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The influence of weather and climate on the reliability of magnetic properties of tree leaves as proxies for air pollution monitoring

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HIGHLIGHTS

- Reliability of enviromagnetic studies of tree leaves in air pollution monitoring is of concern.
- Monthly monitoring revealed anthropogenic time-related k_{lf} enhancement of tree leaves.
- Correlations of k_{lf} of tree leaves with urban dust pollutants were affected by local climate.
- Air humidity explained differences in correlation significance around the world.
- Incorporation of trace metals in the leaf tissue may also play a part.

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ABSTRACT

Monthly monitoring of magnetic properties of *Platanus hispanica* tree leaves was used to assess atmospheric pollution in Madrid (Spain) and its suburban town of Pozuelo de Alarcón. Magnetic susceptibility, isothermal remanent magnetisation and metal concentrations were analysed to study the sources of atmospheric pollutants and their spatial and temporal evolution. In addition to urban dust, our results indicated that lithogenic dust and incorporation of trace metals in the leaf tissue also control the magnetic susceptibility of tree leaves. Global comparisons with cities of different climatic regimes suggest that air humidity is the key factor controlling the relative influence of pollutants, lithogenic dust and biological effects on the magnetic properties of tree leaves. Interaction of the atmosphere and tree leaves depends not only on local meteorology but also on climate. Climate, especially air humidity, and meteorology need to be considered when interpreting the magnetic properties of tree leaves as an atmospheric pollution tool.

1. Introduction

Atmospheric pollution is one of the most important public health problems in urban areas, where anthropogenic suspended particles in the atmosphere are typically associated with a multitude of pollutants. Atmospheric aerosols smaller than 2.5 μm (PM2.5) are especially problematic, due to their increased likelihood of penetration of the respiratory tract and their potential to reach the inner walls of the alveolar ducts, thereby promoting the introduction of toxins into the bloodstream. Concerns over the concentrations of PM2.5 in urban areas stem from their link to short-term mortality rates in cities with high traffic densities and important industrial activities (Galán et al., 1999; Samet et al., 2008; Saurina et al., 1999; Silverman et al., 2010). An increase in mortality rates related to atmospheric particulates can also occur even in areas where the particulate matter (PM) concentration is lower than the official established limits, as was demonstrated by Taracido et al. (1999) for the city of Vigo, in NW Spain. Consequently, air quality assessments and continuous monitoring of its short-term variability are critical for adequate management of urban environmental quality.

Air quality is normally analysed using a network of control stations that measure gases and suspended particles. These stations are notably useful in detecting abnormally high concentrations of contaminants in the air for short periods of time (hours and days). However, their spatial and temporal resolution is generally inadequate for estimating dust transport patterns or long-term effects of contaminants. This last point has been gaining increased attention because prolonged exposure to low-level contamination (diffuse pollution) appears to have a significant influence on people's health, even to a greater extent than sporadic, high-level exposure (Moreno et al., 2003; Samet et al., 2008).

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The analysis of dust passively deposited on urban elements is a good alternative for air pollution monitoring. By studying the magnetic properties of the dust deposited on these elements, it is possible to delimit zones with high air pollution levels, as well as to constrain their origin (Thompson and Oldfield, 1986). This recent application of environmental magnetism is founded on the magnetic nature of part of the particulate matter (Petrovský and Ellwood, 1999), such as magnetite. Trace metals, such as Zn, Cd and Cr, are associated with magnetite in certain aerosols due to the direct incorporation of these metals into the mineral structure during the industrial process (Hansen et al., 1981; Magiera et al., 2011; Moreno et al., 2003). This association between magnetic properties and trace metals can also be produced indirectly due to the simultaneous production of innocuous magnetic particles with the same aerodynamic characteristics as particles enriched in trace element contaminants. Based on this relationship, magnetic particle concentrations can be used as a proxy for the presence and concentration of these atmospheric pollutants (see Rai, 2013 for a recent review). The potential of the magnetic approach is supported by the increasing number of studies that combine traditional analytical methods with the study of magnetic properties of urban dust deposited on objects, plants or samplers (Lu et al., 2008; Maher et al., 2008). The lower costs and simplicity of the magnetic methodologies enable increased spatial and temporal resolution in these types of studies (Dávila et al., 2006), both of which are critical factors in establishing viable detection and monitoring systems. Nevertheless, these methodologies can be significantly affected by the climate and the meteorology in the area under study, especially in the case of magnetic biomonitoring. While tree leaves are efficient natural urban dust accumulators, their complex interaction with the atmosphere must always be considered. To constrain the sources of variability in the magnetic properties of tree leaves, several authors have studied seasonal and inter-species variations in accumulation patterns of atmospheric pollutants (Kardel et al., 2011; Lehndorff et al., 2006; Mitchell et al., 2010; Muxworthy et al., 2001, 2003). These and other studies have evaluated the effects of the weather and meteorological conditions at a local scale, but none has considered these effects on a climatic scale, which involves longer temporal and larger spatial scales. The potential natural variability induced by climate in the magnetic properties of tree leaves must be taken into account when planning a research project.

Our research aimed to ascertain the spatial and temporal evolution of air pollutants in the city of Madrid and the adjacent residential area of Pozuelo de Alarcón (Pozuelo) to determine their origin and fate after they are deposited on the tree leaves. To accomplish this objective, we analysed the magnetic properties and metal concentrations in the urban dust deposited on tree leaves. Our results were subsequently compared with a suite of different cities with diverse demographic, climatological and meteorological conditions to understand what processes and/or thresholds control atmospheric contamination caused by suspended particles. Based on our results, we propose guidelines for establishing criteria for the selection of the most appropriate research methodology, given the climate and meteorological conditions of each study area.

2. Study area and sampling strategy

Our experimental design focused on the detection and assessment of the transfer of pollutants between the localities of Madrid and Pozuelo, in the centre of Spain (Fig. 1). Madrid is the largest urban area in Spain, with a population of more than 3 million inhabitants (3,238,208 in the Municipal Register as of January 1, 2011). The population of Pozuelo is much smaller, with 82,933 inhabitants in its Municipal Register as of January 1, 2011. The large differences between the demographics of both towns allowed for the study of the transference of airborne contaminants from a town with heavy traffic (Madrid) to a residential town with quieter conditions (Pozuelo).

Both Madrid and Pozuelo are located at 600 m above sea level with a Continental Mediterranean climate regime. Winters are cold, with temperatures below 5 °C, and summers are hot with an average temperature of 24 °C in July and August, although maxima above 35 °C are frequent. Annual precipitation exceeds 400 mm, although there is a marked seasonality with minimum rainfall in the summer (www.aemet.es). In addition, there is also a marked gradient in humidity between the wetter NW region and the more arid SE region. In May and July 2007, the predominant wind direction was WNW and WSW, respectively, changing to ENE from September to December (Fig. 2).

Sampling was completed by an environmental company, Aretech Solutions (Advance Research Technologies), in May, July, September, October, November and December 2007. Leaves of *Platanus hispanica* were obtained from trees located in two different areas separated by a *Quercus ilex* forest (Casa de Campo), where the target species was not present. The western area covered a rectangular region of approximately 2.6 × 3 km, located east of Pozuelo. The eastern region was a 2 × 3 km rectangle located west of Madrid (Fig. 1). The distance between sampled trees was approximately 0.5 km in both zones with a density of 9 sample points/km^2. *P. hispanica* occurs broadly in Madrid with an average height of 10 m. The trees blossom in April, their fruits ripen in summer and they began to lose their leaves in autumn. Five leaves were sampled per tree (one tree per sampled point) randomly approximately 2–3 m above the ground. The samples were stored in plastic bags and kept in a refrigerator at 4 °C after every day of sampling.

3. Laboratory methodology

Following the methodology of Dávila et al. (2006), three *P. hispanica* leaves were selected from each sampling site (preferably large and healthy leaves) and 50 cm^2 was cut from their centres to obtain a 150 cm^2 sample from each location to obtain representative data. The cut material was oven-dried at 40 °C and weighed every 4 h till constant weight. This material was then pressed inside standard sized plastic cylinders (2.54 × 2.2 cm) specific for palaeomagnetic measurements to fix the particles. For each sample, the low frequency magnetic susceptibility (k_{lf}) and the isothermal remanent magnetisation (IRM) were measured.

k_{lf} was measured on a MS2 Bartington magnetic susceptibility metre using the MS2B sensor at 0.47 kHz and intercalibrated with the MAGNET network laboratories (Sagnotti et al., 2003). These data were normalised by the dry mass of the leaves after confirming a good correlation with leaf area ($r = 0.903$; $p < 0.01$ and $n = 101$), which could change according to their vegetative cycle. After the k_{lf} measurement, an IRM was induced in a field of 1 T produced by a Magnetic Measurement MMPM9 pulse magnetiser. The remanence generated was measured in a Molspin Minispin spinner magnetometer with a sensitivity of $4.5 \cdot 10^{-5}$ A/m. These analyses were made systematically every five samples to minimise the time between the IRM induction and the subsequent measurement to keep nearly constant superparamagnetic effects on IRM variability.

Major and trace metal concentrations were also determined in 72 samples with high and low magnetic susceptibilities to identify the principal metals present in the leaves. Measurements were made on selected samples obtained in May, September and November. Metal extraction was performed at the University of Vigo according to the method used by Dávila et al. (2006). A second leaching aimed at evaluating the efficiency of a single wash extraction was performed in the samples collected in November. The analytical determinations of Al, Cd, Co, Cu, Fe, Mn, Ni and Zn were carried out in the central research services of the University of Vigo (C.A.C.T.I.) by means of a Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). High quality multi-element and mono-element standard solutions (Merck) were used to obtain the calibration curves. Moreover, the C.A.C.T.I. participates regularly in intercalibration programmes of atmospheric particulate matter analysis, guaranteeing the quality of the results.