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Assessment of species-specific and temporal variations of major, trace and rare earth elements in vineyard ambient using moss bags

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ABSTRACT

Since the methodological parameters of moss bag biomonitoring have rarely been investigated for the application in agricultural areas, two mosses, *Sphagnum girgensohnii* (a species of the most recommended biomonitoring genus) and *Hypnum cupressiforme* (commonly available), were verified in a vineyard ambient. The moss bags were exposed along transects in six vineyard parcels during the grapevine season (March–September 2015). To select an appropriate period for the reliable 'signal' of the element enrichment in the mosses, the bags were simultaneously exposed during five periods (3 × 2 months, 1 × 4 months, and 1 × 6 months). Assuming that vineyard is susceptible to contamination originated from different agricultural treatments, a wide range of elements (41) were determined in the moss and topsoil samples. The mosses were significantly enriched by the elements during the 2-month bag exposure which gradually increasing up to 6 months, but Cu and Ni exhibited the noticeable fluctuations during the grapevine season. However, the 6-month exposure of moss bags could be recommended for comparative studies among different vineyards because it reflects the ambient pollution comprising unpredictable treatments of grapevine applied during the whole season. Although higher element concentrations were determined in *S. girgensohnii* than *H. cupressiforme*, both species reflected the spatio-temporal changes in the ambient element content. Moreover, the significant correlation of the element (Cr, Cu, Sb, and Ti) concentrations between the mosses, and the same pairs of the elements correlated within the species, imply the comparable use of *S. girgensohnii* and *H. cupressiforme* in the vineyard (agricultural) ambient. Finally, both the moss bags and the soil analyses suggest that vineyard represents a dominant diffuse pollution source of As, Cr, Cu, Ni, Fe, and V.

1. Introduction

Air pollution is not a local, but regional and global issue since air pollutants released from one source may be transported in the atmosphere, contributing to or resulting in poor air quality elsewhere (EEA, 2016). Validated monitoring data and air quality maps on the pan-European scale are already available, but still with poor spatial resolution (Tørseth et al., 2012). The majority of fixed monitoring stations are distributed across urban and industrial areas without special attention to the areas with agricultural activities, which continuously emitting significant amounts of air pollutants (Guerreiro et al., 2014). Soil is the final collector for contaminants released by agricultural activities, but also the pollutant emission source to the atmosphere by resuspension processes (Wuana and Okieimen, 2011 and references therein).

Viticulture represents an important agricultural practice in many countries, and long-term use of diverse inorganic (metal-based) and organic pesticides and fertilisers poses serious environmental threats (Komárek et al., 2010). Notwithstanding, Cu-based and synthetic organic fungicides have been extensively used worldwide (Besnard et al., 2001; Wightwick et al., 2008), but nowadays only in organic vineyards with limited doses (EC, 2002). From the 1980s, fertilizers containing rare earth elements (REEs) have been applied in agriculture since they act as a nutrient at low levels (Wen et al., 2001; Zhang and Shan, 2001). Since their utilization is growing worldwide (US EPA, 2012), exposure to this group of emerging pollutants, has also raised questions about their detrimental health effects (Pagano et al., 2015).

To characterise spatial patterns of air pollutants, in the last several decades, moss and lichen biomonitoring has been developed as an easy operational and cost-effective method for air pollution assessment

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(Freitas et al., 1999; Conti and Cecchetti, 2001; Steinnes et al., 2011; Aničić Urošević et al., 2017 and references therein). Due to specific morpho-physiological features (the lack of root system, a large surface area, a number of proton-binding sites on the tissue surface) (González and Pokrovsky, 2014), mosses have been suitable for the biomonitoring of air pollution giving a time-integrated information about the presence of air pollutants. Naturally growing (passive approach) and 'transplanted' (active approach) mosses have been applied for biomonitoring of air pollutants in remote and urban/industrial areas, respectively (Harmens et al., 2010; Adamo et al., 2003; Ares et al., 2012; Aničić Urošević et al., 2017 and references therein). However, passive biomonitoring is hardly applicable to cultivated areas, such as agricultural, where native mosses are not usually available. As an alternative, active moss biomonitoring of trace elements could be performed in agricultural regions, which has been rarely reported thus far (Capozzi et al., 2016a; Capozzi et al., 2016b). Thus, the recommended variables regarding the application of the method in urban and industrial areas – preparation of the moss and transplants, exposure and post exposure treatment (Ares et al., 2012) should be further tested for the agricultural ambient. Thus, this study moves beyond the existing ones in the investigation of the temporal dynamic of element uptake by different moss species. Furthermore, the period of 2-month bag exposure, commonly applied in highly polluted urban/industrial areas, is potentially insufficient for a reliable assessment of ambient pollution in presumably less polluted agricultural areas.

In this study, active moss biomonitoring was performed in a vineyard region, a specific agricultural zone with potential air and soil pollution due to the application of fertilisers and pesticides containing potentially toxic elements. Towards harmonisation of the moss bag methodology, the last review paper (Ares at al, 2012) is respected, but several methodological steps are tested in this study: (*i*) the suitable period of the moss bag exposure in a vineyard ambient, *(ii)* comparison of the element enrichment capacity of two moss species *Sphagnum girgensohnii* and *Hypnum cupressiforme*, mostly explored in the biomonitoring studies, and *(iii)* spatial element distribution in the moss and soil samples across vineyard.

2. Materials and methods

2.1. Study area

The study was conducted in the agricultural area "Oplenac Wine Route" (44°13'36.3" N 20°39'12.4" E). This area is a well-known region for grapevine growing, near Topola settlement, 80 km away from Belgrade, the capital of Serbia. Six vineyard parcels were chosen; three parcels (I, IV and V) are close to the road; two parcels (II and III) are behind parcel I; one parcel (VI) is near the local foundry (Fig. 1). There are no any monitoring stations for air pollution monitoring in this region.

2.2. Experimental setup

Two moss species were chosen for the purpose of moss bag biomonitoring in the vineyard region. One of two used moss species is the most recommended biomonitor species collected from abroad and the another one is naturally present on the territory of Serbia. The moss *Sphagnum girgensohnii* Russow (*S. girgensohnii*) was collected at the end of May 2014 from a pristine wetland area located in the vicinity of Domkino, Dubna (Russia). This locality is well-known as an appropriate background area based on the previous research (Aničić et al., 2009a; Vuković et al., 2016). Another moss species *Hypnum cupressiforme* Hedw. (*H. cupressiforme*) was collected from the protected area "Vršačke planine" (Serbia) which was also selected in the previous studies (Vuković et al., 2015a).

The preparation of the moss material and the exposure of moss bags were performed according to the recommendations given in the review of Ares et al. (2012). Discrepancies from the proposals regarding devitalizing treatments, moss bag shape, and duration of exposure are due to comparison with the previous research in the study region (Aničić et al., 2009a, 2009b; Vuković et al., 2015, 2016). In the laboratory, the green apical parts of the collected moss were separated from the rest of brownish tissue and manually cleaned from extraneous material, i.e., soil particles, leaves, pine needles. Then moss was rinsed thrice with double distilled water (≈ 10 L of water per 100 g of the moss fresh weight with shaking). Such prepared moss was air-dried and gently hand-mixed to obtain a homogeneous material. Approximately 1.5 g of the homogeneous moss was packed in flat 7 × 7 cm nylon net bags with a mesh size of 2 mm. The mesh was previously washed in 0.1 M HNO_3 to eliminate possible contamination. The bag dimension and the moss weight inside were selected to achieve a mass-to-surface ratio of approximately 30 mg cm^{-2} recommended in the review of Ares et al. (2012).

The active moss biomonitoring survey in the vineyard was conducted in 2015 from March 20th to September 20th covering the whole grapevine season. Two moss species (*S. girgensohnii* and *H. cupressiforme*) were exposed in the bags for 2, 4 and 6 month periods. According to the previous studies performed in the urban area (Aničić et al., 2009b), 2-month period should be appropriate for the reliable `signal` of the elements, even REEs, in the exposed mosses. However, in a vineyard ambient, this exposure period might be insufficient, and thus, it was of interest to test a prolonged period of the moss exposure (e.g., 4 months). Six-month bag exposure covers whole grapevine season and could be interesting for intercomparison of air pollution in different vineyards. Specifically, there were five different periods of the moss bag exposure in the agricultural (vineyard) area: three 2-month periods (1M2: March 20 th – May 20 th; 2M2: May 20 th – July 20 th;

Fig. 1. Map of the studied vineyard in the agricultural area "Oplenac Wine Route" (Serbia); the vineyard parcels – I, II, III, IV, V, and VI.