,  $\lambda = 20^\circ 27' \text{ E}$ ,  $H_s = 117 \text{ m}$ ), the moss bag experiment was conducted in five rather symmetric street canyons: Kraljice Natalije (KN), Masarikova Street (MS), Dragoslava Jovanovića (DJ), Obilićev venac (OV), and Knez Mihailova (KM) defined as regular, medium or short ones according to the classification described in Vardoulakis et al. (2003) (Table 1). However, according to the overall aim of the study, special attention is paid on *deep* (DJ) and selected *regular* (MS) street canyons. The

traffic flow measured in the street canyons is presented in Table 1. In all street canyons of Belgrade, moss bags were hung at heights of about 4, 8 and 16 m.

Since in the Belgrade urban area there are no street canyons of the avenue type, the other part of this study was carried out in Moscow, Russia, where the largest avenue street was chosen in the central part of the city: Leninsky prospect (LP) ( $\phi = 55^\circ 40' \text{ N}$ ,  $\lambda = 37^\circ 31' \text{ E}$ ,  $H_s = 118 \text{ m}$ ). The traffic flow in the street part is given in Table 1. In Moscow, moss bags were hung at the street side (on-street) and the backyard side of the canyon (off-street), at heights of about 4, 15 and 28 m.

In both case studies, the first height was chosen in order to gain an insight into the pollution level in the pedestrian zone and also to prevent vandalism or removal. The other two heights were selected arbitrarily because, according to our knowledge, there is no standardized protocol prescribing selection of sites for the study of vertical distribution of trace elements in urban environment. Specifically, the chosen heights of the moss bags exposure in Belgrade and Moscow should represent air pollution bottom, middle and close to roof level of the street canyons. In all study streets, 5 moss bags per heights were hung at specially constructed T-holders and positioned at a distance of about 1–2 m from the wall of the buildings away from any porches, balconies, etc.

The moss bags were exposed for 10 weeks (selected on the basis of the previous study by Anićić et al., 2009c) in the Belgrade and Moscow street canyons during the summer-autumn of 2011. After the exposure period, the moss samples were homogenized and air-dried. Such prepared samples and control moss sample from Belgrade were packed in polypropylene bags, airtight sealed and sent to Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (Dubna) for further analysis.

### 2.3. Sample analysis

Instrumental neutron activation analysis (INAA) was performed at the pulsed fast reactor IBR-2, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. Approximately 0.3 g of well homogenized moss samples (5 subsamples per height per street canyon) were pelletized and taken for measurements of short- and long-lived isotopes. To determine the short-lived isotopes (Mg, Al, Cl, Ca, V, Mn) the samples were packed in polyethylene bags and irradiated for 3–5 min. To determine the long-lived isotopes (Na, K, Sc, Cr, Fe, Co, Ni, Sb, Zn, As, Rb, Sr, Cs, Ba, La, Sm, W, Th, U) the samples were packed in aluminium cups and irradiated for 3 days. Gamma-ray spectra were measured using a HP Ge detector after decay periods of 10 min following the short irradiation and after 3 and 20 days following the long irradiation, respectively.

To determine the initial element concentrations, five subsamples of the initial moss material were subjected to INAA. In addition, three subsamples of the moss from the control bags (handling and stored in the laboratory) were analysed. There were no significant difference between element content in the initial and the control moss which confirmed that there were no any contamination during the bag handling and storage process.

Quality control was provided by using standard reference materials (SRM) of the National Institute of Standard and Technology NIST-2709 San Joaquin Soil, NIST-1632c Coal (bituminous), International Atomic Energy Agency IAEA-433 Marine sediment, and European Reference Material ERM-CC690 Calcareous soil. The analytical results were: up to 5% for Al, As, Ba, Ca, Co, Cs, Fe, La, Mg, Mn, Na, Sb, Sm and Zn; up to 10% for Cl, K, Sc, Sr, U and V; and up to 20% for Cr, Ni, Rb and W. The content of Cu, Sn and Mo appeared to be below the limit of detection, so these elements were excluded from further analysis.

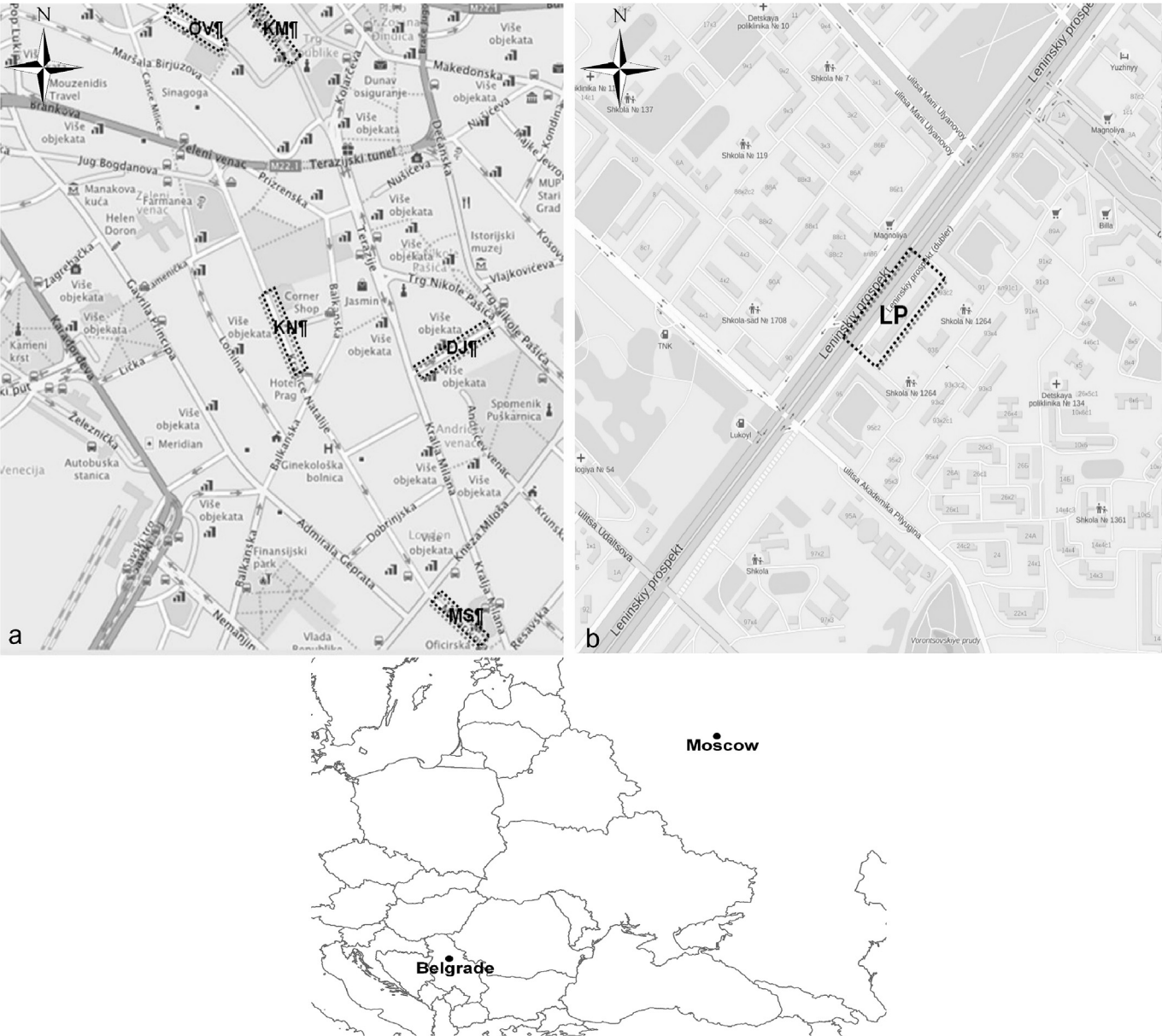


Fig. 1. Map of the studied sites in the Belgrade (a) and Moscow (b) urban areas.

Table 1  
Dimensions and types of the studied street canyons in the Belgrade and Moscow urban areas.

Country	Street name	Street dimensions [m]		H/W	Type	Traffic flow <sup>a</sup> [vehicles per hour]
		Height (H)	Width (W)			
Belgrade	1. St. Kraljice Natalije (KN)	27	20	1.3	regular	1254
	2. Masarikova St. (MS)	25	16	1.5	regular	502
	3. St. Dragoslava Jovanovića (DJ)	25	9	2.7	deep	212
	4. Obilićev venac (OV)	28	22	1.2	regular	332
	5. St. Kneza Mihaila (KM)	25	15	1.6	regular-deep	pedestrian
Moscow	6. Leninsky prospekt (LP)	32	100	0.3	avenue	2500–3000

<sup>a</sup> Traffic flow was estimated using a standard procedure (City Secretariat for Transport of Belgrade, personal communication, and for Moscow city: Guide on highways traffic capacity evaluation (1982)).

2.4. Data analysis

In order to assess the element enrichment of *S. girgensohnii*, relative accumulation factors (RAF) were calculated according to

the equation:  $RAF = (C_{exposed} - C_{initial}) / C_{initial}$ , where  $C_{exposed}$  is the average ( $n = 5$ ) moss content of each element after the exposure,  $C_{initial}$  is the element content before the exposure ( $n = 5$ ).

For the elements with RAF values higher than zero, cluster analysis (CA) was applied using Ward's method as a linkage rule and Euclidean distances as a distance measure. Since the variables had large differences in scaling, base-10 logarithm transformation of all element concentrations was performed prior to CA. Basic nonparametric statistics (Mann–Whitney test) were used to check the significance of differences between the initial and exposed moss element contents at  $p = 0.05$  level. Friedman ANOVA and post hoc test was performed to test for significant differences in the vertical distribution of elements with positive RAF values. The data were processed using StatSoft STATISTICA 8.0.

### 3. Results and discussion

#### 3.1. Belgrade case study

The concentrations of most elements were statistically higher in the exposed moss samples than in the initial ones ( $p < 0.05$ ), indicating that the street canyons where the moss bags were exposed were polluted by the elements in question (Table 2). According to the calculated RAFs, the most accumulated element in the moss was Sb followed by other elements in the descending order: Sm > Zn > V > Sc > Th > Al > Fe > La > U > Cr > Ca > As > Ba > Ni > Co > Sr > Mg > Br > W. In general, for the majority of elements (Al, As, Ba, Co, Fe, Sc, Sm, V and Zn) in the moss, RAF values were the highest for the first height of exposure.

Sodium, K, Cl, Rb, Cs, and Mn concentrations in the exposed moss bags were below the initial concentrations. Some authors also reported the loss of these elements from the exposed moss tissue due to its membrane interruptions and dehydration (Spagnuolo et al., 2011; Aničić et al., 2009b). Varela et al. (2015) reported that both the binding properties of elements and the structure of the moss cell wall define the moss element uptake. The leakage of physiologically active elements such as Na and K may be due to their displacement by other incoming ions with greater covalent binding indices or cell damage (Brown and Wells, 1990; Makholm and Mladenoff, 2005). However, the other elements with low covalent binding indices such as Ba, Al and V were enriched in the moss. The binding sites on the moss cell wall could be assigned to carboxyl, phosphodiester and phosphoryl groups, which have greater affinities for the elements with low covalent binding indices (Varela et al., 2015). In addition, Mn should be also involved with caution in moss biomonitoring surveys because increased Mn concentrations will only be observed in the moss exposed to high concentration of this metal (Boquete et al., 2011).

In all street canyons, statistically significant decrease from the first to the third height of moss bag exposure was observed using Friedman ANOVA in the vertical distribution of elements with positive RAF values ( $\chi^2(2) = 17.15385$ ,  $p = 0.00019$ ,  $n = 285$ ). The results of cluster analysis (CA) for the elements accumulated in the moss bags are given as a dendrogram with two main clusters at a height of 100 (Fig. 2). The first cluster (Sc, Th, Sm, U, La, W, Co, As, and Sb) represents a crust component in the atmospheric

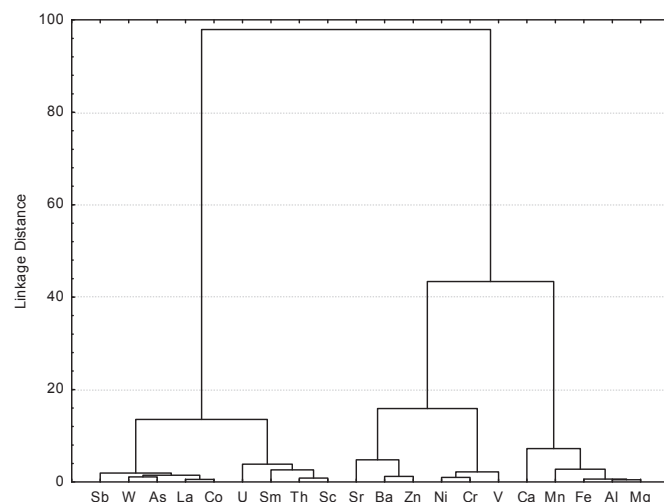


Fig. 2. Dendrogram resulting from the Ward's method of hierarchical cluster analysis of the trace elements in the moss bag samples from the Belgrade street canyons.

deposition. At a height of 15, this cluster contains two smaller ones: a group of rare earth elements (Sc, Th, Sm, and U) and those elements which are naturally enriched in the local soil (W, Co, As, Sb, and La) (Barandovski et al., 2012). At a height of 45, the second cluster (Sr, Ba, Zn, Ni, Cr, V, Ca, Mn, Fe, Al, and Mg) represents a mixture of soil and suspended road dust. The elements grouped in this cluster such as Sr, Ba, Zn, Ni, Cr, and V are reported as traffic-related (Pant and Harrison, 2013; Zechmeister et al., 2005) while the origin of some major elements (Ca, Mn, Fe, Al, and Mg) is attributed to soil resuspension. Air pollution in street canyons could be a combination of both regional and local sources. The first cluster probably represents long-range atmospheric deposition. The other main cluster is a micro-scale element distribution. For example, Lu et al. (2008) reported that urban dust consists predominantly of Fe-rich particles coexisting with anthropogenic heavy metals. The results of CA may represent the groups of elements with a similar uptake mechanism by moss rather than the elements of the same origin. This would explain in our case, why such an element as Sb, which directly originates from road traffic, appears in the same group with such lithogenic elements as La, Sm and Sc.

#### 3.2. Moscow case study

For the Moscow case study RAF values were calculated separately for on- and off-street sides of the avenue (Table 3a and 3b). For both on- and off-street sides, negative RAF values were

Table 2

Average ( $n = 15$ ) relative accumulation factors (RAF) of the elements in moss samples after 10 weeks of exposure in 5 street canyons in the Belgrade urban area.

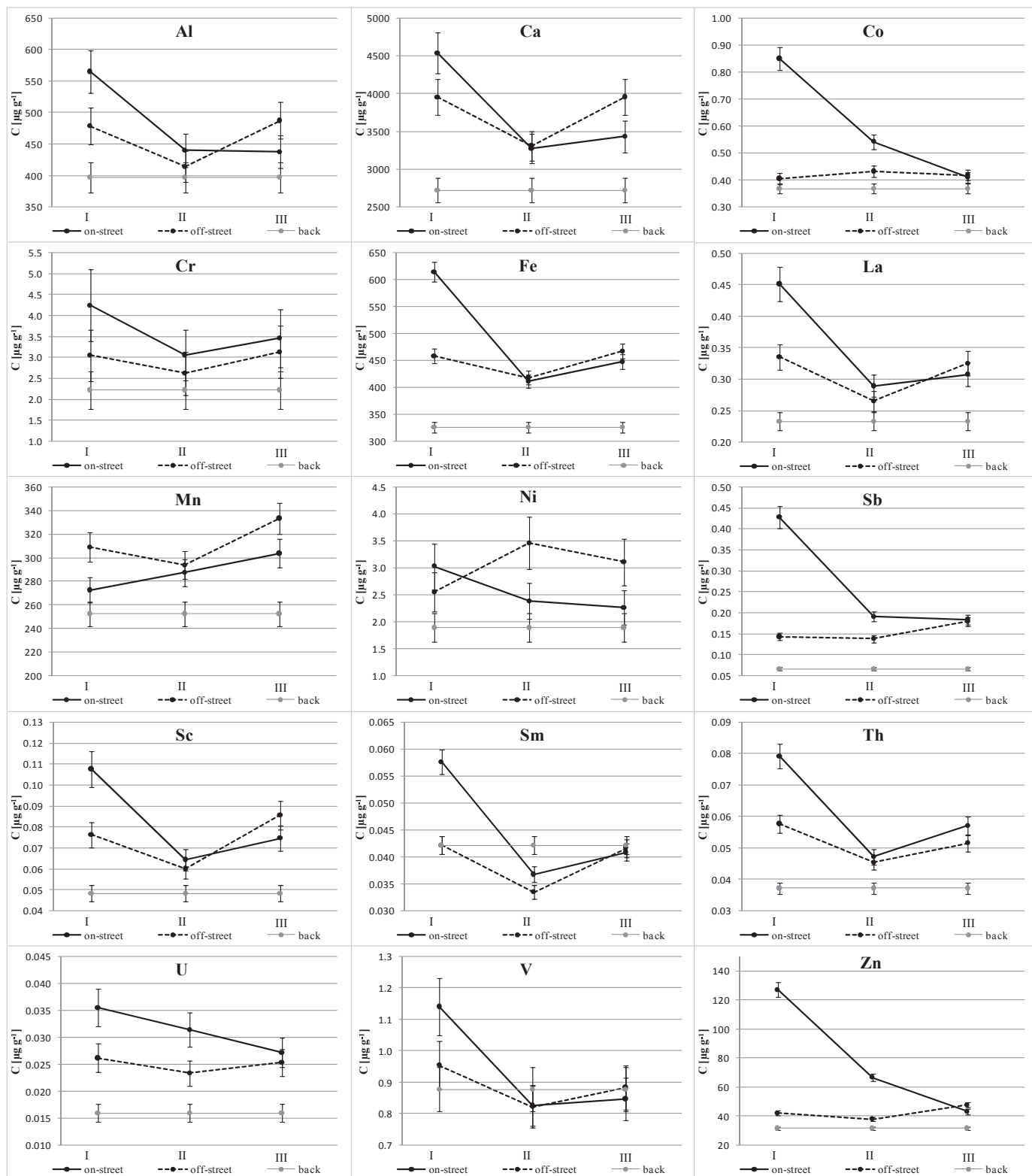
RAF	Element
$\leq 0$	Na, K, Cl, Rb, Cs, Mn,
0–1	Mg, Ni, Co, Sr, W
1–2	Al, Ca, Cr, Fe, As, Ba, La, U
2–10	Sc, V, Zn, Th
>10	Sm, Sb

Table 3

Average ( $n = 15$ ) relative accumulation factors (RAF) of the elements in moss samples after 10 weeks of exposure in the avenue street canyon: on-street (a) and off-street sides (b) in the Moscow urban area.

RAF	Element
<b>a)</b>	
$\leq 0$	Na, Mg, K, Cl, As, Rb, Ba, Cs
0–1	Al, Ca, V, Cr, Ni, Mn, Fe, Sr, La, Sm, W
1–2	Sc, Co, Th, U
2–6	Zn, Sb
<b>b)</b>	
$\leq 0$	Na, Mg, K, Cl, As, Rb, Ba, Cs
0–1	Sc, Al, Ca, V, Cr, Mn, Fe, Co, Zn, Sr, La, Sm, W, Th, U
1–2	Ni, Sb
2–6	~





**Fig. 3.** Vertical distribution of mean element (Al, Ca, Co, Cr, Fe, La, Mn, Ni, Sb, Sc, Sm, Th, U, V, and Zn) concentrations [ $\mu\text{g g}^{-1}$ ] with standard deviation bars in the moss bags exposed for 10 weeks in Moscow avenue (LP): on-street, off-street sides and the initial element concentrations (back); I – the first, II – the second, III – the third height of moss bags exposure above the ground.

obtained for Na, K, Cl, Rb, and Cs with some element (Mg, As and Ba) concentrations exhibiting the accumulation in moss in comparison to the initial ones. For accumulated elements in moss exposed on the on-street side, the highest RAFs were obtained for

Sb and Zn followed by  $\text{Co} > \text{Sc} > \text{U} > \text{Th} > \text{La} > \text{Cr} > \text{Fe} > \text{Sr} > \text{Ca} > \text{Ni} > \text{Al} > \text{Sm} > \text{W} > \text{V}$ . For the off-street side, the order of element RAFs was as follows:  $\text{Sb} > \text{Ni} > \text{Fe} > \text{Ca} > \text{Sr} > \text{Co} > \text{Th} > \text{Zn} > \text{La} > \text{Cr} > \text{Mn} > \text{Al} > \text{Sc} > \text{Sm} > \text{W} > \text{U} > \text{V}$ . The RAF values for the

on-street side were up to 6 while for the off-street side there were no elements with RAFs more than 2.

For most of the elements, the highest concentrations were obtained in the moss bags exposed at the first height (I), both on-street and off-street sides, except Ni which was the most accumulated element at the second height of the off-street side (Fig. 3). Noticeably lower RAF values were observed for the same elements at the other two exposition heights (II and III).

In general, for most accumulated elements on the off-street side the concentrations were lower in comparison with the on-street side for all heights of moss exposure (Fig. 4). Using the Mann–Whitney test statistically significantly higher element concentrations were revealed for Fe, Co, Zn, Sc, Sr, Sb, La, Sm, and U in the moss bags exposed at the first height (I) of the on-street side in comparison with the off-street side ( $p < 0.05$ ). At the second height (II), significantly higher concentrations were observed for Ni, Co, Sr ( $p < 0.05$ ), and at the third height (III) – only for Ba ( $p < 0.05$ ).

The results of cluster analysis (CA) for the elements accumulated in the moss bags in the Moscow avenue canyon are given in Fig. 4. For both the on- and off-street data there was a similar dendrogram structure with two main clusters divided into two smaller ones at a height of 70. The first main cluster in both cases represents a crustal component with some anthropogenically related elements (Sc, La, Sm, Th, U, W, Ni, Cr, Sb, Co, and V). The second cluster (Sr, Ba, Zn, Ca, Mn, Fe, and Al) in both cases consists of soil/road-dust resuspended elements.

### 3.3. Vertical element distribution in deep, regular and avenue street canyons

To compare the vertical element distribution in different type of street canyons, *deep* (DJ) and *regular* (MS) from Belgrade study area were selected. The element accumulation in the moss bags exposed in the Moscow avenue canyon, for both street and off-street sides, followed a similar pattern of relative element accumulation like in the Belgrade case study (Table 2 and 3). It should be noted that in the avenue canyon the number of vehicles per hour is more than twice higher than in *deep* and *regular* street canyons. However, for the majority of elements in the avenue case, RAF values (up to 6), were lower than those obtained for *deep* and *regular* street canyons (up to 13).

In addition to Na, K, Cl, Rb, Cs and Mn the concentrations of which in the Belgrade study were below the initial ones, also the

RAFs of Mg and As in the moss bags exposed in Moscow were very close to zero. A higher level of As in moss exposed in Belgrade could be explained by the regional geological background. There are anomalously high As concentrations in the soil of the Balkan region including Serbia (Barandovski et al., 2012).

The comparison of vertical profiles of the selected elements (Al, As, Ba, Co, Cr, Fe, Ni, Sb, Sc, Sm, V, and Zn) in the moss bags in *deep*, *regular* and *avenue* street canyons is presented in Fig. 5. These elements are usually considered as anthropogenically related. For all types of street canyons, the highest element contents were observed at street level, i.e. at the first studied height (4 m). This is confirmed by other authors who also found that moss bags exposed at heights of about 4 m were more efficient in retaining contaminants related to traffic pollution. Adamo et al. (2011) reported the highest element (Al, As, Ba, Co, Fe, Pb, Ti, V and Zn) enrichment in the *Hypnum cupressiforme* bags exposed in the Naples urban area at 4 m in comparison with those exposed at 12 and 20 m. In the same study area, no differences were obtained in the vertical distribution of Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn in *H. cupressiforme* moss bags exposed at 3, 6 and 9 m in the street canyon. In addition, in the study of Ares et al. (2014), *Sphagnum denticulatum* moss bags were exposed at 8 different heights (0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 m) at industrial, urban and rural areas. Although variable results were observed in this study, the most replicable results were obtained for Cd, Cu, Hg, Pb and Zn determined in the moss bags exposed at 2.5 and 4 m. Taking into account practical considerations (e.g. to avoid vandalism) an exposure height of 4 m is recommended for moss bag exposure (Vuković et al., 2013; Ares et al., 2014).

Variation in the vertical gradient of moss element concentrations in the urban street canyons presumably depends on the street canyon geometry (e.g. height/width and length/height ratio), prevailing winds and local air turbulence (De Nicola et al., 2009; Oke, 1988; Vardoulakis et al., 2003). When the average wind speed is below  $1.5 \text{ m s}^{-1}$ , the main wind vortex within deep and regular street canyons tends to disappear and the air stagnates in the street (De Paul and Sheih, 1986) increasing the level of pollutants. It was the case in the Belgrade studied street canyons, which is described in detail in Vuković et al. (2013), so the moss element concentrations were elevated in comparison with the Moscow avenue canyon. In avenues, the main wind vortex is elongated while the wind direction at a street level is opposite to the wind direction at a roof-top level, i.e. from the downwind to the upwind side of buildings. It is generally expected that residence times of non-

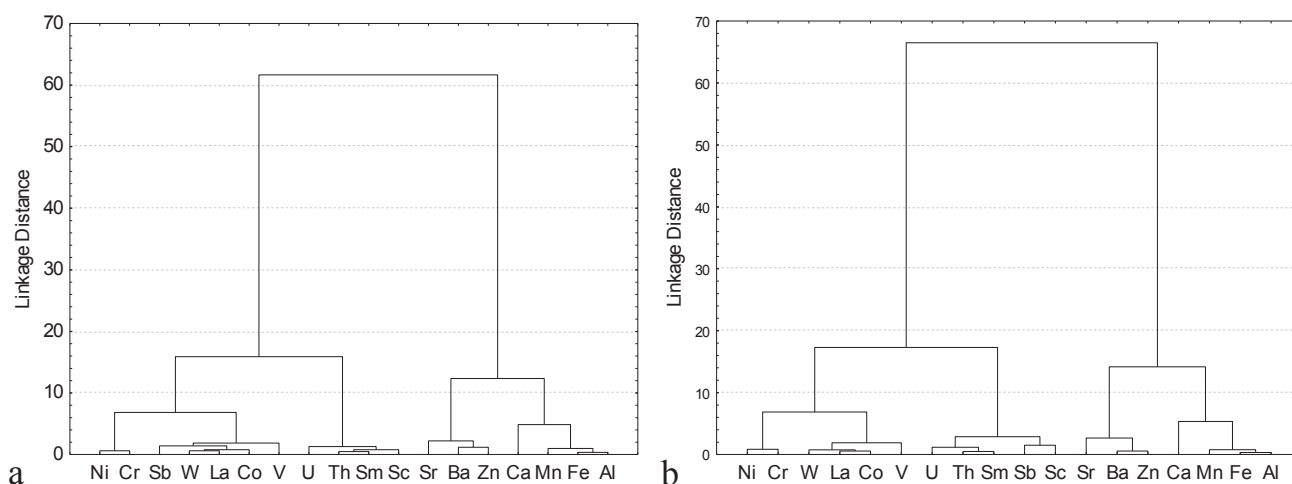
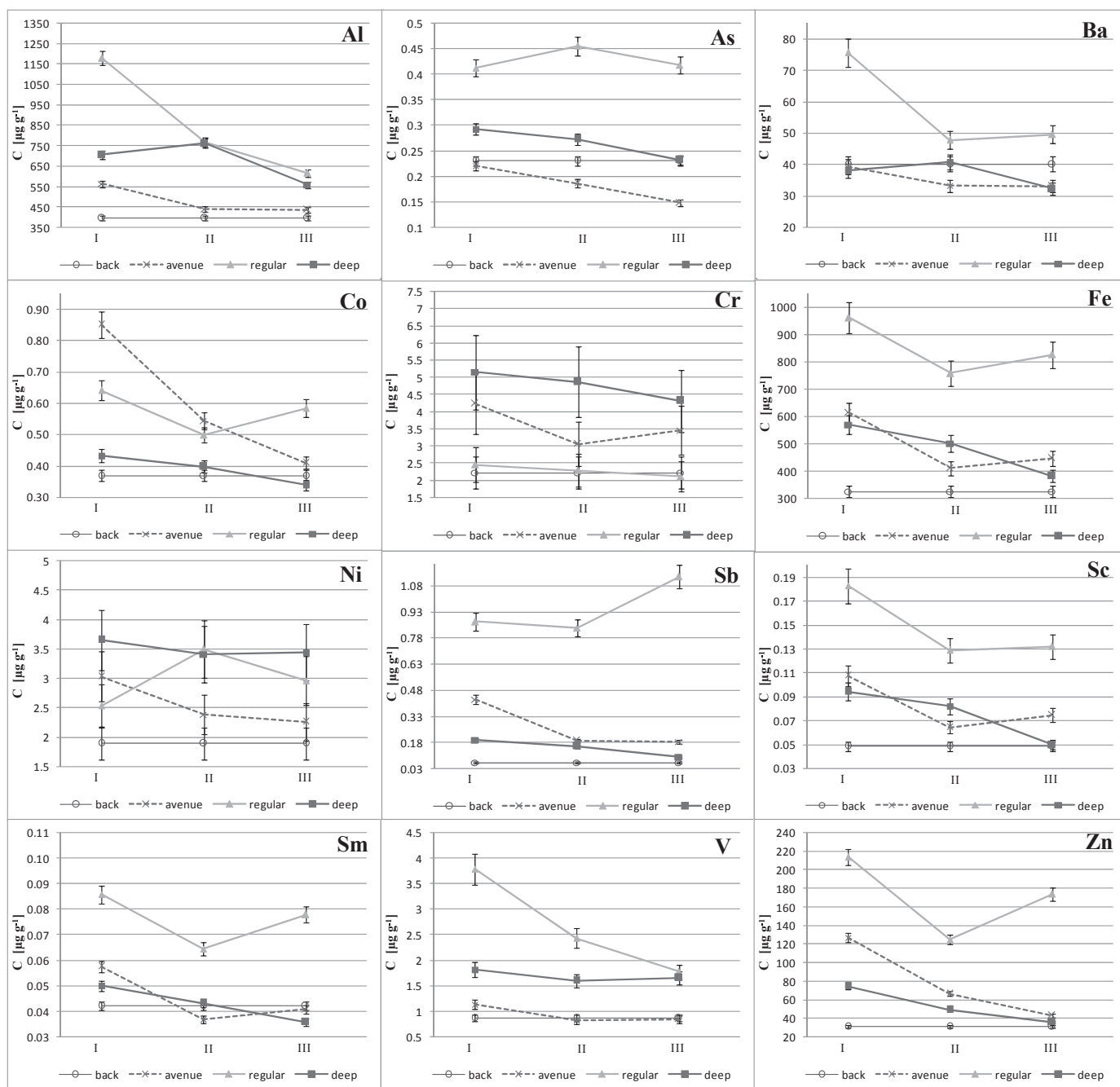


Fig. 4. Dendrogram resulting from the Ward's method of hierarchical cluster analysis of the trace elements in the moss bag samples exposed at the on-street (a) and off-street (b) sides in the Moscow avenue canyon.



**Fig. 5.** Vertical profiles of mean element (Al, As, Ba, Co, Cr, Fe, Ni, Sb, Sc, Sm, V and Zn) concentrations [ $\mu\text{g g}^{-1}$ ] with standard deviation bars in the moss bags exposed for 10 weeks in deep (DJ), regular (MS) and avenue (LP) street canyons and the initial element concentrations in the unexposed moss (back); I—the first, II—the second, III—the third height of moss bag exposure above the ground.

reactive pollutants are smaller in avenue low-rise canyons compared to deep canyons (Murena and Ricciardi, 2005). It could be concluded that with increasing moss exposure height in the avenue street canyons, the ambient concentrations for the majority of the elements become lower due to a specific wind flow regime (Oke, 1988).

#### 4. Conclusions

Active moss biomonitoring using *S. girgensohnii* species was applied for the assessment of major and trace element distribution in different types of street canyons—deep, regular and avenue. After

the exposure time a significant enrichment of most determined elements was found in all study street canyons. The highest concentrations were found for Sb, Zn or Sc while the lowest values were observed for Al, Cr, Ni, Sr and W. Using cluster analysis groups of the elements possibly originated from natural (e.g. Al, Ca and Fe) and traffic pollution sources (e.g. Sb, Zn, Ni and Ba) were revealed. However, the results of cluster analysis may represent the groups of elements with both a similar uptake mechanism by moss and the same origin.

In all types of the study street canyons, the highest element contents were observed at the first height (4 m), i.e. in the pedestrian breathing zone. In the avenue, the moss element enrichment is

considerably lower for most determined elements despite higher traffic intensity in this street. Thus, it could be assumed that the type of canyons, i.e. geometry, plays a major role in the element concentration in the air. When comparing on- and off-street sides of the avenue the latter demonstrated lower contents for most elements.

The results demonstrate that active monitoring using *S. girgensohnii* could be an effective method to study element small-scale spatial patterns in complex topography of urban areas.

### Conflict of interest

The authors declare that there are no conflicts of interest.

### Acknowledgement

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