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Evergreen or deciduous trees for capturing PAHs from ambient air? A case study☆

Flavia De Nicola [a, *], Estefanía Concha Graña [b], Purificación López Mahía [b], Soledad Muniategui Lorenzo [b], Darío Prada Rodríguez [b], Rubén Retuerto [c], Alejo Carballeira [c], Jesús R. Aboal [c], J. Ángel Fernández [c]

[a] Dipartimento Scienze e Tecnologie, Università degli Studi del Sannio, Via Port'Arsa 11, 82100 Benevento, Italy
[b] Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Departamento Química Analítica, Facultad de Ciencias, Universidade da Coruña, 15071 A Coruña, Spain
[c] Área de Ecología, Departamento de Biología Funcional, Facultad de Biología, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

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ABSTRACT

Tree canopies play a key role in the cycling of polycyclic aromatic hydrocarbons (PAHs) in terrestrial ecosystems, as leaves can capture PAHs from the air. In this study, accumulation of PAHs was compared in an evergreen species, *P. pinaster*, and in a deciduous species, *Q. robur*, in relation to some physio-morphological characteristics. For this purpose, pine needles and oak leaves collected from different sites across Galicia (NW Spain) were analysed to determine PAH contents, specific leaf area, stomatal density and conductance.

Leaves and needles contained similar total amounts of PAHs. The major contribution of particle-bound PAHs in oak (the concentrations of 4- and 5-ring PAHs were two times higher, and those of 6-ring PAHs five times higher in oak than in pine) may be related to the higher specific leaf area (13 and 4 $cm^2\ g^{-1}$ dry mass in respectively oak and pine). However, the major contribution of vapor-phase PAHs in pines may be affected by the stomatal conductance (two times higher in pine than in oak). Moreover, an increase in the diameter at breast height of trees led to an increase in accumulation of PAHs, with pine capturing higher amounts of low and medium molecular weight PAHs. The study findings underline the potential role of trees in improving air quality, taking into account the canopy biomass and life cycle.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants, emitted from both anthropogenic and natural sources by incomplete combustion of organic material such as fossil fuels and plant biomass. PAHs can exist in the air in vapor phase (low molecular weight PAHs) or can be adsorbed onto airborne particulate matter (high molecular weight PAHs), depending on their physico-chemical properties (Kameda, 2011). Given that PAHs can be transported over long distances through several environmental compartments, and taking into account the associated health risks due to their carcinogenicity and toxicity (IARC, 2010), PAHs are considered environmentally hazardous compounds. PAHs have thus recently been included in official air quality standards (EEA, 2012), and their monitoring is required. To evaluate the impact of PAH pollution on environmental compartments, is crucial to track pollution emission sources. PAH diagnostic ratios, i.e. the concentration ratios of specific pairs of PAHs, are generally used as tool to identify the origins of PAHs, being each source featured with a specific emission profile (Guo et al., 2003; Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012). Different chemical reactivity, volatility, and solubility of PAHs could affect diagnostic ratios, thus is important to use PAHs with similar physico-chemical properties, i.e. with same molecular mass, thus minimizing this error.

The capture and accumulation of PAHs by trees play a key role in the environmental fate of these compounds in terrestrial ecosystems. Leaves, representing the exchange surface between air and vegetation, are always taken into account in modelling PAH cycling (Behrendt and Brüggemann, 1993; Priemer and Diamond, 2002).

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* Corresponding author.
E-mail address: fdenicol@unisannio.it (F. De Nicola).

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During the transfer of PAHs from air to leaves, gaseous PAHs move via the stomatal pathway or diffuse into the cuticle and further inside the leaf (Bakker et al., 2001), whereas particle-bound PAHs are deposited on the leaf surface (Belis et al., 2011). Plant metabolism (i.e. gas exchange), leaf morphology (e.g. surface area, trichomes and roughness) and anatomy (e.g. density of stomata and presence of cuticular waxes and polymeric lipids) can therefore affect the ability of different plant species to capture PAHs from the air (Bakker et al., 2001; Howsam et al., 2001; Li and Chen, 2014; Simonich and Hites, 1995; Wagrowski and Hites, 1996). The influence of some ecological parameters (e.g. specific leaf area and leaf area index) on the uptake of PAHs by trees has recently been investigated (Terzaghi et al., 2015).

In the past few decades, oak and pine species have been widely used for biomonitoring airborne PAHs (De Nicola et al., 2011; Howsam et al., 2001; Lehndorff and Schwark, 2004; Orecchio, 2007; Piccardo et al., 2005; Ratola et al., 2011; Sun et al., 2010). The pedunculate oak *Quercus robur* L. (*Fagaceae*) and the maritime pine *Pinus pinaster* Ait. (*Pinaceae*) are both widely distributed across Europe. The southwest range of *Q. robur* is limited by the Iberian Peninsula, and *P. pinaster* typically occurs in areas of Europe affected by Mediterranean climatic conditions, although it grows better in areas with an Atlantic influence. In Galicia (NW-Spain), *P. pinaster* is the most common forest species, with pure stands occupying an area of 390 000 ha, while pure stands of *Q. robur* cover an area of 187 000 ha (data from 3rd Spanish National Forest Inventory DGCONA, 2002). The epidermal cells of mature leaves of this oak are covered by a continuous layer of wax superimposed with numerous wax crystalloids (Gülz and Mueller, 1992). While the cuticle of maritime pine needles has numerous closely aligned rows of stomata (Garcia Álvarez et al., 2009). Differences in anatomy, morphology and physiology of oak leaves and pine needles can affect how each species interacts with air pollutants.

The main objectives of this study were to compare the capacity of the leaves of an evergreen gymnosperm, *P. pinaster*, and a deciduous angiosperm, *Q. robur*, to accumulate PAHs, as well as to investigate the relationships between PAH content and some leaf characteristics. For this purpose, we measured the PAH burdens in pedunculate oak and maritime pine trees distributed across the study area, and we determined the values of several ecophysiological parameters (specific leaf area, stomatal density and stomatal conductance). Understanding the role of leaf characteristics in PAH accumulation is essential for choosing species to biomonitor PAHs in the air. In addition, quantifying the rate of capture of PAHs from the air by each plant species is also important.

2. Material and methods

2.1. Leaf sampling

The sampling method used in the present study has previously been described (Aboal et al., 2004). Briefly, the sampling sites were situated in rural areas throughout Galicia (NW-Spain, Fig. 1A). A total of 43 sampling sites (Fig. 1B) where both *Q. robur* and *P. pinaster* were present were selected (Aboal et al., 2004). At each sampling site, one branch (ca. 4 cm in diameter) was cut at a height of 5 m from 30 trees of each species. Sampled branches were sequentially directed towards each cardinal point, and the sequence was repeated with the fifth tree. Fifty shaded leaves, all about six months old, were collected from each oak specimen, and all newly emerging needles, also about six months old, were collected from each of the pine branchlets (Aboal et al., 2001). Sampling was carried out in July 1999 at coastal sites and in September 1999 at inland sites. In the first sampling survey, the weather was quite dry and the level of precipitation was very low. Heavy rainfall occurred during the second sampling survey (i.e. strong rainstorms that washed the leaves and needles). In an attempt to standardize the samples and overcome any effects of the different rain washing due to the form of pine and oak crowns, such as to the different weather conditions, both leaves and needles were washed in distilled water for 15 min with shaking (after removal of epiphytic organisms, insect eggs, fungi and debris from all samples). The samples were then homogenized in a variable speed blender (Waring Laboratory Blender, Torrington, USA), dried at room temperature and ground into an ultra-fine powder (Retsch ZM-100, Haan, Germany). These samples were stored for several years (between 1999 and 2014) in glass recipients in darkness at 18 °C (see Ares et al., 2009 for the effectiveness of this storage); the headspace was minimized to prevent loss of chemical compounds, via volatilization or oxidative reactions, during storage.

2.2. Leaf characterization

To determine any differences between the two species in leaf characteristics, five sampling sites (A2, B3, B8, 5D1 and J4 in Fig. 1B) were delimited in September 2015, and 10 trees of each species were selected for sampling in each. At least four fully expanded leaves from the last age cohort (at 5 m height) were obtained from each tree to determine the characteristics outlined below.

2.2.1. Specific leaf area and stomatal density

The specific leaf area (SLA) was estimated as the one-sided projected area of foliage per unit dry mass (cm^2 leaf area g^{-1} dry mass) (Pérez-Harguindeguy et al., 2013). The projected leaf area was determined with a portable leaf area meter (AM100, ADC BioScientific Ltd, Hoddesdon, England), and the leaf mass determined to the nearest 0.0001 g (Mettler Toledo AJ100, Columbus, USA), after oven-drying at 40 °C to constant weight. SLA is important as it represents the surface available for air pollutant exchange per unit of leaf-dry mass investment (Nizzetto et al., 2008), and it influences the rate of uptake of PAHs by vegetation (Terzaghi et al., 2015). Once the SLA was determined, the corresponding leaf surface was calculated for each species by means of the previously established relationship between tree diameter and leaf biomass (Diéguez-Aranda et al., 2009).

Stomatal density (stomata number mm^{-2}) was determined by counting stomata with Cell Sens software in four 400 × 400 μm frames of micrographs captured at 40× with a digital camera (Olympus SC30, Olympus Corporation, Tokyo, Japan) coupled to a microscope (Olympus CX41). Impressions of the abaxial and adaxial mid-portions of leaf surfaces (stomata are absent from oak adaxial surface) were obtained by applying a thin layer of clear nail polish to the leaves. The dried nail polish impressions were peeled from the leaves with the aid of clear adhesive tape and mounted on a slide. In the context of this research, stomatal density is important as vascular plants may exert some control of gas-exchange rates, and therefore on the uptake of air pollutants, by varying the number of stomata per unit of leaf area.

2.2.2. Stomatal conductance

The total conductance to CO_2 (mol CO_2 m^{-2} s^{-1}) measures the rate of carbon dioxide uptake through the leaf stomata. This represents the reciprocal of the physical resistance to the movement of gases from the air towards the interior of the leaf. Stomatal density, stomatal pore width and the degree of opening of the stomata together determine stomatal conductance (Larcher, 1995). Conductance is useful for assessing the impact of air pollutants on plant metabolism (Smith and Lytle, 1997; Tomar and Jajoo, 2014). Measurements were made between 11:00 and 13:00 h on days when conductance was unlikely to be restricted by temperature or