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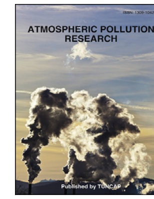

Assessment of vertical element distribution in street canyons using the moss *Sphagnum girgensohnii:* A case study in Belgrade and Moscow cities

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A B S T R A C T

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.

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 hotspots 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 (Aničić 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 (Aničić 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 (Aničić 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 × 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 ($\varphi = 44°49'$ N, $\lambda = 20°27'$ E, $H_s = 117$ 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) ($\varphi = 55°40'$ N, $\lambda = 37°31'$ E, Hs = 118 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 Aničić 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 errors 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.