MICROSCOPICAL ANALYSIS OF PARTICULATE MATTER INTERCEPTED BY MOSS-BAGS IN URBAN, INDUSTRIAL AND AGRICULTURAL AREAS OF THREE EU COUNTRIES

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Introduction

The particulate matter (PM) represents an important transport form of heavy metals in the atmosphere (WHO, 2013), recently recognized by the International Agency for Research on Cancer (IARC) as one of the pollutants most affecting human health and closely associated with increased cancer incidence (EEA, 2015). High costs and technical constrains often hamper an adequate evaluation of airborne particulate load. The use of moss-bags represents a cost effective alternative to evaluate PM deposition. It consists of the exposure of mosses inside nylon bags according a rationale design with the aim to evaluate the air quality (Capozzi et al., 2016a; 2016b; Ares et al., 2012). Mosses are in fact well-known biomaterials able to adsorb and entrap different type of airborne particles (Adamo et al., 2007; González et al., 2016). According to the above considerations, the aims of this work were: 1) to describe the nature of PM adhering to leaf surfaces of the moss *Pseudoscleropodium purum* (Hedw.) M. Fleisch. after 12 weeks exposure in bags in urban, industrial and agricultural sites of Italy, Austria and Spain; 2) to relate PM size and relative chemical composition to site-specific land use; 3) to identify different markers of possible PM pollutant source.

Methods

The moss *P. purum* was collected in undisturbed areas and treated and exposed according to Capozzi et al. (2016b). Moss samples were exposed for 12 weeks in the 2013 winter in three EU countries (Austria, Italy, Spain), choosing in each country three sites belonging to different land uses: urban, industrial and agricultural. Ten leaves from three to five shoots of moss material exposed in each site were observed under a SEM (JEOL JSM 5310) in SE and BSE modes and analyzed by energy-dispersive X-ray spectroscopy (EDX; Oxford INCA). A total of 10 representative areas of 10.000 μm^2 each (100 x 100 µm) were examined for particle counting by ImageJ open source software and characterization by EDX.

Results

After exposure, heterogeneous particles (from regular- to amorphous-shaped and from 1 to 40 µm) and in form of single particle or aggregates were observed on *P. purum* leaflets, particularly on adaxial leaf surfaces and the leaf-stem intersection points. The particles were classified according to their equivalent diameter

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into different size classes (PM1.0, PM2.5, PM10, >PM10). Biological materials, such as plant-derived fragments, fungal hyphae, spores and pollens were observed as well. In general, in the urban and industrial sites the amount and density of particles *per* leaf were higher than in the agricultural sites. Similarly, large aggregates (~ 30-40 μm) and fine PM (Ø < 2.5 μm) were only found in industrial and urban sites. In all investigated sites, submicroscopical EDX analysis frequently revealed particles made by Si, Al and Fe, mostly as Si-Al or Fe-Si associations, indicating an important contribution of soil dust (mainly in form of silicates, clay minerals and quartz) to airborne PM. Titanium, occurring exclusively in urban and industrial sites, was also likely derived from resuspension of soil dust particles. Iron was also found in association with other elements, in particular Ni and Cr, in a metallic or oxide nature, especially in moss-bags exposed in urban and industrial sites. Potassium and Mg salts, and calcium carbonates and oxalates were found abundantly on leaf surfaces, particularly in moss samples exposed in agricultural sites. Sulfur-metal (Fe, Ni, Ba) associations were detected in moss leaflets exposed in the Spanish industrial site, suggesting occurrence of pyrite, barite and nickel sulfite/sulfates in PM. The results from PM characterization were consistent with the observed differences in moss uptake between the exposure sites.

Conclusion

Many studies highlighted the efficiency of moss exposed in bags to retain particulate matter, but only few of them are focused on a morphological/numerical/chemical characterization of particles. This study represented a further confirmation of the close association between PM entrapped by moss surface and moss elemental uptake. Different land uses appear to be associated to the deposition of specific particle size class and composition, with a commonly frequent soil dust contribution. Morphological and chemical characterization of PM entrapped by mosses might be useful to track possible sources of air pollution.

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