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Moss bag biomonitoring of airborne toxic element decrease on a small scale: A street study in Belgrade, Serbia

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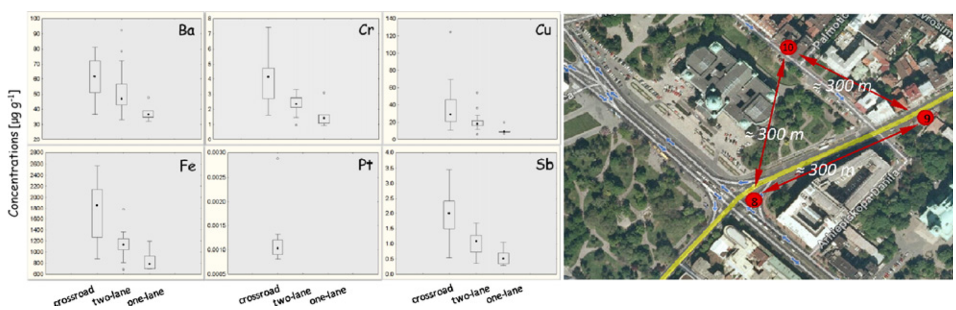
HIGHLIGHTS

- The moss element decline was observed along crossroads and two- and one-lane streets.
- The moss element content was correlated with the counted traffic flows ($r > 0.65$).
- Pedestrian zones could not be assumed as urban pollution background.
- Sb, Cu and Cr have been marked as reliable tracers of traffic pollutant emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

A database of potentially hazardous substances, necessary for estimating the exposure of humans to air pollutants, may be deficient because of a limited number of regulatory monitoring stations. This study was inspired by undeniably harmful effects of human long-term exposure to intense traffic emissions in urban area. Moss bag biomonitors were used to characterize spatial variation of airborne toxic elements near crossroads and two- and one-lane streets. The *Sphagnum girgensohnii* and *Hypnum cupressiforme* moss bags were exposed for 10 weeks to 48 sampling sites across Belgrade (Serbia) during the summer of 2014. In addition, oven-drying pretreatment of the moss bags was tested. During the experimental period, traffic flows were estimated at each site by counting the number of vehicles during the rush hours. The concentrations of 39 elements were determined in the moss samples. There was no significant difference between the results obtained for nontreated and oven-dried moss bags. For the majority of elements, the moss bags identified a common pattern of decrease in the concentration from crossroads to two- and one-lane streets. The exposed moss bags were enriched with Sb, Cu and Cr. The correlation coefficients ($r = 0.65$–0.70) between the moss concentrations of Cr, Cu, Fe and Sb and the site-counted traffic flows also confirmed a dependence of the airborne element content on traffic emissions. A strong correlation with traffic flows makes Sb, Cu and Cr reliable traffic tracers.

1. Introduction

The transport sector represents the dominant source of air pollution in urban areas. Traffic-related air pollutants, including particulate matter (PM) associated with toxic elements, are widespread. These pollutants are often found in higher concentrations in areas near urban

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micro-environments such as major roads, crossroads, junctions and bus stations. Increase of air pollutants beyond the limit values has been associated with many hazardous health effects (European Environment Agency, 2013; United States Environmental Protection Agency, 2013).

Epidemiological studies commonly use data from one or few stations of regulatory monitoring network to estimate personal exposure to PM (Brauer, 2010). However, the results of recent studies have indicated that monitoring stations may not accurately characterize complexities of the spatial dispersion of PMs in an urban area (Wilson et al., 2005; Brauer, 2010). Concentrations of traffic-related air pollutants show dramatic temporal and spatial variations from on-road to near-road micro-environments. For example, particles with size <2.5 μm (<PM2.5), volatile organic compounds (VOCs), NO and polycyclic aromatic hydrocarbons (PAHs) have demonstrated steep gradients in concentrations that attain elevated levels near- and on-road, and a return to background level at distances of approximately 150–200 m (Hagler et al., 2009; Karner et al., 2010).

Regulatory network of air quality monitoring has been typically designed to assess regional and temporal variations of air pollution. For micro-scale setting, sampling sites should be placed at a distance of at least 25 m from the edge of crossroads and not on the carriageways of roads (Directive 2004/104/EC; Directive 2008/50/EC). Because of this, examination of long-term on-road exposure of pedestrians, commuters, cyclists and workers (e.g. drivers and policemen) to traffic-related toxic elements requires alternative approaches (Brauer, 2010).

Biomonitoring represents a simple and cost-effective alternative to regulatory monitoring of air quality. Moss is the most efficient biomonitor available to entrap air pollutants. It lacks a developed root system and thus obtains nutrients from air. Moreover, the high cation exchange capacity of moss increases its adsorbent efficiency (Brown and Bates, 1990). 'Moss bag technique' was introduced by Goodman and Roberts (1971), and it has been developing over the last several decades as an efficient method of active moss biomonitoring of hazardous air pollutants such as heavy metals, non-metals and PAHs (Vasconcelos and Tavares, 1998; Adamo et al., 2003; Ares et al., 2009; Cao et al., 2009; Salo and Mäkinen, 2014; Calabrese et al., 2015; Kosior et al., 2015). This method has been particularly useful for conducting a detailed survey of diversely polluted micro-environments within urban areas, where native mosses are usually absent because of predominantly paved and landscaped surfaces. In contrast to instrumental measurements, moss bags do not require power supply and maintenance. Thus, the moss bag technique could be applied to obtain a satisfactory spatial resolution of monitoring sampling sites, and consequently a detailed database. Another important difference between the moss bag technique and instrumental measurements is sampling time. Instrumental measurements are usually restricted to short time periods, providing daily concentration of pollutants, whereas moss bags act as a long-term integrator of air pollutants providing average concentration. Long-term sampling is prerequisite for the assessment of cumulative exposure to a certain pollutant that has hazardous effect on human health.

The purpose of this study was to assess the level of airborne toxic elements near highly traffic-burdened crossroads and two- and one-lane streets, using the moss bag technique. It is hypothesized that distance decline of toxic element concentrations exists from crossroads to two- and one-lane streets depending on the traffic burden. The aim was also to assess if the moss bags could reflect this phenomenon. The specific objectives were related to the methodological aspects of the application of moss bag technique. The main reason for selecting a particular moss species is its abundance in the study region. Thus, we studied whether (1) two moss species could be interchangeably used for biomonitoring purpose and (2) recommended oven-drying pretreatment of moss bags (Giordano et al., 2009; Ares et al., 2012) is necessary before moss exposure in active biomonitoring studies.

2. Materials and methods

2.1. Study area

The study was conducted in the urban area of Belgrade (44°50′–44°44′N and 20°22′–20°32′ E at 70–250 m altitude). The city is the capital of Serbia, situated at the confluence of the rivers Sava and Danube, with approximately 1.7 million inhabitants.

The biomonitoring survey was conducted from June 15 to August 15, 2014. During the experimental period, the average daily air temperature was 22.5 °C, the prevailing wind direction was WNW, the average daily wind speed was 2 m s^{-1} and the average relative air humidity and total rainfall were 68% and 225 mm, respectively (Republic Hydrometeorological Service of Serbia, 2014).

2.2. Traffic flow estimation

During the experimental period, traffic is considered to be the major source of air pollution, particularly toxic elements, because of the absence of heating systems. To estimate the contribution of traffic intensity to the toxic element concentrations in air, traffic flows were counted. For each study site, traffic flows were recorded by video cameras for later off-site counting. The vehicle fleet was classified into categories of passenger cars, buses, trams, trolleys, motorcycles and light- and heavy-duty vehicles. Traffic flows of each vehicle category were counted for 15 min during the rush hours (7:00–9:00 am and 4:00–6:00 pm) on Wednesdays and Sundays of June and July. The average traffic flows during the experimental period were estimated from these counts (Table 1), using a procedure recommended by the Secretariat for Transport of Belgrade (personal communication).

2.3. Moss bags — sampling, bag preparation and pre- and post-exposure treatments

Two moss species were chosen for moss bag biomonitoring: the most recommended biomonitor species obtained from abroad and the other one, common for the study area. Thus, at the end of May 2014, the moss *Sphagnum girgensohnii* Russow (*S.g.*) was collected from a pristine wetland area located near Dubna, Russia. This area is considered to be an appropriate background site in the previous research (Aničić et al., 2009a, 2009b). The moss *Hypnum cupressiforme* Hedw. (*H.c.*) was obtained from the protected area 'Vršačke planine', Serbia, which is also selected in the previous study (Vuković et al., 2015a). In the laboratory, the green apical parts of the mosses were separated from the brown tissue and manually cleaned of soil particles, plant remains and epiphytes with care. Subsequently, moss material was rinsed thrice with double-distilled water (~10 L of water per 100 g of moss dry weight and 10 min of shaking). Such prepared mosses were air-dried and gently hand-mixed to obtain a homogeneous material. Approximately 1.5 g of the homogeneous moss was packed loosely in 7 × 7 cm nylon net bags with mesh size of 2 mm. The net was previously washed in 0.1 M HNO_3 to eliminate any contamination. The bag dimensions were selected to obtain a moss weight/surface area ratio of approximately 30 mg cm^{-2} for each square centimetre of bag surface, which was suggested by Ares et al. (2012). Simultaneously, the researchers indicated that a higher moss entrapment capacity for particles could be reached if the ratio of moss weight to surface area of the bag is lower (Ares et al., 2014).

To minimize the influence of possible moss growth on element uptake during the experimental period, Giordano et al. (2009) and Ares et al. (2012) recommended an oven-drying devitalizing pretreatment of moss before its exposure in the field. However, in the previous survey (Aničić et al., 2009b), a poor vitality of moss was evident after exposure, because of dry continental climate conditions in the study area. To test the recommended devitalizing moss pretreatment, one half of the prepared moss bags were oven-dried (dry moss, $DM_{S.g.}$ and $DM_{H.c.}$) at 120