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# PRELIMINARY DATA OF MOSS-BAGS TECHNIQUE IN AN URBAN AREA (PLOVDIV, BULGARIA)

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**Abstract**

Moss-bags with *Sphagnum girgensohnii* were used for indicating the status of air pollution at four sites in the town of Plovdiv (Bulgaria). A novel hanging system for the moss collectors was applied. The levels of 22 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, P, Pb, S, Sr, U, V, Zn) in the exposed and unexposed mosses for three periods were determined by FAAS and ICP-MS. Time-depending and site-depending changes of elements were assessed.

**Key words:** urban atmosphere, active biomonitoring, moss-bags, *Sphagnum girgensohnii*

**Introduction.** Some moss species were successfully applied for more than 30 years for assessing the atmospheric depositions of heavy metals and toxic elements in background and polluted areas. The mosses naturally occur in many terrestrial ecosystems, but the anthropogenic factors can be responsible for the so-called "moss desert" in urban areas. In such cases, the passive biomonitoring is not useful and the active biomonitoring as "bags technique" comes to replace it [1].

This technique has a lot of advantages: well-defined exposure time, known original concentration of elements in the biomonitor, flexibility both in site selection and number of stations that can be chosen, uniformity of entrapment surface. The major limitations of the method are in the unknown collection efficiency for different contaminants in different biomonitors and, therefore, the impossibility to standardize the exposure time for the exact species in bags and/or for urban, industrial or other source of pollution.

This study is a very small part of a large programme for passive and active biomonitoring with tree leaves, tree-rings, herbaceous species, mosses and lichenized fungi applied for a wide evaluation of the urban conditions in various towns within the Balkan Peninsula. The suggested work is the first application of the moss-bags technique in the town of Plovdiv.

**Materials and methods.** ***Study area and sampling.*** *Sphagnum girgensohnii* Russ. (nomenclature followed [2]), grown in a background mountain area (42°37′ N, 23°19′ E, altitude 1710 m in Vitosha Mountain), was used as a suitable active biomonitor of air pollution. The town of Plovdiv (42°09′ N, 24°45′ E), one of the most populated cities in Bulgaria (over 365 000 inhabitants on 102 $km^2$), was selected as a study area. The unwashed material (3 g) in nylon mesh (10 × 10 cm) was exposed at four important sites in the town of Plovdiv (north, east, west and central part) from May to October 2010 (Fig. 1). A novel hanging system at the same height from the ground was used (Fig. 2). At the beginning and every week each moss-bag was carefully damped with drops of distilled water. The mosses exposed for one, three and five months were collected by the end of each period respectively and stored in clean, labelled polyethylene bags until chemical analysis.

***Analytical methods.*** About 1 g ground plant material was treated with 5 ml 65% $HNO_3$ (Merck) for 24 h at room temperature. The wet-ashed procedure was assisted by a Microwave Digestion System CEM MDS 81D. Samples were treated for 5 min at maximum power (600 W) in closed vessels. After cooling, the vessels were opened and 2 ml $HNO_3$ and 3 ml 30% $H_2O_2$ were added and were left to react for 1 h. The vessels were closed and treated by the Microwave Digestion System for 10 min again at 600 W for full digestion of the organic matter. The filtrate was diluted with double distilled water up to 50 ml. All samples, blanks and standards were spiked with internal standards – Ge 50 ppb and Rh 5 ppb final concentration in the solutions. Calibration standards Multy VI (MERCK) were freshly prepared from 1 to 1000 ppb in 0.05 volume% HNO3 (p.a.). Monostandard of Hg 100 ppt was also used in the calibration. Signals of suitable isotopes for the tested elements have been measured twice in both modes – without and with helium gas collision cell. The concentrations of 22 micro- and macroelements were analyzed by FAAS (Zn, Fe, K, Mg, Mn, Na, Cu, Ca) using Atomic Absorption Spectrometer PERKIN-ELMER 4000 and ICP-MS (Al, S, P, Cr, V, Co, Ni, As, Sr, Mo, Cd, Hg, Pb, U) with instrument Agilent 7700 (2009).

***Statistical analysis.*** To determine the significant differences occurring between assessed element content in moss bags in four sites and three periods, one-way ANOVA was applied. Data analyses using STATISTICA 7 for Windows (StatSoft CR) were conducted.

**Results and discussion.** The element content in transplant material of moss biomonitor before exposure could be compared (Fig. 3). The elements K (up to 7 times), P and Mo decreased their values in comparison with the unexposed *Sphagnum girgensohnii*. No significant changes were proved for the rest of the analyzed elements. Loss of K in *Sphagnum girgensohnii* after exposure has also

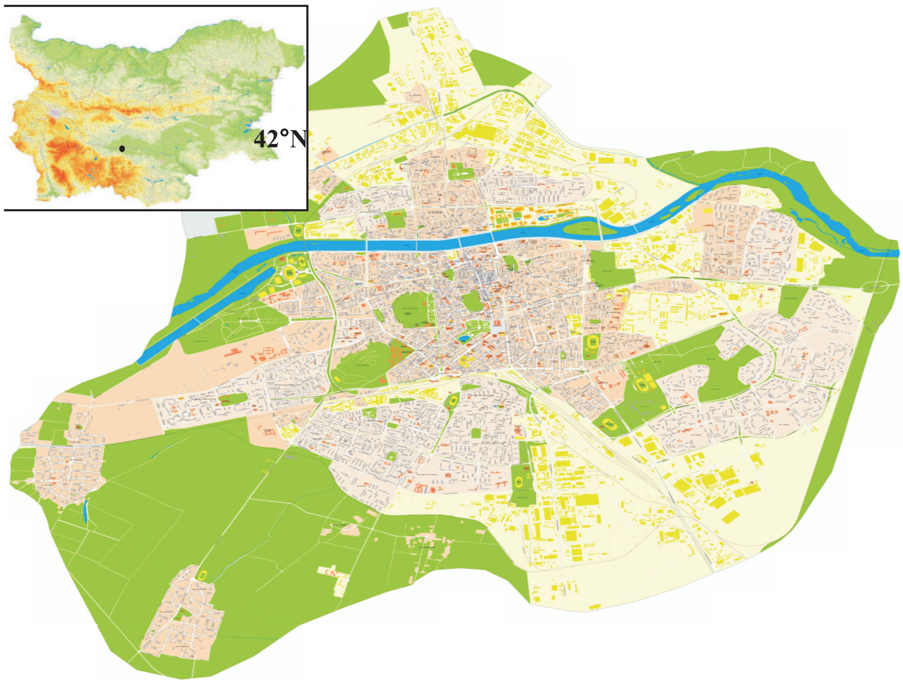


Fig. 1. Town of Plovdiv: moss-bags sites

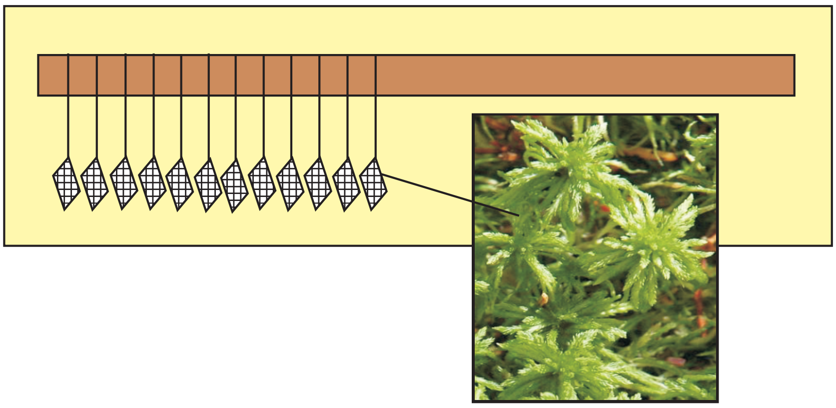

Fig. 2. Hanging system of applied biomonitor

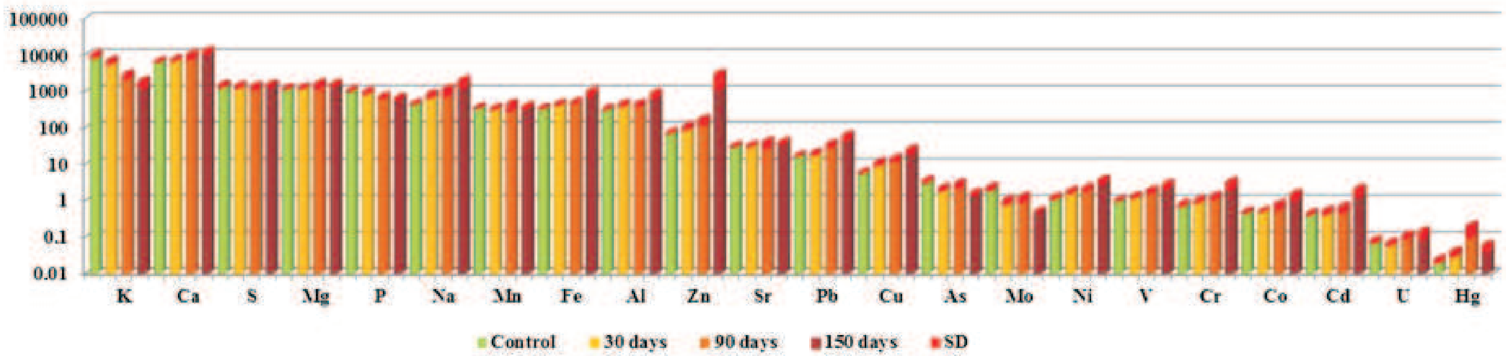


Fig. 3. Time-depending differences in the element content of moss-bags (mg kg$^{-1}$)

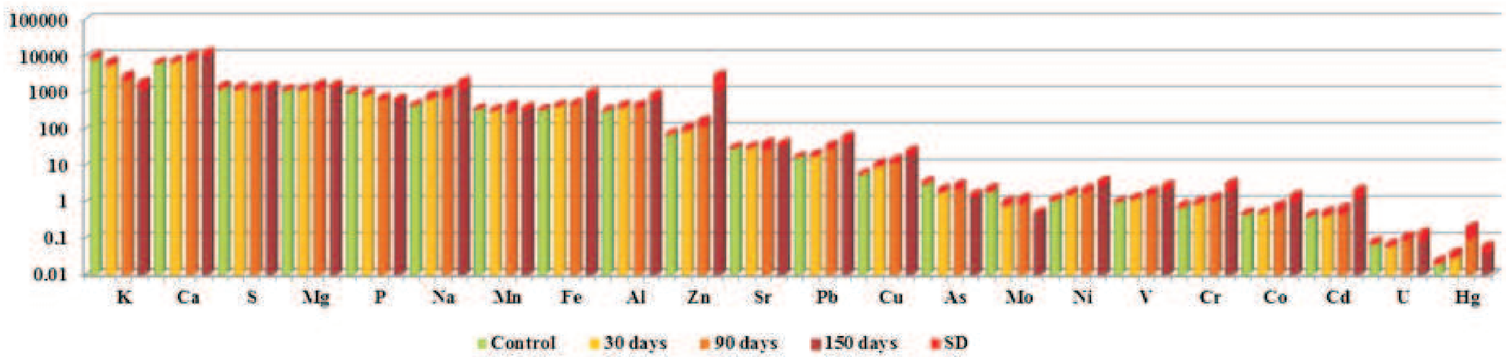


Fig. 4. Site-depending differences in the element content of moss-bags (mg kg$^{-1}$)

been observed in other studies in Romania [3] and Sofia (Bulgaria) [4]. Loss of K in *Sphagnum capillifolium* bags in Naples (Italy) is mentioned in [5].

For the periods of 30, 90 and 150 days, the elements Na, Al, Ca, V, Cr, Fe, Co, Ni, Cu, Sr, Cd, Pb, and especially Zn increased significantly their concentrations in moss-bags. The accumulation found was with highest significance for Zn, Cd, Pb, Cr, Cu and Na, due to heavy motor vehicle traffic, power plants and non-ferrous metallurgy located at 5 km (SE) from the town. No significant changes were proved for the rest elements.

The elements As, Mo and U had insignificantly higher content in the unexposed *Sphagnum girgensohnii* in comparison with exposed samples. The possible reason was the higher level of these elements in the background area for the material in Vitosha Mountain. An interesting result for this group (As, Mo, U) was the dynamics during the tested periods: insignificant decrease of the concentrations between control and exposed moss after 30 days, then increase to day 90, and new insignificant decease till day 150. As these elements are connected with burning processes of the fuels, which during the summer were not so heavy, a possible reason were the emissions of the non-ferrous metallurgy located nearby and the predominant wind from south to north.

The relative accumulation factors (RAF) calculated as mean content of each element after 150 days of exposure in all locations divided by the content of each element before exposure were highest for Cr (6), followed by Al, Co, Fe, Na, Ni, V and Zn (3–4).

48 positive and 16 negative correlations were proved for the analyzed elements. The strongest positive one was found for Fe, V, Cr, Co, Cu, Cd, Pb, Zn and Ni. These elements were the priority pollutants in the town of Plovdiv also selected by the parallel passive biomonitoring. The negative correlations were between K and Pb, Cu, Ni and Fe, and the group of As, Mo, Hg with the group of Mg, Ca, Mn, and Sr.

The same moss species (*Sphagnum girgensohnii*) in bags was tested in the town of Belgrade, Serbia in 2005/2006 [6]. Our results for As, Mn and Cd were higher, 3–2 times respectively; similar Pb and Zn content, and lower concentrations of Al, V, Cr, Fe, Ni and Cu (5 to 8 times).

The measured As in bags with the same species was higher (2.5 times) compared to the published values [4] for the city of Sofia. The elements Al, V and Zn (3 times) were lower in the atmosphere of Plovdiv assessed by moss-bags technique.

The site-depending differences are presented in Fig. 4. The mean content of each element proved insignificant differences for K, S, Mg P, Mn and Sr in bags exposed in north, east, central and west sites.

A tendency to enlarge the number of the maximal values of the chemical elements (S, Fe, Al, Ni, V, Cr, Co) by approaching the central part, along one of the major traffic arteries, was found. The east zone was characterized with maximum values of Zn, Pb, As, Cd, Cu, U and Hg. None of the analyzed elements had maximum value in the west site. The applied cluster analysis proved close groups of north and west sites, connected then with the central zone and quite separated east site.

**Conclusions.** First attempt was presented to describe and assess the atmospheric pollution levels in the town of Plovdiv using moss-bags for three periods. This study confirms moss *Sphagnum girgensohnii* as efficient element accumulator in bags exposed in an urban area. The differences between the changes of concentrations in the biomonitor in the four investigated locations could not be explained by some evident pollution patterns. Further studies in other periods/seasons of moss-bags exposure are needed to confirm the achieved results. This preliminary study is also a base for comparative analysis with the atmospheric assessment in urban areas.

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