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Monitoring of trace element atmospheric deposition using dry and wet moss bags: Accumulation capacity versus exposure time

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ABSTRACT

To clarify the peculiarities of trace element accumulation in moss bags technique (active biomonitoring), samples of the moss *Sphagnum girgensohnii* Rusow were exposed in bags with and without irrigation for 15 days up to 5 months consequently in the semi-urban area of Belgrade (Serbia) starting from July 2007. The accumulation capacity for 49 elements determined by ICP-MS in wet and dry moss bags was compared. The concentration of some elements, *i.e.* Al, V, Cr, Fe, Zn, As, Se, Sr, Pb, and Sm increased continuously with exposure time in both dry and wet moss bags, whereas concentration of Na, Cl, K, Mn, Rb, Cs, and Ta decreased. Irrigation of moss resulted in a higher accumulation capacity for most of the elements, especially for Cr, Zn, As, Se, Br, and Sr. Principal component analysis was performed on the datasets of element concentrations in wet and dry moss bags for source identification. Results of the factor analysis were similar but not identical in the two cases due to possible differences in element accumulation mechanisms.

1. Introduction

Biomonitoring is a rapid and economical method that has commonly been used for assessing environmental quality and potentially detrimental effects of pollutants to the biosphere [1,2]. Various effective bioindicators have been used so far for assessment of the state of natural ecosystems. These include mosses and lichens, which are commonly regarded as the best bioindicators of air quality as they can accumulate elements to a far greater level than is necessary for their physiological needs. Moreover, mosses can accumulate and concentrate toxic substances that may be present even in low concentrations in the local environment.

Uptake and retention of elements by moss is aided by: (i) numerous small leaves and intricate surfaces (large area/volume ratio); (ii) high permeability of tissue to water and elements; (iii) high water retention capacity; (iv) high cation exchange capacity, due to binding sites on the cell wall [3,4]. Generally, accumulation of trace elements depends on their supply in air, their solubility in water, water availability and humid condition [5,6].

The use of native mosses as biomonitors is a convenient way of determining levels of trace elements atmospheric deposition [7–10]. However, where samples of epiphytic mosses have been difficult to find at locations of interest, such as in urban and industrial areas, transplanted moss has been employed as an option. The "moss bags" technique [11,12] is one of the active biomonitoring methods, where a suitable moss species is sampled from an area with negligible influence from air pollution, properly cleaned from foreign materials, packed into nylon mesh bags, and then exposed at specific locations for defined periods of time to trap deposited elements. *Sphagnum* moss species are most suited for the moss bag method due to their very high element retention properties [13]. Mäkinen [14] found that bags filled with peat and cotton wool will have retention capacities of only 43% and 35% respectively in the comparison to the capacity of a typical *S. moss* bag.

Particulate matter is a predominate form of trace elements emissions in urban areas and uptake capacity of mosses mainly depends on passive physico-chemical entrapment and adsorption of elements on cell walls. Total element contents of mosses may be considered as the result of a balance between an input from wet and dry deposition, and output determined by: (i) washing of particulate materials by rain; (ii) leaching of some ions due to precipitation (especially acid rain); (iii) cation displacement, depending on their relative affinities for binding sites and concentrations; (iv) cellular damage due to environmental stress [3].

The exposure period is especially critical in moss biomonitoring surveys [4]. If exposure time is too long, saturation of exchange sites

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on the moss membrane may occur, and preferential displacement or exchange of elements as well. Also, heavy metals and other elements may "occupy" the exchange sites on moss membrane cells, so that they are effectively immobilized [15]. Little and Martin [12] and Ratcliffe [16] found an exposure period of 4 weeks to be optimal. Goodman et al. [17] found that the retention of metals by moss-bags was directly proportional to the exposure time and was linear for up to 10 weeks for Co, Ni, Cu, Zn, Cd, and Pb. Displacement and saturation effects can be avoided by using the minimum exposure periods necessary for detecting trends. The other factor is the bag design, which should keep the humidity of the sample at a stable level to avoid drying [2].

The aim of this study was to assess study cumulative properties of moss *Sphagnum girgensohnii* bags (dry and irrigated – wet) with time as the relations between element accumulation and exposure time at different climatic conditions are not well understood.

2. Experimental

2.1. Study area

The study was carried out on the roof terrace of the Institute of Physics, ($\varphi = 44^\circ 51'$N, $\lambda = 20^\circ 23'$E, $H_s = 92$ m) situated on the right bank of the Danube in Zemun (suburb of Belgrade). Belgrade has a moderate continental climate. The year-round average temperature is 11.7 °C, the hottest month is July, with an average temperature of 22.1 °C; annual precipitaion is about 700 mm.

The main source of ambient particulates is old vehicles. Leaded gasoline is still widely used. There are several large heating plants, run with natural gas or crude oil and many smaller plants run only with crude oil. Fuel used for domestic heating is mainly coal or crude oil, as well as natural gas introduced during the last few years. A detailed description of the Belgrade study area was given in Aničić et al. [18].

2.2. Experimental design

The moss, *S. girgensohnii* Rusow, was collected in May 2007 from a pristine wetland area located near Dubna, Russian Federation ($\varphi = 56^\circ 44'$N, $\lambda = 37^\circ 09'$E, $H_s = 120$ m). This background area was chosen on the basis of results obtained by Culicov et al. [19].

In the laboratory, the moss was cleaned from soil particles and other foreign matter and air-dried. About 3 g of air–dried moss was packed loosely in 10×10 cm^2 bags of nylon net with 1-mm mesh size. The untreated samples were stored in the laboratory at room temperature until exposure.

Using specially constructed holders (1.5 m high) (Fig. 1) placed on a roof terrace, 5–10 m above the street level, the moss bags were exposed to the atmospheric deposition for different exposure periods (0.5–5 months) between June and November 2007. Thus, the moss bags were exposed for ten consecutive 15-day periods. Different treatments, with and without irrigation, were applied to the exposed moss in parallel [20]. The bags were wetted by placing them on the top of a cellulose (100%) sponge with the bottom immersed in distilled water. The whole setup was placed in a polyethylene box (130 mm × 110 mm × 80 mm). Bidistilled deionized water was added to the boxes at intervals of several days depending on the meteorological conditions (precipitation and temperature).

To check for possible contamination, the elemental composition of the unexposed sponge was determined after acid digestion, and the concentrations of all elements reported were below the detection limits. The polyethylene boxes were cleaned before use by soaking in 0.1% nitric acid for 48 h and washed with bidistilled water. Sampling and preparation of moss bags were carried out wearing polyethylene gloves.

Fig. 1. Experimental setup: (A) dry, and (B) wet moss bags.

2.3. Chemical analyses

Initial concentration levels were determined in the unexposed moss material to be considered for the experiments. The moss from exposed bags was removed from the nylon net and air-dried at room temperature. The samples were manually homogenized and dried to constant weight at 40 °C. After drying, portions of approximately 0.5 g of moss (dry weight) were digested for 2 h in an ULTRACLAVE microwave digester with 8 ml of concentrated nitric acid (Merck ultra pure) using a standard temperature program. After cooling to room temperature the digested samples were diluted with double-distilled and deionized water to a total volume of 60 ml. The concentrations of 49 elements (Be, Na, Mg, Al, Si, P, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, As, Se, Rb, Sr, Y, Nb, Mo, Cd, Te, Cs, Ba, La, Ce, Pr, Sm, Eu, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, and U) were determined by inductively-coupled plasma mass spectrometry (ICP-MS). The homogeneity tests were performed on five sub-samples of 0.5 g taken from eight randomly chosen moss bags. The homogeneity was evaluated based on the variation in the concentration of the measured elements which were determined by ICP-MS. The results of the test showed no significant difference within the moss bag sub-samples. The relative standard deviation of these results varied from 3% to 6%. Accordingly, one sample (0.5 g) from each bag was analyzed throughout the experiment.

Quality control was performed using two international moss reference samples [21] and tea leaves GBW-07605 (Institute of Geophysical and Geochemical Exploration, Langfang, China). Those reference materials were analyzed in triplicate along with the survey of moss bags samples. The results for the reference materials were within 90–115% (analyzed/certified values, %) of certified values for the measured elements. Blank samples were also analyzed to assess possible contamination during sample preparation.