ARTICLE IN PRESS

Atmospheric Environment xxx (2009) 1–9

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution

R Mitchell*, B.A. Maher

Centre for Environmental Magnetism and Palaeomagnetism, Lancaster Environment Centre, University of Lancaster, Farrer Avenue, Lancaster, LA1 4YQ, UK

ARTICLE INFO

Article history:
Received 17 November 2008
Received in revised form
23 January 2009
Accepted 28 January 2009

Keywords:
Magnetic biomonitoring
Roadside tree leaves
Vehicle pollution
Atmospheric modelling dispersion,
Lancaster, UK

ABSTRACT

Inhalation of particulate pollutants below 10 μm in size (PM_{10}) is associated with adverse health effects. Here we use magnetic remanence measurements of roadside tree leaves to examine levels of vehicle-derived PM around Lancaster, UK. Leaf saturation remanence (SIRM) values exhibit strong correlation with both the SIRM and particulate mass of co-located, pumped-air samples, indicating that these leaf magnetic values are an effective proxy for ambient PM_{10} concentrations. Biomagnetic monitoring using tree leaves can thus provide high spatial resolution data sets for assessment of particulate pollution levels at pedestrian-relevant heights. Leaf SIRM values not only increase with proximity to roads with higher traffic volumes, but are also ~100% higher at 0.3 m than at ~1.5–2 m height. Magnetic and SEM data indicate that the particle populations are dominated by spherical, iron-rich particles ~0.1–1 μm in diameter, with fewer larger, more angular, silica-rich particles. Comparison of the roadside leaf-calculated PM_{10} concentrations with PM_{10} concentrations predicted by a widely-used atmospheric dispersion model indicates some agreement between them. However, the model under-predicts PM_{10} concentrations at 'urban hotspots' such as major–minor road junctions and traffic lights. Conversely, the model over-predicts PM_{10} concentrations with distance from the road wherever one tree is screened by another, indicating the filtering/protective effect of roadside trees in leaf.

1. Introduction

The presence in the atmosphere of pollutant particles below 10 μm (PM_{10}), particularly those below 0.1 μm ($PM_{0.1}$), is of current concern due to adverse health effects associated with their inhalation (e.g. Calderón-Garcidueñas et al., 2004; Morris et al., 1995; Oberdörster, 2000; Pope et al., 2004). Indeed, particulate matter is thought to be the most harmful pollution component widely present in the environment (Donaldson, 2003), with no known level at which adverse health effects do not occur (Bealey et al., 2007).

European Air Quality Standards for PM_{10} were established in 1999 (regulation 99/30/EG), with daily maxima set at 50 μg m^{-3}, not to be exceeded more than 10 times annually, with a maximum annual mean of 40 μg m^{-3}. Tighter regulation will become effective in 2010; 50 μg m^{-3} not to be exceeded more than 7 times in a year with a 20 μg m^{-3} maximum annual mean (excluding Scotland, 18 μg m^{-3}, and Greater London, 23 μg m^{-3}). Where these levels are regularly exceeded, Air Quality Management Areas (AQMA) are ordered, in which mitigation measures must be enforced in order to lower the ambient PM_{10} concentrations.

In the UK, and elsewhere in western Europe, increased implementation of mitigation techniques has led to a decline in industrially-sourced PM emissions; however, vehicle usage is increasing annually (DfT, 2007). This is combined with an increase in diesel-fuelled vehicles, particularly light vans (DfT, 2007) which, compared with petrol vehicles, produce up to 2 orders of magnitude more PM_{10} (e.g. Nicolay, 2000; Rudell et al., 1999), enriched in toxic heavy metals such as Pb, Zn and Fe (e.g. Huhn et al., 1995; Harrison and Jones, 1995).

Various parameters, such as NO_2, polycyclic aromatic hydrocarbon (PAH), and volatile organic compound (VOC) levels, have been used in addition to PM mass and reflectance measurements, to identify and characterize ambient pollution levels and sources (e.g. Kingham et al., 2000; Fischer et al., 2000; Kaur et al., 2005; Xie et al., 2003) but many of these analyses are time-consuming, expensive and may not provide a robustly representative measure of pollutant exposure to pedestrians or drivers (e.g. Urbat et al., 2004).

Dispersion of pollution particles is affected by road geometry, street canyon effects and meteorological conditions, particularly

* Corresponding author. Tel.: +44 1524 510221.
E-mail address: r.mitchell@lancaster.ac.uk (R. Mitchell).

1352-2310/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2009.01.042

wind speed and direction (e.g. Micallef and Colls, 1999; Xie et al., 2003). Atmospheric dispersion modelling systems such as ADMS-urban (CERC Ltd., Cambridge, UK) or AERMOD (US Environmental Protection Agency) use traffic count, speed and composition, in addition to predefined emission factors, to estimate vehicle-derived particulate emissions, and estimate their dispersion. It is possible to use measurements from PM_{10} monitors to calibrate/validate models (e.g. Micallef and Colls, 1999), allowing estimation of pollution levels at greater spatial resolution than measurement methods can currently enable. However, detailed knowledge of 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). To reduce this uncertainty, techniques capable of measuring urban pollutants at greater spatial resolution are required.

Strong correlation has been demonstrated between leaf saturation magnetic remanence (SIRM) and susceptibility values and the presence of anthropogenic ferrimagnetic particles produced by industrial and vehicular combustion, and metal abrasion (Flanders, 1994; Matzka and Maher, 1999; Hoffmann et al., 1999; Gautam et al., 2004; Knab et al., 2001; Maher et al., 2008; Halsall et al., 2008). Magnetic techniques, which are sensitive, fast and relatively cheap to carry out, have the potential to provide unprecedentedly high spatial density data sets for assessment of pollution levels (Matzka and Maher, 1999; Muxworthy et al., 2003; Gautam et al., 2005; Maher et al., 2008; Szönyi et al., 2008). Biomagnetic pollution monitoring uses plant leaves as natural biomonitors, as they provide a large surface area for PM collection (Matzka and Maher, 1999; Urbat et al., 2004; Gautam et al., 2005), and require no power source or protection from vandalism. A further benefit of this approach is the ability to obtain leaf samples from heights of pedestrian relevance, in contrast with conventional sampling station inlets, which are fixed at heights often in excess of 2.5 m. Because PM_{10} concentration and composition change with height (Tuch et al., 2003; Maher et al., 2008), samples obtained closer to head height can be assumed to have more relevance for human exposure.

Here, we report a biomonitoring study (based in Lancaster, UK) which first examines co-located leaf and pumped air sample measurements, in order to assess how representative leaf magnetic values are of ambient particulate concentrations. Second, we examine the mineralogy and particle characteristics of leaf PM_{10}. We then use the biomagnetic data to calculate PM_{10} concentrations for comparison with concentrations estimated by a conventional dispersion model. We show that biomagnetic monitoring can be used to: provide robust quantitative estimates of PM_{10} concentrations, at much higher spatial resolution than from conventional pollution monitoring; highlight target areas for mitigation of human exposure levels; and estimate the screening/filtering effects of roadside vegetation.

2. Study area

Lancaster is a small town in north-west England (2001 population 133,914; National Statistics, 2001) with little industry but high levels of traffic, particularly on the main ring road which surrounds a pedestrianized town centre.

An air quality management area (AQMA) order was declared in Lancaster based on NO_2 data (from diffusion tube sampling in 2004), which indicated potential exceedence of the mean NO_2 annual air quality standard (AQS) around the city centre's one-way traffic system (Fig. 1). Conversely, for PM_{10}, non-compliance with the UKAQS was recorded (at Lancaster's sole conventional fixed monitoring station, adjacent to sampling site 1; Fig. 1), on only four occasions in 2006. The annual PM_{10} measured at the city centre site was 24.0 μg m^{-3} (from tapered element oscillating microbalance (TEOM) measurements), compared with, for example, 47.4 μg m^{-3} at London, Marylebone and 19.5 μg m^{-3} in Inverness (UK National Air Quality Archive, 2008). In order to investigate traffic-derived pollution in greater spatial detail across this contentious area, we sampled roadside leaves at a number of sites (sites 1–7; Fig. 1) within the perimeter of the city ring road.

3. Methods

3.1. Sampling

Most of the leaf samples were collected in early autumn 2007 from sites in close proximity to the southern loop of the ring road (Fig. 1), with a few additionally from background and suburban areas. Leaves were only collected from lime trees (*Tilia platyphyllos*), in order to avoid possible species-dependent differences in PM collection (e.g. Ferretti et al., 1995; Moreno et al., 2003). Samples consisting of 6 leaves were collected (08/10/07) from trees distributed over the Lancaster area; given previous reports of height-dependent pollution concentrations (Maher et al., 2008), samples were taken from adult head height (~1.5–2 m) and, where available, at ~0.3 m height. Exposure times were standardized by selecting the youngest leaves with the least senescence (as sampling was done in late autumn, even these leaves had been exposed for many weeks). Over a period of 3 h, 30 trees were sampled; samples were placed in plastic bags to avoid contamination. Sampling was repeated one day later (09/10/07); all samples were refrigerated at 5 °C before being returned to the laboratory for analysis. The surface area of each leaf was measured by pixel counting of their scanned images (Matzka and Maher, 1999); each sample of 6 leaves was then prepared for magnetic analysis by folding the leaves to fit, immobile, inside a 10 cc plastic pot.

For independent analysis of ambient PM_{10} concentrations, pumped air samples (120 L) were collected at a rate of 2 l min^{-1} for 1 h, from each sampled tree location, using SKC Leyland Legacy personal monitors fitted with magnetically clean ($SIRM = 1 \times 10^{-10}$ $Am^2/1 \times 10^{-3}$ $m^2 = 1 \times 10^{-7}$ A) PTFE filters (1 μm pore size). After exposure, filters were immediately placed in magnetically clean ($SIRM = 4 \times 10^{-10}/2 \times 10^{-3}$ $m^2 = 2 \times 10^{-7}$ A) 10 cc plastic pots and taken to the laboratory for magnetic analysis.

3.2. Magnetic measurements

A range of magnetic properties was measured for the leaf and air filter samples, in order to identify their major magnetic minerals and dominant magnetic grain size (many magnetic properties are grain size-dependent, since grain size determines the number of magnetic domains into which a crystal can sub-divide). All magnetic measurements were carried out at the Centre for Environmental Magnetism and Palaeomagnetism (CEMP) at Lancaster University. Magnetic susceptibility was initially measured, using a Bartington susceptibility meter, on a subset of samples. Values for both wet (fresh) and dry samples were small and negative, indicating that despite the late-season sampling, the concentration of magnetic particles was insufficient to overwhelm the diamagnetic nature of the water and organic content of the leaves. This indicates that, unlike cities like Rome (Szönyi et al., 2008), Lancaster's levels of particulate pollution are too low for leaf magnetic susceptibility to be used as a pollution proxy.

The susceptibility of anhysteretic remanent magnetization (χ_{ARM}) was then measured; this parameter is especially sensitive to the presence of sub-micrometre magnetic particles (Özdemir and Banerjee, 1982; Maher, 1988). The ARM was imparted at

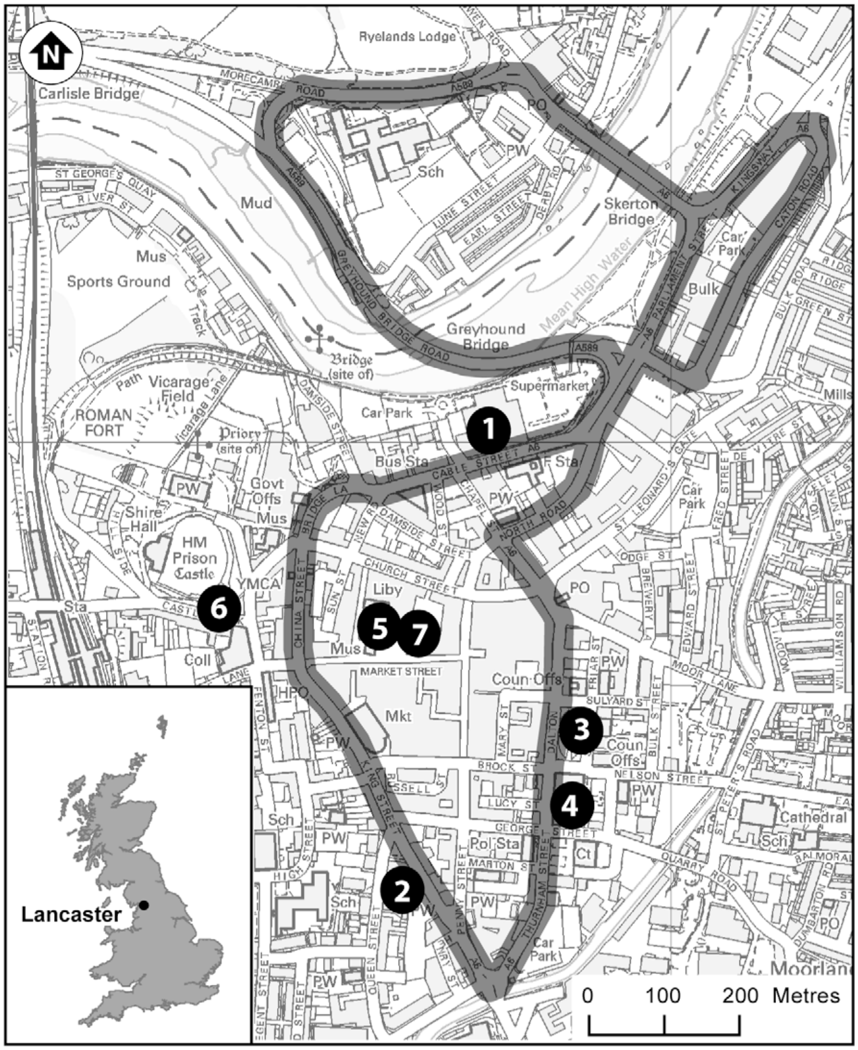

Fig. 1. Location map indicating the AQMA Order 2004 boundaries (grey band), this study's urban sampling sites and Lancaster's location within the UK.

80 milliTesla (mT) in a 0.08 mT dc biasing field (using a Molspin demagnetizer with ARM attachment), and subsequently AF-demagnetized in fields of 20, 50 and 100 mT.

Room-temperature remanent magnetisation (IRM) was then incrementally acquired (in dc fields at 20, 50, 100 and 300 mT) using a Molspin pulse magnetizer. The 'saturation' remanence (SIRM), acquired by subjecting samples to an applied magnetic field of 1 T generated using a Newport electromagnet, was used to indicate the total concentration of magnetic particulates (Muxworthy et al., 2003). The high-field remanence (% HIRM), i.e. the % remanence acquired at fields between 300 mT and 1 T $(((SIRM_{1T} - IRM_{300mT})/SIRM)100)$ indicates remanence acquisition by high-coercivity antiferromagnetic minerals, like haematite (αFe_2O_3) and goethite (αFeOOH). The samples were then stepwise AF demagnetized at 20, 50 and 100 mT. In order to identify any diagnostic magnetic transitions, low-temperature leaf remanence properties were measured by cooling samples to 77 K (-196 °C) with liquid nitrogen, in the absence of an applied field. Remanence was then imparted at 1 T using a Newport electromagnet. The sample was subsequently measured repeatedly in the zero-field sample space of the Molspin magnetometer as the sample warmed to room temperature. (A type T thermocouple was used to measure the rate at which the sample warmed, prior to the magnetic analysis, to allow time to be substituted for temperature during the magnetic measurement sequence).

All leaf remanence values were measured using a Molspin Minispin magnetometer (sensitivity level $\sim 1 \times 10^{-8}$ A) and normalized for leaf surface area (Matzka and Maher, 1999). The magnetometer was calibrated routinely (i.e. after ~ten sample measurements) against a laboratory rock specimen, in turn independently checked through international inter-laboratory calibration undertaken through the MAG-NET research programme (Sagnotti et al., 2003). Magnetic measurements of the pumped air filters were carried out using an Agico JR-6 magnetometer (cross-calibrated with the Molspin magnetometer) and normalized for surface area.

3.3. Scanning electron microscopy

Finally, subsamples of leaf, filter and potential source materials were mounted on carbon stubs and, without further pre-treatment, scanning electron microscopy was carried out (at the Dept. of Earth Sciences, Glasgow University) using an environmental SEM (FEI Quanta 200F) equipped with a Pegasus 2000 energy dispersive X-ray microanalysis (EDX) system. For particle size determinations, measurement was made of the longest axis of each of 100 particles

Please cite this article in press as: Mitchell, R, Maher, B.A., Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution, Atmospheric Environment (2009), doi:10.1016/j.atmosenv.2009.01.042

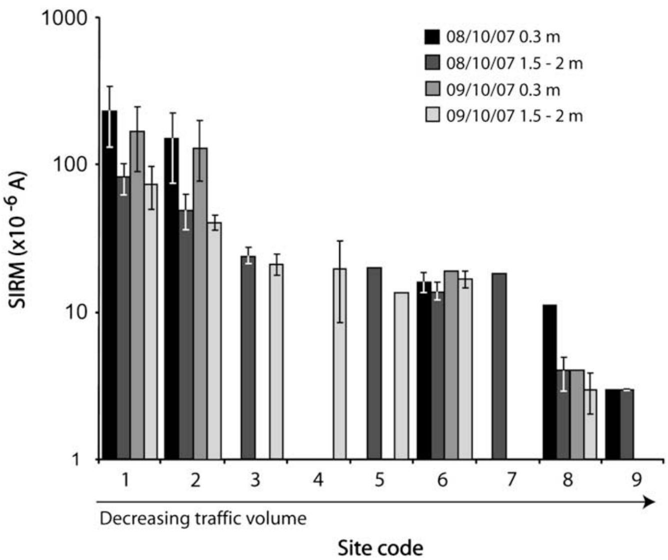

Fig. 2. Mean SIRM (and s.d.) values of leaves sampled at various locations around Lancaster, UK. Data presented are mean values for all samples from each sampling height, at each site on 08/10/07 and 09/10/07. Between the two sampling days, there was heavy rainfall (9 mm between 1 am and 6 am 09/10/07). Data only available for one day at Sites 4, 7 and 9. The greatest decrease is observed at sites with greater traffic flows (possibly due to the presence of more, but less well adhered, particles).

from the enlarged SEM images. For elemental analyses, elemental maps were obtained for 18 separate particle groupings (i.e. encompassing several hundreds of particles).

4. Results

4.1. Leaf magnetic values and particulate pollution

Leaf magnetic remanence values (X_{ARM}, SIRM and $\%IRM_{100}$ and $\%IRM_{300}$), from nine sampled locations across the AQMA and at background parkland and suburban sites, are presented in Appendix 1. SIRM values are minimal for background and suburban trees and increase with proximity to roads with higher traffic volumes (Fig. 2). For leaves sampled from a heavily-trafficked section of the ring road (Site 1, Fig. 1), the mean leaf-area normalized SIRM value at 1.5–2 m was 81×10^{-6} A. This compares with a mean background value (from trees sampled at a suburban park) of 3×10^{-6} A (Site 9, Fig. 1), resulting in roadside SIRM enrichment ratios (ER) of 27. This is consistent with the enrichment ratio observed on a road with a similar traffic flow in Norwich (ER 26.7, sample date 1999) (Maher et al., 2008). The maximum roadside enrichment ratio for any individual sampled tree, occurring at 0.3 m height at Site 1, was >100 (i.e. maximum SIRM $= 332 \times 10^{-6}$ A, see Appendix 1). Individual samples (Sites 1, 2 and 3, see Appendix 1) displayed notably high SIRM values wherever traffic remains stationary for periods of time, specifically, at minor–major road junctions and at traffic lights. With just one exception, the mean lime tree leaf remanences were reduced (by 12–64%) after a rainfall event between the two sampling days (Fig. 2). Only at Site 5 (sheltered by buildings on three sides) did the remanence increase, by ~20%.

At all sites where leaves were sampled at 0.3 m and 1.5 m height, SIRM values were up to 50% lower at 1.5–2 m than at 0.3 m height (Appendix 1).

To assess how representative the tree leaves are as surfaces for PM collection, pumped air samples (120 L) were collected for 1 h at each sampled tree location. There is strong correlation both between pumped air filter and mean leaf SIRM values ($R^2 = 0.9$, $n = 18$, $\sigma = 0.01$; Fig. 3a), and between the filter SIRM and filter particulate mass ($R^2 = 0.9$, $n = 18$, $\sigma = 0.01$; Fig. 3b). The mean leaf SIRM values are thus strongly correlated with the pumped air particulate concentration ($R^2 = 0.8$, $n = 18$, $\sigma = 0.01$; Fig. 3c).

At all locations except one, filter SIRMs were higher at ~0.3 m than ~1.5 m height (Appendix 1). For example, the air filter from 0.3 m height at the major road location (Site 1) displayed SIRM values ~4 × the background site (Site 9); the filter from 1.5 m height SIRM values ~2.5 × background. At the one exceptional site (Site 7), the SIRM of the higher filter sample was ~1.8 × that of the lower sample. This site also displayed the highest % HIRM value of any of the sites.

4.2. Magnetic mineralogy and particle characteristics

The leaves acquired most magnetic remanence at low applied fields; ~20% was acquired below 20 mT, ~45% by 50 mT and ~75% by 100 mT. This indicates the presence of magnetically 'soft' material (i.e. easily magnetized and demagnetized), such as magnetite (Fe_3O_4). Between 21 and 26% of the SIRM was acquired between 100 and 300 mT, with up to 9% acquired above 300 mT (% HIRM). However, for all but one site, ~99% of this 0.1–1 T remanence was removed by AF demagnetization at 100 mT. This apparently paradoxical behaviour, with remanence acquisition particularly at intermediate fields (100–300 mT) but its ready subsequent demagnetization, probably reflects the presence of some partially oxidized, 'maghemitised' magnetite (Liu et al., 2002; Maher et al., 2004). In contrast, the samples from Site 7, which display the highest % HIRM value (~9%), retain ~50% of their HIRM upon demagnetization. Such magnetic behaviour is characteristic of haematite of ~0.2 µm grain size (Maher et al., 2004). This site comprises a city centre 'pedestrianised' road with access only for commercial vehicles and garbage collection.

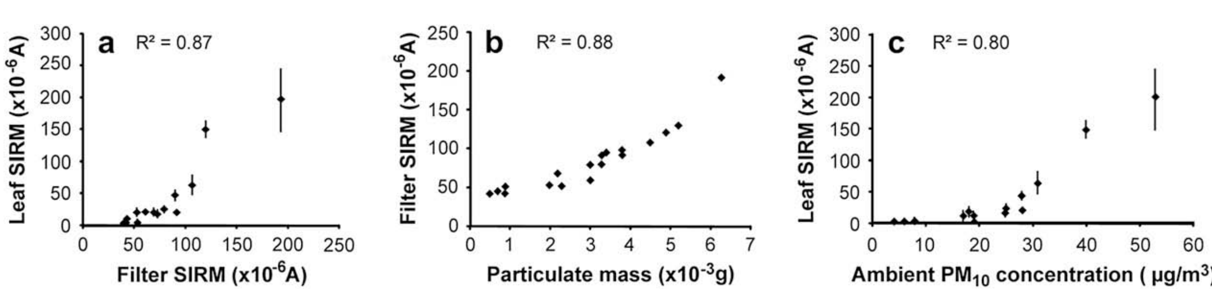

Fig. 3. Correlations (R^2 values) between (a) leaf and filter SIRM values ($R^2 = 0.9$, $n = 14$, $\sigma = 0.01$), (b) filter SIRM and pollutant particulate mass ($R^2 = 0.9$, $n = 18$, $\sigma = 0.01$) and (c) leaf SIRM and ambient PM_{10} concentrations ($R^2 = 0.8$, $n = 14$, $\sigma = 0.01$). NB: At some filter sites, leaves were not available at each sample height . At sites sampled on both sampling days, the mean of the day 1 and day 2 leaf SIRM data is used (the range also indicated on the figure).

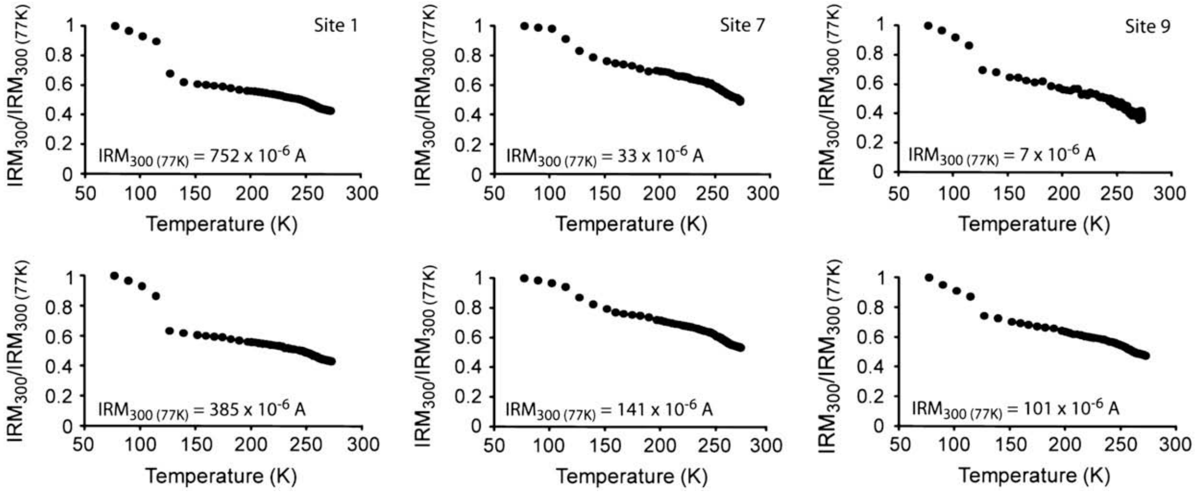

Fig. 4. IRM_{300mT}/temperature data normalized for values acquired at 77 K; leaf (top) and filter (bottom) samples obtained from various locations. Verwey transitions are apparent in all samples at temperatures ranging between 114 and 127 K, diagnostically indicating the presence of magnetite and/or partially-oxidized magnetite at each site. The differing degrees of demagnetization may reflect varying degrees of magnetite oxidation and/or the possible presence of some admixed SP particles (e.g. Özdemir et al., 1993).

Upon warming from 77 K, the $SIRM_{77K}$ shows varying degrees of remanence loss between 114 and 127 K for all of the leaf and air filter samples, associated with the Verwey transition (Fig. 4). This diagnostically identifies magnetite and/or partially-oxidized magnetite as the dominant leaf and filter magnetic component (Halgedahl and Jarrard, 1995; Özdemir et al., 1993). The continued steady loss in remanence beyond the Verwey transition may indicate either multidomain relaxation effects and/or unblocking of superparamagnetic (SP) magnetite particles (e.g. Muxworth et al., 2002).

Identification of magnetite as the dominant magnetic component of the leaf particles enables assessment of their magnetic grain size, through use of key magnetic ratio parameters (independent of magnetic concentration and particularly sensitive to changes in magnetic grain size). Fig. 5 shows comparison of the leaf and air filter χ_{ARM}/SIRM ratios and median destructive field (MDF_{ARM}) values with those for magnetites of known grain size (Maher, 1988), and indicates that the dominant size of the leaf and filter magnetic particles is between ~0.1 and 1 μm (Özdemir and Banerjee, 1982; Maher, 1988).

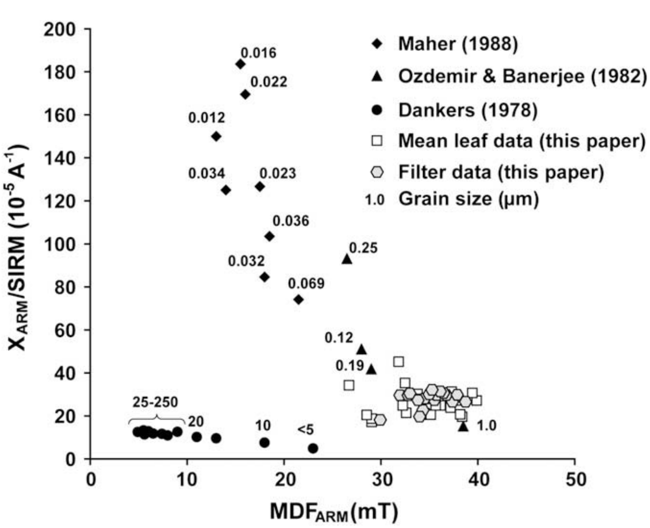

Fig. 5. Comparison of leaf and filter χ_{ARM}/SRM ratios and MDF_{ARM} values with magnetite particles of known grain sizes (Maher, 1988; Dankers, 1978; Özdemir and Banerjee, 1982).

SEM analysis of the leaf and co-located air filter particles identifies the presence of a range of particle sizes, morphologies and compositions. Particles appear concentrated along ridges in the leaf surface (Fig. 6a & c). Many of the finer particles (<500 nm) are agglomerated, most likely due to magnetic interactions between particles. More than 50% of the sub-micrometre particles comprise rounded spherules (Fig. 6e, arrowed in Fig. 6c & d), in contrast to the larger particles which generally exhibit a more angular morphology. Elemental analysis by EDXA indicates that many of the sub-micrometre particles, both on the leaves and for vehicle exhaust particles collected on a filter, are typically iron-rich, whilst the larger, more angular particles appear characterized by higher concentrations of aluminium and silica (e.g. Fig. 7a and b).

4.3. Comparison of leaf-calculated PM_{10} with modelled PM_{10}

Given the strong correlation demonstrated between the magnetic properties of roadside tree leaves and the particulate mass and concentration of co-located pumped air samples, leaf magnetic values can be used as a robust, quantitative proxy for particulate pollution. They can therefore be used to test modelled predictions of urban PM_{10}. Here, we compare the leaf-calculated mean PM_{10} concentrations with predictions from a widely used dispersion model, ADMS -Urban (CERC, 2009) of PM_{10} concentrations in Lancaster (Fig. 8). These two independent data sets show some, albeit limited, correlation ($R^2 = 0.6$, $n = 24$, $\sigma = 0.01$). However, notable disparities also occur. The model under-estimates PM_{10} concentrations at heavily-trafficked roads, major–minor road junctions and traffic lights, and over-estimates PM_{10} at sites with multiple trees (Fig. 8). Similarly, this model over-predicts PM_{10} concentrations at the 'background', parkland site.

5. Discussion

The data presented here demonstrate that despite the different time windows of sampling, the actively-sampled pumped air samples ($2\ l\ min^{-1}$ for 1 h during peak traffic flow) and the passively-collecting leaf samples (~days) display strong direct correlation of their SIRM values. This suggests that the leaves collect a representative portion of traffic-derived particulates, which are dominantly produced during the two periods of peak traffic flow per day (Mitchell and Maher, in prep.) Further, strong correlation exists

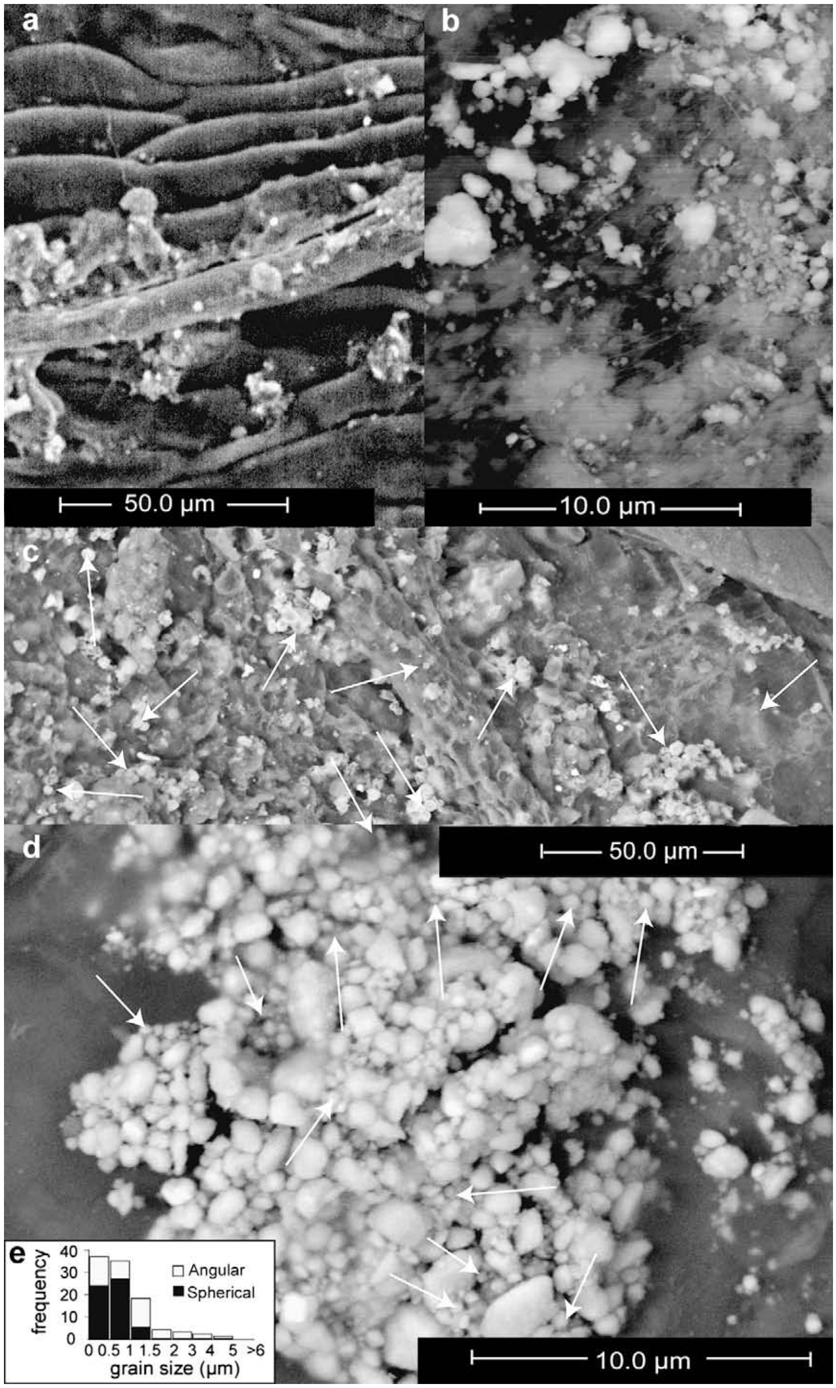

Fig. 6. SEM images of roadside leaves and pumped-air filter: (a) Site 5, particulate pollutants preferentially collected along ridges in the leaf surface; (b) Site 1, air filter co-located with the tree sample shown in (d); (c) and (d) Site 1, roadside tree leaf, showing mixture of particle sizes and morphologies including numerous spherules (arrowed) as well as more angular particles; (e) histogram of particle size and morphology count from Site 1.

between the air filter SIRMs and the filter PM_{10} mass and ambient PM_{10} concentrations. This demonstrates that a) leaves provide a robustly representative surface for collection of PM_{10} pollutant particles, and b) magnetic measurements of roadside leaves provide a robust, quantitative proxy for ambient PM_{10} particulate concentrations in this traffic-dominated urban setting.

As shown by the low-temperature IRM analyses, the dominant magnetic mineral present in the particle assemblages is magnetite, some of which may be partially oxidized to maghemite (and contributing the intermediate $IRM_{100-300mT}$ which is subsequently unstable upon af demagnetization). For one site (site 7), haematite probably contributes the % HIRM which is stable upon af demagnetization. Comparison of the leaf and air filter magnetic ratio data with those for magnetites of known grain size indicates a dominant magnetic grain size of ~0.1–1 μm, very similar to the mean grain size reported by Muxworth et al. (2002) for pollutant particles sampled in Munich. However, the varying temperature and degree of expression of the Verwey transition may indicate some suppression of the transition, possibly caused by the presence of SP magnetic particles (i.e. $<\sim 0.03$ μm) and/or partially oxidized

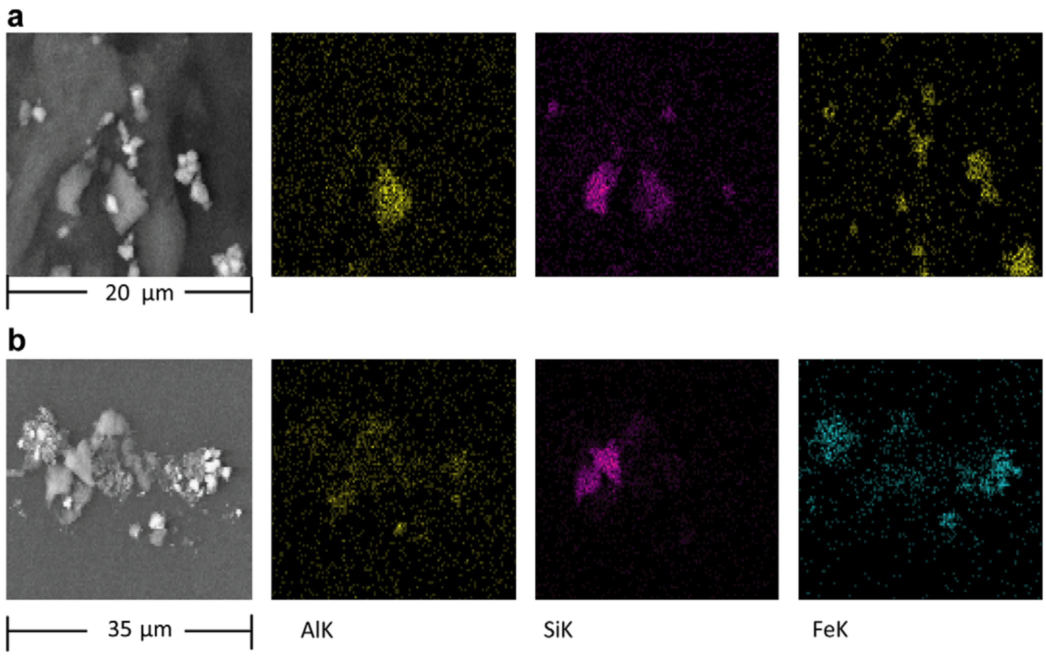

Fig. 7. EDXA for (a) leaf and (b) pumped-air filter, indicating respective contents of aluminium, silica and iron.

magnetite (Özdemir et al., 1993). The decreasing remanence (and possible SP 'unblocking') beyond the Verwey also suggests the presence of some SP grains (Muxworthy et al., 2002). Since, particles <0.1 µm have the greatest potential for adverse impacts on human health (Donaldson, 2003), further analysis of our leaf and air filter particles is currently underway, using transmission electron microscopy in order to resolve the sub-micrometre grain population.

Independent analysis of the particulate pollutants by SEM identifies particle morphologies comprising a mix of spherical, iron-rich, combustion-derived particles (especially within the sub-micrometre size range) and larger (up to 5 µm), more angular

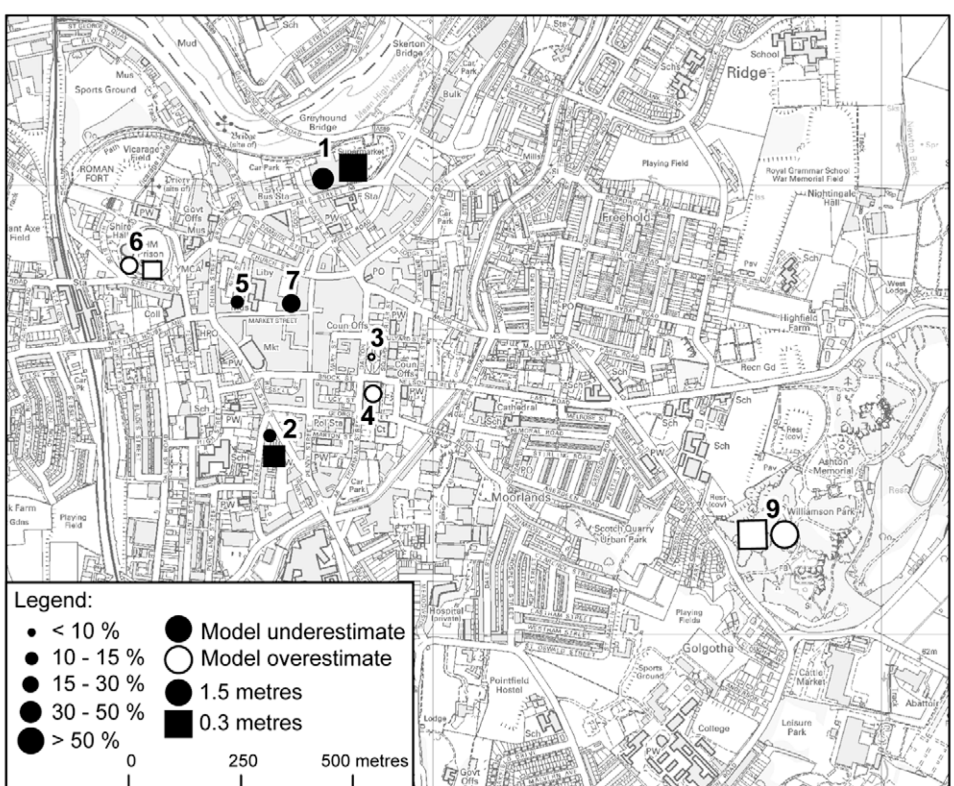

Fig. 8. Residuals (%) of modelled PM_{10} concentrations from correlation with leaf-calculated PM_{10} concentrations at 0.3 and 1.5–2 m.

Please cite this article in press as: Mitchell, R, Maher, B.A., Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution, Atmospheric Environment (2009), doi:10.1016/j.atmosenv.2009.01.042

particles. The larger particles are dominantly associated with the presence of Al and Si. Similar assemblages of particles are present on the leaf surfaces, the co-located air filters and on a filter used to collect car exhaust emissions.

Pumped air filter and, where available, leaf SIRM values were higher at 0.3 m height than those at ~1.5–2 m at all but one location (Site 7). Site 7 is unusual in that it is located beneath a city-centre shop front, adjacent to a bench surrounded by discarded cigarette butts. It is possible that frequent exposure to cigarette smoke could explain both the unexpectedly high leaf SIRM value (18×10^{-6} A, Appendix 1) in an area where vehicle access is restricted, and the higher filter SIRM values at 1.5 m compared with 0.3 m height. This site also displayed the highest and most stable % HIRM values, indicative of the presence of magnetically 'hard' haematite. These HIRM values are consistent with those measured for indoor air where cigarette smoking is thought to have occurred (Halsall et al., 2008). Conversely, Jordanova et al. (2006) report low coercivity values for a range of branded cigarette ashes.

Some correlation exists between the leaf-calculated PM_{10} concentrations and the PM_{10} concentrations predicted by the ADMS for the Lancaster area. However, this model under-estimates at 'urban hotspot' locations (Gokhale and Raokhande, 2008) such as at traffic junctions and traffic lights. Improved correlation between the modelled and mean-calculated PM_{10} concentrations ($R^2 = 0.7$, compared with $R^2 = 0.6$, at a 1% significance level; $n = 24$) can be obtained if the traffic flow speed data in the model are decreased by 30% (Gokhale and Pandian, 2004) at such locations. This speed adjustment appears to be required in order to reflect traffic congestion on short road sections preceding these 'hotspots' within the study area. Conversely, the model over-estimates PM_{10} concentrations at sites with multiple trees, such as at the background site here, Site 9. As the ADMS-urban model takes into account effects of vehicle movements and distance from road, this over-estimate must reflect some other factor. The lower PM_{10} concentration likely reflects the screening and filtering effects of the adjacent trees.

It has been reported that reductions in PM_{10} concentrations of up to 20% can be achieved in the presence of co-located trees (e.g. Bealey et al., 2007). A similar decrease in PM_{10} concentrations (15%) was observed here wherever one tree was screened by another. Magnetic methods may thus be used as a rapid and efficient method to examine the efficacy of tree screening for pollution reduction purposes. They can also enable effective selection of sites for targeting of tree planting to enable maximum PM_{10} scavenging and reduction in human pollution exposure. Results from this study indicate that ambient PM_{10} concentrations are greatly increased at 'urban hotspots' especially at traffic junctions and traffic lights, maximizing potential for UKAQS non-compliance. Targeting of mitigation measures, including tree-planting, at such critical sites will be most effective in reducing pollution exposure. The high spatial resolution provided by biomagnetic monitoring is of key potential value for designing and optimizing vegetative screening of pollution. Such data thus might usefully be included in modelling studies of urban tree planting and its potential efficacy for pollution reduction (e.g. Bealey et al., 2007; Mcdonald et al., 2007). Given the health implications of exposure to particulate pollution, the mitigation offered by targeted screening by trees appears presently an under-used resource in pollution reduction.

6. Conclusions

- Measured magnetic properties (SIRMs) of roadside tree leaves exhibit strong correlation with ambient PM_{10} concentrations, and thus represent a robust, quantitative proxy for roadside particulate pollution.
- As measured both by roadside leaf SIRMs and co-located pumped air samples, roadside PM_{10} concentrations are ~100% greater at 0.3 m than at 1.5 m height. This indicates that fixed monitoring stations with inlets at ~3 m height do not collect pedestrian-relevant particle concentrations.
- Magnetic granulometry of the leaf and filter particulates indicates a dominant grain size of ~0.1–1 μm. An SEM particle count independently confirms this, with a high proportion of the sub-micrometre particles comprising iron-rich spherules.
- Rainfall events lower both ambient PM_{10} concentrations and roadside lime tree leaf magnetic values.
- Biomagnetic monitoring can provide unprecedentedly high spatial resolution data on PM_{10} concentrations and distributions, enabling identification of pollution 'hotspots' (requiring targeted mitigation) and mapping of PM_{10} concentrations into epidemiological and pollution exposure modelling studies.
- Biomagnetic monitoring can be used to 'ground-truth' pollution dispersion models. In the current study, such a model under-estimates traffic-derived PM_{10} concentrations at those locations where traffic remains stationary for intervals (traffic lights, minor–major road junctions), and over-estimates at sites screened by trees.
- Biomagnetic monitoring can contribute significantly to mitigation and pollution reduction measures, enabling rapid assessment of the degree of scavenging/filtering of PM_{10} by roadside vegetation. Further, planting and/or enhanced maintenance of roadside trees can be effectively targeted towards those areas delivering most of the roadside PM_{10} dose, whether to pedestrians, drivers or adjacent properties. Inclusion of biomagnetic data in urban modelling studies can contribute to the optimization and feasibility of urban tree planting for pollution reduction.

Acknowledgements

We are grateful to Jennifer Roberts from Lancaster Girls' Grammar School, who kindly assisted with sampling of tree leaves across the city, and Duncan Whyatt for helpful comments on an earlier version of this paper. We would also like to thank the referees for their insightful and helpful comments. This study was supported by a NERC (CASE) Studentship award (to RM) and a Royal Society Wolfson Research Merit award (to BAM).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2009.01.042

References

Bealey, W.J., Mcdonald, A.G., Nemitz, E., Donovan, R., Dragosits, U., Duffy, T.R., Fowler, D., 2007. Estimating the reduction of urban PM_{10} concentrations by trees within an environmental information system for planners. Journal of Environmental Management 85, 44–58.

Calderón-Garciduеñas, L., Reed, W., Maronpot, R.R., Henriquez-Roldan, C., Delago-Chavez, R., Calderon-Garciduenas, A., Dragustinovis, I., Franco-Lira, M., Aragon-Flores, M., Solt, A.C., Altenburg, M., Torres-Jardon, R., Swenburg, J.A., 2004. Brain inflammation and Alzheimer's-like pathology in individuals exposed to severe air pollution. Toxicologic Pathology 32, 650–658.

CERC, 2009. Who uses ADMS-Urban?. http://www.cerc.co.uk/software/ urban.htm accessed (15.01.09).

Dankers, P.H, 1978. Magnetic properties of dispersed natural iron oxides of known grain size. PhD thesis, University of Utrecht.

Department for Transport, 2007. Transport Trends 2007 Edition. HMSO, London.

Donaldson, K., 2003. The biological effects of coarse and fine particulate matter. Occupational and Environmental Medicine 60, 313–314.

Ferretti, M., Cenni, E., Bussotti, F., Batistoni, P., 1995. Vehicle-induced lead and cadmium contamination of roadside soil and plants in Italy. Chemistry and Ecology 11 (4), 213–228.

Fischer, P.H., Hoek, G., Van Reeuwijk, H., Briggs, D.J., Lebret, E., Van Wijnen, J.H., Kingham, S., Elliott, P.E., 2000. Traffic-related differences in outdoor and indoor concentrations of particles and volatile organic compounds in Amsterdam. Atmospheric Environment 34, 3713–3722.

Flanders, P.J., 1994. Collection, measurement, and analysis of airborne particulates from pollution in the environment. Journal of Applied Physics 75, 5931–5936.

Gautam, P., Blaha, U., Appel, E., Neupane, G., 2004. Environmental magnetic approach towards the quantification of pollution in Kathmandu urban area, Nepal. Physics and Chemistry of the Earth, Parts A/B/C 29, 973–984.

Gautam, P., Blaha, U., Appel, E., 2005. Magnetic susceptibility of dust-loaded leaves as a proxy of traffic-related heavy metal pollution in Kathmandu city, Nepal. Atmospheric Environment 39, 2201–2211.

Gokhale, S., Pandian, S., 2004. A semi-empirical box modeling approach for predicting the carbon monoxide concentrations at an urban traffic intersection. Atmospheric Environment 14, 7940–7950.

Gokhale, S., Raokhande, N., 2008. Performance evaluation of air quality models for predicting PM_{10} and $PM_{2.5}$ concentrations at urban traffic intersection during winter period. Science of the Total Environment 394, 9–24.

Halgedahl, S.L., Jarrard, R.D., 1995. Low-temperature behavior of single-domain through multidomain magnetite. Earth and Planetary Science Letters 130, 127–139.

Halsall, C.J., Maher, B.A., Karloukovski, V.V., Shah, P., Watkins, S.J., 2008. A novel approach to investigating indoor/outdoor pollution links: combined magnetic and PAH measurements. Atmospheric Environment 42, 8902–8909.

Harrison, R.M., Jones, M., 1995. The chemical composition of airborne particles in the UK atmosphere. Science of the Total Environment 168, 195–214.

Hoffmann, V., Knab, M., Appel, E., 1999. Magnetic susceptibility mapping of roadside pollution. Journal of Geochemical Exploration 66, 313–326.

Huhn, G., Schulz, H., Staerk, H.J., Toelle, R., Scheuermann, G., 1995. Evaluation of regional heavy metal deposition by multivariate analysis of element contents in pine tree barks. Water, Air and Soil Pollution 84, 367–383.

Jordanova, N., Jordanova, D., Henry, B., Le Goff, m, Dimov, D., Tsacheva, T., 2006. Magnetism of cigarette ashes. Journal of Magnetism and Magnetic Materials 301, 50–66.

Kaur, S., Nieuwenhuijsen, M.J., Colvile, R.N., 2005. Pedestrian exposure to air pollution along a major road in central London, UK. Atmospheric Environment 39, 7307–7320.

Kingham, S., Briggs, D., Elliott, P., Fischer, P., Erik, L., 2000. Spatial variations in the concentrations of traffic-related pollutants in indoor and outdoor air in Huddersfield, England. Atmospheric Environment 34, 905–916.

Knab, M., Appel, E., Hoffmann, V., 2001. Separation of the anthropogenic portion of heavy metal contents along a highway by means of magnetic susceptibility and fizzy c-means cluster analysis. European Journal of Environmental Engineering and Geophysics 6, 125–140.

Liu, Q., Banerjee, S.K., Jackson, M.J., Zhu, R., Pan, Y., 2002. A new method in mineral magnetism for the separation of weak antiferromagnetic signal from a strong ferrimagnetic background. Geophysical Research Letters 29 (12), 1565. doi:10.1029/2002GL014699.

Maher, B.A., 1988. Magnetic properties of some synthetic sub-micron magnetites. Geophysical Journal 94, 83–96.

Maher, B.A., Karloukovski, V.V., Mutch, T.J., 2004. High-field remanence properties of synthetic and natural submicrometre haematites and goethites: significance for environmental contexts. Earth and Planetary Science Letters 226, 491–505.

Maher, B.A., Moore, C., Matzka, J., 2008. Spatial variation in vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves. Atmospheric Environment 42 (2), 364–373.

Matzka, J., Maher, B.A., 1999. Magnetic biomonitoring of roadside tree leaves: identification of spatial and temporal variations in vehicle-derived particulates. Atmospheric Environment 33, 4565–4569.

Mcdonald, A.G., Bealey, W.J., Fowler, D., Dragosits, U., Skiba, U., Smith, R.I., Donovan, R.G., Brett, H.E., Hewitt, C.N., Nemitz, E., 2007. Quantifying the effect of urban tree planting on concentrations and depositions of PM10 in two UK conurbations. Atmospheric Environment 41, 8455–8467.

Micallef, A., Colls, J.J., 1999. Measuring and modelling the airborne particulate matter mass concentration field in the street environment: model overview and evaluation. The Science of the Total Environment 235, 199–210.

Morris, W.A., Versteeg, J.K., Bryant, D.W., Legzdins, A.E., Mccarry, B.E., Marvin, C.H., 1995. Preliminary comparisons between mutagenicity and magnetic susceptibility of respirable airborne particulate. Atmospheric Environment 29, 3441–3450.

Moreno, E., Sagnotti, L., Dinarés-Turrell, J., Winkler, A., Cascella, A., 2003. Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves. Atmospheric Environment 37, 2967–2977.

Muxworthy, A.R., Schmidtbauer, E., Petersen, N., 2002. Magnetic properties and Mössbauer spectra of urban atmospheric particulate matter: a case study from Munich, Germany. Geophysical Journal International 150, 558–570.

Muxworthy, A.R., Matzka, J., Davila, A.F., Petersen, N., 2003. Magnetic signature of daily sampled urban atmospheric particles. Atmospheric Environment 37, 4163–4169.

National Statistics, 2001. The Census in England and Wales. http://www.ons.gov.uk/census/index.html accessed (01.10.08).

Nicolay, S., 2000. A simplified LCA for automotive sector – comparison of ICE (diesel and petrol), electric and hybrid cars. 8th LCA case studies Symposium. SETAC – Europe.

Oberdörster, G., 2000. Toxicology of ultrafine particles: in vivo studies. Philosophical Transactions of the Royal Society of London, A 358, 2719–2740.

Özdemir, Ö., Banerjee, S.K., 1982. A preliminary magnetic study of soil samples from west-central Minnesota. Earth and Planetary Science Letters 59 (2), 393–403.

Özdemir, Ö., Dunlop, D.J., Moskowitz, B.M., 1993. The effect of oxidation on the Verwey transition in magnetite. Geophysical Research Letters 20 (16), 1671–1674.

Parker, S.T., Kinnersley, R.P., 2004. A computational and wind tunnel study of particle dry deposition in complex topography. Atmospheric Environment 38, 3867–3878.

Pope, C.A., Hansen, M.L., Long, R.W., Nielsen, K.R., Eatough, N.L., Wilson, W.E., Eatough, D.J., 2004. Ambient particulate air pollution, heart rate variability, and blood markers of inflammation in a panel of elderly subjects. Environmental Health Perspectives 112, 339–345.

Rudell, B., Blomberg, A., Helleday, R., Ledin, M.C., Lundback, B., Stjernberg, N., Horstedt, P., Sandstrom, T., 1999. Bronchoalveolar inflammation after exposure to diesel exhaust: comparison between unfiltered and particle trap filtered exhaust. Journal of Occupational and Environmental Medicine 56, 527–534.

Sagnotti, L., Rochette, P., Jackson, M., Vadeboin, F., Dinares-Turell, J., Winkler, A., Maher, B.A., 2003. Inter-laboratory calibration of low-field magnetic and anhysteretic susceptibility measurements. Physics Earth Planetary Interiors 138, 25–38.

Szönyi, M., Sagnotti, L., Hirt, A.M., 2008. A refined biomonitoring study of airborne particulate matter pollution in Rome, with magnetic measurements of *Quercus Ilex* tree leaves. Geophysical Journal International 173 (1), 127–141. doi:10.1111/j.1365-246X.2008.03715.x.

Tuch, Th.M., Wehner, B., Pitz, M., Cyrys, J., Heinrich, J., Kreyling, W.G., Wichmann, H.E., Wiedensohler, A., 2003. Long-term measurement of size-segregated ambient aerosol in two German cities located 100 km apart. Atmospheric Environment 37, 4687–4700.

Urbat, M., Lehndorff, E., Schwark, L., 2004. Biomonitoring of air quality in the Cologne conurbation using pine needles as a passive sampler – part I: magnetic properties. Atmospheric Environment 38, 3781–3792.

Xie, S., Zhang, Y., Qi, L., Tang, X., 2003. Spatial distribution of traffic-related pollutant concentrations in street canyons. Atmospheric Environment 37, 3213–3224.