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Improved biomonitoring of airborne contaminants by combined use of holm oak leaves and epiphytic moss

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HIGHLIGHTS

- Distinctive traits of leaves and mosses differently rule bioaccumulation.
- Mosses efficiently accumulate airborne elements, due to the CEC and high surface/mass ratio.
- Holm oak leaves mainly accumulate PAHs due to the waxy cuticle and stomata.
- The combined use of leaves and moss is a promising tool to monitor airborne pollutants.

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ABSTRACT

Concentrations of 12 elements (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) and 16 EPA-listed PAHs were detected in *Quercus ilex* leaves and the epiphytic moss *Leptodon smithii* collected at urban, periurban and extraurban holm oak stands, in two Italian Regions (Campania and Tuscany). Levels of environmental contaminants were generally higher in leaves and moss from urban areas than periurban and extraurban ones and samples from Campania had the highest PAH content. The epiphytic moss accumulated higher concentrations of trace elements than leaves and the latter showed a higher accumulation capability for PAHs, especially for those with low molecular weight. The different bioaccumulation in leaves and moss were explained in terms of their distinctive morphological and ecophysiological characteristics. The combined approach seems a promising tool for the monitoring of a wide range of pollutants in Mediterranean urban and extraurban environments.

1. Introduction

Due to technical difficulties and high-cost of atmospheric pollutant monitoring, the European Air Quality Directives 2004/107/EC and 2008/50/EC only demand for the determination of few atmospheric contaminants (e.g. Pb, Cd, As, Ni, Hg and benzo[a]pyrene). Plant biomonitors are an useful tool, complementary to automatic monitoring devices, because they provide time-integrated information on atmospheric depositions of a large number of persistent pollutants and permit to draw deposition maps at different scales (Alfani et al., 2000; Fernández et al., 2007; Smodiš, 2007; Giordano et al., 2009; De Nicola et al., 2011). For an appropriate use of biomonitors, it is of a paramount importance to evaluate their specific ability in the uptake and accumulation of contaminants in different climatic and environmental conditions.

Mosses and tree leaves are among the most used biomonitors of persistent atmospheric contaminants. The small number of suitable moss species living in urban and periurban environments has encouraged the use of moss transplants to monitor air quality (Aničić et al., 2009; De Nicola et al., 2013; Giordano et al., 2013). When native mosses are used as biomonitors, the choice widely falls on pleurocarpous species, which differently from acrocarpous mosses, have large carpets almost totally insulated from the substrate and are less affected by contamination from soil particles (Zechmeister et al., 2008; Spagnuolo et al., 2009). Mosses have no roots and are largely dependent upon wet and dry atmospheric depositions for water and nutrient supplies (Bargagli, 1998; Sardans and Peñuelas, 2005). The bioaccumulation of airborne elements is favoured by their high surface to mass ratio and one-cell thick leaves. Moss leaves, without waxy cuticle and with high CEC

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(cation exchange capacity), bind ions to anionic polysaccharides into the cell wall or entrap/adsorb airborne particles (Pérez-Llamazares et al., 2011; Spagnuolo et al., 2011).

Tree leaves intercept airborne particles and their waxy cuticle can incorporate lipophilic organic contaminants but the root uptake can contribute to total concentrations of some pollutants in all plant parts (Howsam et al., 2000; Aničić et al., 2011).

Many airborne elements and polycyclic aromatic hydrocarbons (PAHs) are among environmental contaminants of major concern because they are persistent and are released by many anthropogenic sources, such as waste incineration, industrial processes and vehicles (Bargagli, 1998; Mastral et al., 2003). Whereas most airborne metals are bound to particulate matter, atmospheric PAHs are partitioned between gas and particulate phases, depending on their molecular weight and environmental conditions (Riederer, 1990; Mastral et al., 2003). Thus, the leaves of several plant species have been widely used in biomonitoring of both airborne elements and PAHs (e.g. Lehndorff and Schwark, 2004, 2010; Sun et al., 2010), whereas native moss species have been widely employed to assess atmospheric deposition of metals and rarely those of PAHs (e.g. Gerdol et al., 2002; Ares et al., 2009).

This work aims at comparing the ability of native epiphytic moss *Leptodon smithii* and leaves of *Quercus ilex* (holm oak) to accumulate a wide spectrum of elements and PAHs not routinely monitored in automatic devices and to discuss the results in the light of their different morpho-physiological characteristics. *Q. ilex* woods are a climax community of Mediterranean regions and in Italy holm oak trees have been widely used in the landscaping of urban and periurban parks and gardens. In order to test similarity/difference in pollutant uptake and accumulation by moss shoots and holm oak leaves, the samples were collected in sites with different anthropogenic pressure, mesoclimatic and environmental conditions of two Italian Regions: Campania and Tuscany.

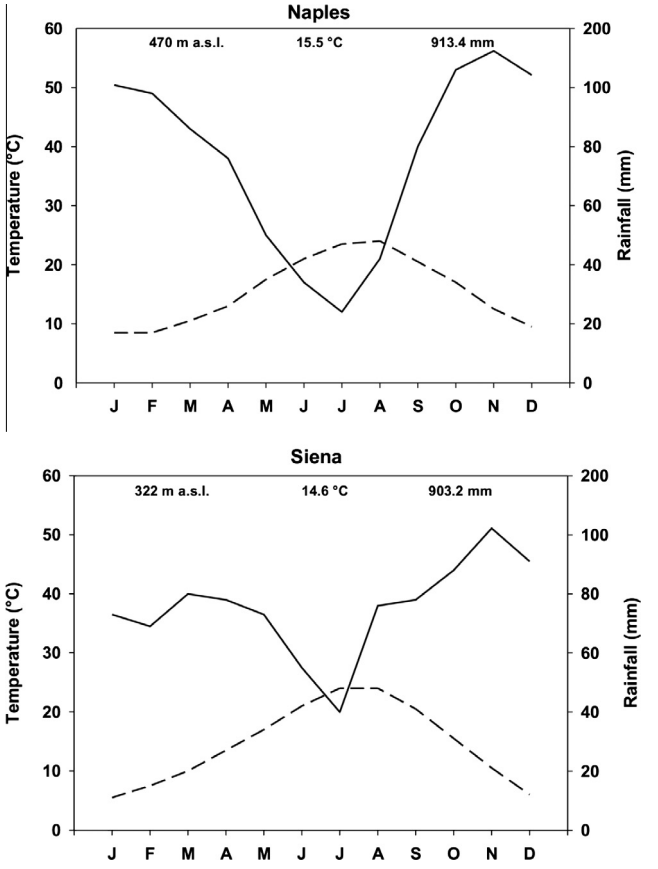

Fig. 1. Climatic diagrams for Campania (Naples) and Tuscany (Siena). Dashed and continue lines for temperature and precipitation curves, respectively.

2. Materials and methods

2.1. Plant material

Q. ilex L. (holm oak) is an evergreen oak representing the potential natural vegetation community in Mediterranean area, where it is found as mono-species woodlands in natural areas and as remnant woods in periurban and urban areas. This species is widely used in biomonitoring, being its leaves capable to accumulate organic and inorganic pollutants (Alfani et al., 2000; Orecchio, 2007).

L. smithii Hedw. is a pleurocarpous moss of the Mediterranean climax vegetation, rarely occurring on bare rocks, and preferring tree bark of humid, close woods up to 3000 m above sea level. The species is common on holm oak bark and has been used in a previous biomonitoring survey carried out in Campania Region (Spagnuolo et al., 2009).

2.2. Sampling

In Campania and Tuscany, characterised by a typical Mediterranean climate (Fig. 1), the sampling sites were located in urban (U), periurban (PU) and extraurban (EU) holm oak woodlands (Table 1). The U sites were located in urban parks embedded in the cities of Naples and Siena, for Campania and Tuscany, respectively. Naples and Siena provinces are characterised by a maximum population density >8000 and <500 inhabitants km^{-2}, respectively; the major land use types are: agriculture (54%), urban/industrial (28%) and forest/natural greenland (17%) for Naples province, and agriculture (58%), forest/natural greenland (41%) and urban/industrial (1%) for Siena province. Each PU site was within 5 km from the respective U site, whereas EU sites were located at 100 and 70 km from U sites, for Campania and for Tuscany, respectively.

At each site, in May 2009, 15–20 holm oak trees were selected. From the outer part of each canopy, at about 3–4 m above the ground, mature (1-year old) and healthy leaves were collected and successively all the leaves were pooled in a homogeneous sample. On the same holm oak trees, at a height of 1–2 m above the ground, small green clumps of the epiphytic moss *L. smithii* (not elder than 2- or 3-years) were collected and carefully mixed to obtain a homogeneous sample. Dead or extraneous material was removed from moss samples under a binocular.

The samples were oven dried (75 °C) for element analysis and stored at −20 °C until PAH analysis, without washing. Concentrations of trace and major elements and PAHs were reported as average of three replicates, on a dry weight basis.

2.3. Chemical analyses

2.3.1. Major and trace elements

As fully reported in Baldantoni et al. (2009), oven dried moss and leaf samples were powdered in a planetary ball mill (Retsch, PM4) and subsequently mineralised with the addition of HNO_3 and HF (2:1 = v:v) in a micro-wave oven system (Milestone, Ethos). Total element concentrations were measured in sample solutions by atomic absorption spectrometry (PerkinElmer, AAnalyst 100) via graphite furnace (Cd, Cr, Cu, Ni and Pb) or via flame (Ca, Fe, K, Mg, Mn, Na and Zn). The percentage recovery of each element in standard reference material (Apple leaves, NIST SRM 1515) was used to correct the quantification of the investigated elements.