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Chemical and magnetic analyses on tree bark as an effective tool for biomonitoring: A case study in Lisbon (Portugal)

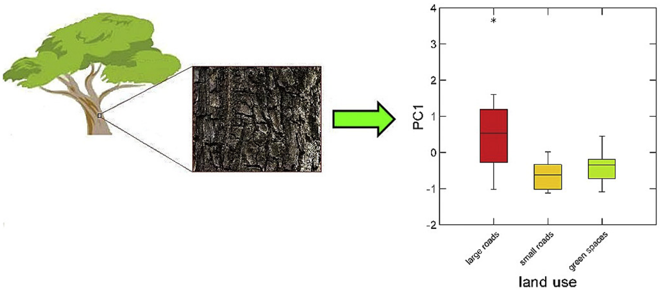
Daniele Brignole [a], Giuliana Drava [a, *], Vincenzo Minganti [a], Paolo Giordani [a],
Roeland Samson [b], Joana Vieira [c], Pedro Pinho [c, d], Cristina Branquinho [c]

[a] *Department of Pharmacy, University of Genova, Viale Cembrano 4, Genova, Italy*
[b] *Department of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, Antwerpen, Belgium*
[c] *Centre for Ecology, Evolution and Environmental Changes, Faculdade de Ciências, Universidade de Lisboa, Campo Grande C2, Lisboa, Portugal*
[d] *Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*

HIGHLIGHTS

- Tree bark is known to be a reliable tool for biomonitoring.
- Bark magnetic properties can be used as a proxy of the overall metal loads.
- Magnetic and chemical analyses have been combined for studying urban environments.

GRAPHICAL ABSTRACT



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ABSTRACT

Tree bark has proven to be a reliable tool for biomonitoring deposition of metals from the atmosphere. The aim of the present study was to test if bark magnetic properties can be used as a proxy of the overall metal loads of a tree bark, meaning that this approach can be used to discriminate different effects of pollution on different types of urban site. In this study, the concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, V and Zn were measured by ICP-OES in bark samples of *Jacaranda mimosifolia*, collected along roads and in urban green spaces in the city of Lisbon (Portugal). Magnetic analyses were also performed on the same bark samples, measuring Isothermal Remanent Magnetization (IRM), Saturation Isothermal Remanent Magnetization (SIRM) and Magnetic Susceptibility (χ). The results confirmed that magnetic analyses can be used as a proxy of the overall load of trace elements in tree bark, and could be used to distinguish different types of urban sites regarding atmospheric pollution. Together with trace element analyses, magnetic analyses could thus be used as a tool to provide high-resolution data on urban air quality and to follow up the success of mitigation actions aiming at decreasing the pollutant load in urban environments.

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* Corresponding author.
E-mail address: drava@difar.unige.it (G. Drava).

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1. Introduction

Air quality is a crucial factor for human health (Kelly and Fussell, 2015; WHO, 2013); air pollutants (e.g. particulate matter, trace elements, nitrogen oxides, sulphur oxides) have been associated to an increased risk of lung cancer mortality (Chen et al., 2016b; Pope et al., 2002; Raaschou-Nielsen et al., 2016),to the outbreak of cardiovascular and pulmonary diseases (Chen et al., 2016a) and to several other pathologies (Davidson et al., 2005; Jung et al., 2015; Ribeiro et al., 2014). Thus, an effective air quality monitoring process is a key point to be aware of the spatial and temporal patterns of contaminants. This can allow relating the concentrations of pollutants with the possible effects on human health, with the aim of planning and implementing regulatory policies to reduce emissions, as well as tracking the emission decrease (Nowak et al., 2015; WHO, 2017).

In the past decades, many studies on pollutants (Jarup, 2003; Nriagu, 1979; Pacyna and Pacyna, 2001; Schwarze et al., 2006) have been focused on trace elements which may represent a serious health threat even at low concentrations (Tørseth et al., 2012). However, despite the relevance of the European policy for air pollution reduction, only few monitoring stations are currently monitoring metals throughout the continent (EEA, 2017). This lack of monitoring data affects the reliability of high-resolution models of air pollution, which are needed both to define the real population exposed and to plan mitigation strategies. Additionally, urban areas are not homogeneous and may considerably differ from sites where air quality monitoring stations are located. Factors such as microclimatic conditions (e.g. local winds), the presence or absence of green spaces and particular situations such as a stop light in uphill roads might interfere with the air quality in small distances (Llop et al., 2012). Therefore, in order to obtain information with high spatial resolution, other tools to monitor atmospheric pollutants are needed. Biomonitors of air pollution (e.g. lichens, tree bark and leaves) are reliable tools for assessing the effects of pollution on the biotic component of ecosystems, providing complementary information with respect to traditional chemical-physical monitoring (Nimis et al., 2002) and have the potential to deliver data with high spatial resolution.

Among indicators, tree bark has been extensively used to assess air pollution (Cucu-Man and Steinnes, 2013; Drava et al., 2016; El-Hasan et al., 2002; Minganti et al., 2016) because of its ability to accumulate atmospheric trace elements during many years, both through wet and dry deposition. Although the mechanisms of metal accumulation in the bark are not yet fully understood, the uptake of pollutants from the roots can be considered negligible (Catinon et al., 2008, 2011). Consequently, tree bark reflects the concentration of pollutants in the atmosphere, even though it does not allow relating the accumulation of trace elements to a defined period of time (Drava et al., 2017).

Depending on physical and chemical processes acting in the atmosphere, metals emitted from pollution sources may be accumulated under different forms that may influence the magnetic fingerprint of living organisms. This characteristic has led to an increasing application of different magnetic techniques, i.e. Isothermal Remanent Magnetization (IRM), Saturation Isothermal Remanent Magnetization (SIRM), Magnetic Susceptibility (χ), for biomonitoring purposes. Magnetic measurements are usually applied to leaves (Hofman et al., 2014; Kardel et al., 2012; Maher et al., 2008; Matzka and Maher, 1999; Szonyi et al., 2008), dust (Qiao et al., 2013; Sipos et al., 2014; Zhang et al., 2012), soil samples (Lourenco et al., 2012; Lu and Bai, 2006) or mosses and lichens (Salo et al., 2012; Salo and Makinen, 2014; Vukovic et al., 2015), but there are very few data in the literature about the application of these techniques to tree bark samples (Kletetschka et al., 2003) and they do not relate the data with measured metal concentrations.

As a novel approach, in this study we compared the element concentrations in tree bark with the results obtained by magnetic techniques. The aims of this study were: i) to test whether magnetic intensity in tree bark is a good proxy of the overall metal loads of the bark; ii) to test whether the two methods can discriminate among the trees located in different types of urban site (green spaces, small roads and large roads).

For achieving these goals the concentrations of selected trace elements (As, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, V and Zn) were measured in bark samples of *Jacaranda mimosifolia* collected from trees in different areas of the city of Lisbon (Portugal). The choice of the trace elements was made according to: i) the possible impact on human health; ii) the sensitivity of the analytical method and iii) the possibility to have good reproducibility and accuracy. On the same samples SIRM, IRM and χ were performed to characterize their magnetic properties. The choice of the sampling sites took into consideration the absence of industrial activities directly influencing the central area of the city.

2. Materials and methods

2.1. Sampling

Sampling was carried out in Lisbon, the capital city of Portugal. Lisbon metropolitan area has a population of 2.8 million people and is located in the estuary of river Tagus. It has a typical Subtropical-Mediterranean climate according to Köppen climate classification, with hot dry season and a mild wet season. The annual average temperature is 17.4 °C and the total annual precipitation 705.8 mm (averages from 1981 to 2010, IPMA).

Bark samples were collected in January and February 2016 from trees of *Jacaranda mimosifolia* in 34 sites. The tree species was chosen according to: i) the widespread presence in the urban area; ii) the roughness of the trunk, assuming that more rugose trunk can trap more dust/pollutants than smooth bark surface.

After a preliminary investigation of the distribution of *Jacaranda* trees in the survey area, a number of sites were selected where the species occurred and, among these, 34 sites were chosen on the basis of a stratified random sampling. Lacking information from an adequate number of monitoring stations or from other possible descriptors of atmospheric pollution, a proxy variable for traffic intensity was used. Therefore, sites were categorized according to their land use (Llop et al., 2017) into: i) large roads (two or more lanes); ii) small roads (one lane); and iii) green spaces (presence of green areas/urban parks even if very small). For each site, the closest 3 trees were selected (except for two sites, where only two trees were available).

A small portion of tree bark (approximately 30 cm^2) was removed at a height between 1.5 and 2.0 m all around the tree circumference, using a stainless-steel knife. The bark samples collected were put in a plastic bag and taken to the laboratory, where they were freeze-dried and homogenized in 25 mL Teflon grinding jars using a MM 400 Mixer Mill (Retsch, Germany).

2.2. Trace element analysis

About 0.10–0.15 g of the samples were mineralized using 5 mL of 65% (m/m) nitric acid (for trace metal analysis from Scharlau, Spain) in closed Teflon PFA vessels heated in a microwave digestion system MDS 2000 (CEM Corporation, U.S.A.). After cooling, the solutions were transferred into 25 mL volumetric flasks and diluted to volume using ultra-pure (>18 MOhm cm) water (Elgastat UHQ, Elga Ltd., U.K.). All glassware used was washed with 3 M nitric acid and rinsed with ultra-pure water.