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Biomagnetic monitoring of industry-derived particulate pollution

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Biomagnetic techniques are used for quantitative mapping of particulate pollution at uniquely high spatial resolution and to distinguish between differently-sourced PM_{10}.

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ABSTRACT

Clear association exists between ambient PM_{10} concentrations and adverse health outcomes. However, determination of the strength of associations between exposure and illness is limited by low spatial-resolution of particulate concentration measurements. Conventional fixed monitoring stations provide high temporal-resolution data, but cannot capture fine-scale spatial variations. Here we examine the utility of biomagnetic monitoring for spatial mapping of PM_{10} concentrations around a major industrial site. We combine leaf magnetic measurements with co-located PM_{10} measurements to achieve inter-calibration. Comparison of the leaf-calculated and measured PM_{10} concentrations with PM_{10} predictions from a widely-used atmospheric dispersion model indicates that modelling of stack emissions alone substantially under-predicts ambient PM_{10} concentrations in parts of the study area. Some of this discrepancy might be attributable to fugitive emissions from the industrial site. The composition of the magnetic particulates from vehicle and industry-derived sources differ, indicating the potential of magnetic techniques for source attribution.

1. Introduction

In recent years, identification of the adverse health effects associated with exposure to particles smaller than 10 μm aerodynamic diameter (PM_{10}), particularly those smaller than 2.5 μm in diameter ($PM_{2.5}$), has been an active and growing research area. Short-term (<1 h) exposure to peak levels of PM_{10} has been strongly associated with adverse cardiovascular and respiratory health impacts (e.g. Curtis et al., 2006; Schwarze et al., 2006). However, epidemiological and toxicological studies also indicate that longer-term cumulative exposure to relatively small increases ($<10\ \mu g\ m^{-3}$) in ambient PM_{10} and $PM_{2.5}$ concentrations impact adversely on human health (e.g. COMEAP, 2009). Additionally, Pope et al. (2009) have shown a marked improvement in health outcomes in response to programmes of active reduction of ambient particulate pollution concentrations. Their findings suggest that reductions in ambient particulate pollution concentrations of just $10\ \mu g\ m^{-3}$ are associated with increased life expectancy, independent of socioeconomic, demographic or lifestyle (e.g. smoking habits) factors.

However, the specific causal links between the degree of exposure and the likelihood/severity of adverse health impacts within a population remain uncertain, and calculated risk estimates also differ between studies (e.g. Schwarze et al., 2006). This may be due at least in part to the reliance of many epidemiological studies on exposure data from relatively low spatial-resolution networks of monitoring stations (e.g. up to 5 miles from residences; e.g. Karr et al., 2006; Woodruff et al., 2006). Such coarse-scale data are a limiting factor in determining dose response relationships at an individual rather than population level, due to finer-scale variations in particulate pollution concentration and/or size across the urban environment (e.g. Brook et al., 2004; Monn, 2001), depending on particle source.

A global increase in implementation of mitigation techniques (e.g. Balat, 2008; Minguillón et al., 2009) has led to a decline in emissions of industrially-sourced particulate matter (e.g. EEA, 2008). However, despite decreasing pollution emissions from industrial point sources, monitoring shows that industry continues to impact on local and regional particle concentrations at a range of distances from the source (e.g. Sharma and Tripathi, 2008; Wang et al., 2010). Our ability to fully understand and quantify, and hence manage down, such contributions is currently limited by the scarcity of monitoring data that are generally available. While temporal resolution is high, spatial coverage tends to be poor,

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limiting our ability to resolve between, for example, multiple sites of emission.

In an effort to address the low spatial density of conventional fixed monitoring stations, PM_{10} surfaces have been modelled. Atmospheric dispersion modelling systems such as ADMS 4.1 (CERC Ltd., Cambridge, UK; CERC, 2010) or AERMOD (US Environmental Protection Agency; U.S. EPA, 2010a) are widely used to model emissions from industrial pollution sources for regulatory purposes. Dispersion models use meteorological data, stack height and diameter, in addition to estimates of emission quantities, temperature and exit velocity, to model the dispersion of industry-derived particulate emissions. However, validation data at high spatial resolution are sparse, and quality of model parameters can be limited; for example, emission data are often approximated from diurnally-trended monthly fuel usage, while data taken from the nearest meteorological station to the study area may not be fully representative due to local-scale variability. Additionally, detailed knowledge of all emissions (especially on complex sites) and the effects of varying terrain on PM dispersion and deposition is limited at present, resulting in uncertainty in modelled results (e.g. Parker and Kinnersley, 2004).

There is thus a need for high spatial-resolution particulate pollution monitoring techniques which are able to capture local variation in pollutant concentration.

Biomagnetic monitoring, using tree leaves as sampling surfaces, can generate high spatial-resolution PM_{10} proxy data. Whilst urban anthropogenic particulates may consist of a complex mixture of organic and inorganic components, they almost invariably contain magnetic particles, which derive from iron impurities in the fuel. Upon combustion, a non-volatile magnetic residue is formed, often a mixture of ferrimagnetic (magnetite/maghemite-like) and imperfectly antiferromagnetic (haematite-like) iron oxides. In urban particulates, a strong correlation has been observed between magnetic susceptibility/remanence and PM_{10} concentrations (e.g. Morris et al., 1995; Muxworthy et al., 2003; Sagnotti et al., 2006; Szönyi et al., 2008), as a proxy for particulate pollution concentrations. Magnetic techniques are sensitive and rapid (e.g. Matzka and Maher, 1999; Muxworthy et al., 2003; Maher et al., 2008; Szönyi et al., 2008). Tree leaves provide particularly good sampling surfaces as they are already prevalent throughout the urban environment and require no power source or protection from vandalism. Whilst this approach is limited, for deciduous species, to the in-leaf season (i.e. ~ 8 months p.a.), the spatial resolution of PM_{10} mapping enabled by this technique represents a step change improvement in current data availability.

This study focuses on deciduous tree leaves, reflecting both species availability in the study area (S. England) and previously established species inter-calibration data (Mitchell et al., 2010). In order to identify ambient particulate pollution levels, it is necessary to use leaves from tree species which reach dynamic equilibrium with ambient PM_{10} concentrations rapidly, i.e. by surface capture of particles (Mitchell et al., 2010) rather than internal uptake of particles into the leaf structure (e.g. Lehndorff et al., 2006). Leaves from the deciduous species used here (Methods section below) have been found to reach magnetic dynamic equilibrium (e.g. Chamberlain and Chadwick, 1972) at the roadside after ~ 6 days (Mitchell et al., 2010) compared to an equilibration time of >2 years for evergreen species (e.g. Lehndorff et al., 2006).

Variations in leaf shape and surface morphologies are the probable cause of variations in particulate dry deposition velocities to the leaf surface of different tree species. Deposition velocity of particles to ridged/hairy leaf surfaces is likely to be much greater than to smooth/waxy leaves. Consistent deposition velocities have been reported for several tree species (e.g. Freer-Smith et al., 2005; Mitchell et al., 2010). Magnetic measurements of leaves from several deciduous species can thus be inter-calibrated (Mitchell et al., 2010), optimising sampling density and resultant spatial resolution of the proxy PM_{10} data.

Previous work has shown that magnetic biomonitoring can be a robust, quantitative technique for identifying ambient concentrations of anthropogenic PM_{10}; strong correlation has been demonstrated between leaf saturation remanent magnetisation (SIRM) and/or magnetic susceptibility (χ) values and the amount of combustion- and/or abrasion-derived pollution particles on the leaf surface (e.g. Halsall et al., 2008; Maher et al., 2008; Szönyi et al., 2008). Correlations between magnetic parameters and toxic metals, such as lead, zinc and iron, have also been identified (e.g. Lu and Bai, 2006; Maher et al., 2008; Morton-Bermea et al., 2009).

Here, we report a biomagnetic study which monitored particulate pollution around a large combustion plant in the U.K.. The site has 1 chimney stack, ~200 metres tall, with annual mean emission rates ~ 6 $m\,s^{-1}$ (range = 0.1–11.89 $m\,s^{-1}$). First, we examine leaf-magnetic data, combined with co-located ambient PM_{10} concentrations (from SidePak AM510 personal aerosol monitors), in order to assess how representative leaf magnetic values are of ambient particulate concentrations. We then use the biomagnetic data to quantify PM_{10} concentrations at high spatial resolution, and compare the leaf-derived and measured PM_{10} concentrations with those predicted by a conventional dispersion model. Finally, we briefly compare the magnetic characteristics of vehicle- and industry-derived pollutant particles from sites in the U.K.

2. Methods

A pilot biomagnetic study was carried out in 2006, with leaves sampled from 12 sites along north and east transects (9 km N and 11 km E) originating at the elevated stack of a large combustion plant located in England. Subsequently, leaves from 52 sites around the plant were sampled at monthly intervals from May to September, 2008, with an additional campaign in September 2009 (Fig. 1). Rainfall and transient inputs of relatively 'non'-magnetic PM_{10} from distal sources (e.g. tropical/subtropical dust storms) can affect the attainment of dynamic equilibrium between leaf surface and ambient PM_{10} concentrations (Sagnotti et al., 2006). Available fixed monitoring station data indicate that the sample locations used in this study were not influenced by transient peaks in long range transported particulates. To minimise any local meteorological effects, sampling was always done within two consecutive, rain-free days.

With the exception of the 2006 pilot study (when both high tree and low shrub canopy samples were collected), leaf samples were collected at 1.5–2 m height from trees located at >30 m from any road, in order to minimise the contribution from immediately adjacent sources, such as traffic (e.g. Hoffmann et al., 1999; Szönyi et al., 2008). To obtain data at highest possible spatial resolution, using the previously-established inter-species calibration (Mitchell et al., 2010), the following tree species were sampled: birch (*Betula pendula*), beech (*Fagus sylvatica*), lime (*Tilia platyphyllos*), field maple (*Acer campestre*), ash (*Fraxinus excelsior*), sycamore (*Acer pseudoplatanus*), elder (*Sambucus nigra*), elm (*Ulmus procera*), and willow (*Salix alba*).

All leaf samples were refrigerated at 5 °C before being taken to the Centre for Environmental Magnetism and Palaeomagnetism (CEMP) at Lancaster University for magnetic analysis using the protocol outlined in Mitchell and Maher (2009). Appendix 1 provides a short explanation of the magnetic parameters used.

Co-located PM_{10} concentration data were collected from a subset of sites (37) over the whole sample area during the September 2009 campaign, using handheld SidePak AM_{510} personal aerosol monitors.

3. Results

3.1. Leaf magnetic values and particulate pollution

In the initial pilot study (2006), leaf magnetic enrichment ratios (ER) were measured for leaves from 12 locations along north and east sampling transects (Fig. 2). Leaves were collected from both high (>1.5 m) and low (<0.5 m) canopy vegetation. For calculation of the ERs, all values were divided by a 2006 background (leaf area-normalised) SIRM value (measured >10 km from the source) of 3×10^{-6} A; this value is consistent with measured background