Geophys. J. Int. (2008) **173**, 127–141 doi: 10.1111/j.1365-246X.2008.03715.x

A refined biomonitoring study of airborne particulate matter pollution in Rome, with magnetic measurements on *Quercus Ilex* tree leaves

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Accepted 2007 December 19. Received 2007 December 19; in original form 2007 June 6

SUMMARY

Elevated levels of airborne particulate matter (PM) are a current problem for air quality in many major metropolitan areas. Many European cities have tightened the PM limits in the air, due to advances in monitoring PM levels. In order to establish guidelines for monitoring and curbing anthropogenic PM output, a better understanding of its origin, composition and diffusion is required. Biomonitoring of magnetic properties of tree leaves has been suggested previously to be a good approach to measure pollution levels in cities both in space and time. We report on a magnetic biomonitoring study of PM in the city of Rome, conducted from 2005 October to December. We collected approximately 180 different sample sets of tree leaves of *Quercus ilex*, an evergreen oak widely distributed in Rome, at 112 different locations. Specific magnetic susceptibility χ of the leaf is used as a fast, easy and cost-effective proxy to assess levels of primary anthropogenic airborne PM pollution. Highly polluted areas correlate with high traffic areas, with an average susceptibility value of $\chi = 3.2 \times 10^{-7}$ m^3 kg^{-1}. Low traffic zones are characterized by values more than an order of magnitude lower at $\chi = 1.4 \times 10^{-8}$ m^3 kg^{-1}, and the background magnetic susceptibility is around $\chi = 2.6 \times 10^{-9}$ m^3 kg^{-1}. The data show that distance dependence from the source is the most significant factor for the concentration of magnetic PM, and that pollution levels and sources can be reliably delineated by measuring magnetic susceptibility values on tree leaf samples of *Q. ilex*. A new protocol for magnetic susceptibility measurements is proposed, in order to account for changes due to water evaporation in the leaves as a function of time after collection of the samples. Additional magnetic analyses, such as acquisition of artificial remanences and hysteresis properties, were used to characterize the mineralogy and grain size of the magnetic PM. The results indicate that the population of ferrimagnetic phases have a homogenous composition and grain size throughout the investigated area.

Key words: Environmental magnetism; Rock and mineral magnetism.

1 INTRODUCTION

Airborne particulate matter (PM) is considered to be the largest contributor to the problem of urban air pollution. It has been shown that PM particle size correlates positively with mortality numbers (e.g. Morris *et al.* 1995; Pope & Dockery 1999; Wichmann & Peters 2000). Decreasing particle size is closely connected to increasing toxicity, with the greatest physiological effect from ultrafine particles <100 nm. Particles in this so-called nanoparticle range have an adverse effect on health, as they are inhaled much more deeply in the human lungs (Muxworthy *et al.* 2002; Morawska *et al.* 1998). In 1999, the European Union passed Regulation 99/30/EG on PM limits, and these were put into effect on 2005 January 1 with an option to further tighten limits in 2010. For the case in which these limits are exceeded, the authorities are obliged to enact counteractive measures to lower PM content in the air. Due to the increased awareness in the dangers associated with high PM concentrations, there is an immense interest for qualitative and quantitative means to measure and monitor PM emissions both over shorter and longer periods of time. Furthermore, surveillance of individual areas of heavy traffic or areas close to other pollution sources can lead to

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better mitigation plans. In developing countries, industrial emissions and traffic-related pollution are a serious problem due to spreading urbanization and insufficient environmental regulations (Goddu *et al.* 2004). Fast, reliable, easy-to-apply proxy methods with low costs and personal demands are paramount particularly in these regions.

Magnetic minerals in aerosols may be derived from combustion processes related to industry, domestic heating or vehicles, as well as from abrasion products from street surfaces and brake systems (e.g. Hoffmann *et al.* 1999; Petrovsky & Ellwood 1999; Knab *et al.* 2001; Jordanova *et al.* 2004). Therefore, magnetic parameters, notably magnetic susceptibility, are possible proxies to monitor the regional distribution of air PM pollution or relative changes in an area over time. In the past, magnetic properties have been used to identify atmospheric industrial and traffic pollution in cities by studying dust directly collected on roads (Gautam *et al.* 2004; Goddu *et al.* 2004) or accumulated in filters (Xie *et al.* 2000; Gillies *et al.* 2001; Muxworthy *et al.* 2001; Spassov *et al.* 2004; Sagnotti *et al.* 2006) and on tree leaves (Matzka & Maher 1999; Moreno *et al.* 2003; Urbat *et al.* 2004). They have also been used to characterize pollution in soils (e.g. Flanders 1999; Hoffmann *et al.* 1999; Petrovský *et al.* 2000, 2001; Gautam *et al.* 2004; Jordanova *et al.* 2004, 2006; Veneva *et al.* 2004; Spiteri *et al.* 2005; Magiera *et al.* 2006). A European-wide study, conducted under the European Fifth Framework Project MAG-NET, had one of its goals to characterize pollution levels in major cities. Results showed the usefulness of magnetic biomonitoring methods as a quick, cost-effective method to monitor pollution levels in cities (MAGazine issues 4 and 5; *cf.*, http://www.geo.uu.nl/∼magnet/). Evergreen species were found to be effective accumulators of PM, because their leaves may be up to 3 years old and, therefore, provide a better time-averaged signal (Moreno *et al.* 2003). It is important that trees are widely spread across the sampling area and typical for the region.

In this study, we show that the simple measurement of magnetic susceptibility is sufficient to delineate spatial airborne anthropogenic PM pollution, whereas more elaborate magnetic methods, such as analyses of laboratory produced remanent magnetizations, hysteresis properties and temperature-dependent susceptibility can provide information on the mineralogy and grain size of the PM magnetic fraction which can then be used as an indicator of various pollution sources (e.g. Sagnotti *et al.* 2006; Szönyi *et al.* 2007). Szönyi *et al.* (2007) demonstrated that magnetic measurements made on samples from a single leaf showed a lower variation in magnetic properties than seen from a population of leaves sampled over a wider area. Therefore, measurements on a single leaf are considered to be representative for PM concentration at a specific location. This study is concerned with refined magnetic monitoring in the city of Rome. Magnetic PM10 content of tree leaves is mainly ascribed to circulating vehicles (Matzka & Maher 1999; Moreno *et al.* 2003), although there may be other sources of short duration, such as building constructions or natural fires.

This study has three main goals. The first is to expand the existing biomonitoring study of Moreno *et al.* (2003) within the city limits of Rome in order to achieve an improved spatial distribution map of pollution, with emphasis on the dependence of magnetic properties with the distance from the monitored roads. The second goal is to investigate the effects of different sampling procedures and laboratory methods on the overall magnetic properties of the leaf samples, with particular regards to the change in the magnetic properties as a function of timing of the measurement after collection. The third goal is to improve the characterization of the magnetic particles in the airborne PM by means of standard rock magnetic techniques.

2 METHODOLOGY

2.1 Location and study area

Rome is the capital of Italy with 2.7 million inhabitants in the city itself and a total of 3.8 million in the metropolitan area. Heavy street traffic is found throughout the city, and historical considerations have prevented excavation of a widespread public underground transportation system, still limited to two lines only. Rome never developed an industrial sector and it has little industrial activity today, most of which is in information technology.

This study extends in latitude from 41°50′N to 41°55′N and in longitude from 012°28′E to 012°32.5′E. The sampling campaigns were carried out from 2005 October to December with samples collected from 112 different sampling locations (Fig. 1). We adopted the same sampling strategy used in the work of Matzka & Maher (1999) and Moreno *et al.* (2003): at each site, six to eight leaves were detached from the outer canopy of a single tree at a height of about 1.5–2 m above the ground. At each site, the leaves were stored in a paper envelope for transportation, and not packed in plastic pots/cubes as formerly done by Matzka & Maher (1999) and Moreno *et al.* (2003). The magnetic measurements started the day after the sampling in the palaeomagnetic laboratory of the Istituto Nazionale di Geofisica e Vulcanologia (Rome). A total of 181 sample sets were collected, due to repetitive sampling of the same tree under different conditions (i.e. weather, distal/proximal side of the tree with respect to the road). The site localities were selected according to the availability of *Q. ilex* tree leaves. Tuch *et al.* (2003) emphasized that sampling height is important with regard to the composition of the contributing PM sources. They found that sampling up to 4 m above the surface favoured monitoring PM resulting from vehicular emissions, whereas sampling at heights of about 10 m higher favoured domestic heating or long-range sources.

The selected sites represent different traffic conditions, varying from urban parks and protected green areas along the ancient Appian Way (Via Appia Antica), which is a natural park with very low traffic volume on weekdays and none on Sundays, to roads and congested intersections with very high levels of motorized traffic throughout the entire day, including weekends. Low-field magnetic susceptibility is a parameter that is easily and quickly measured. Earlier studies have shown a correlation between magnetic susceptibility and intensity of artificial remanences (Moreno *et al.* 2003) and between susceptibility and the effective PM10 content in monitored air stations, in absence of significant inputs of natural dust from distant sources (Sagnotti *et al.* 2006). Therefore, magnetic susceptibility was chosen as the routine magnetic parameter to monitor the spatial distribution of urban pollution.

2.2 Quercus ilex

Q. ilex is an evergreen oak tree very common in the central and southern parts of Italy and around the Mediterranean region. It grows in mild climates and is a typical perennial of the Mediterranean shrub and woodlands commonly known as 'macchia mediterranea'. It is a resistant plant that can grow on poor soils or in adverse conditions, such as polluted city areas. Since the 16th century, *Q. ilex* was planted as ornamental tree in Rome and its surroundings.

The tree can easily be recognized by the presence of its acorn, whereas the tree leaves come in different shapes and sizes. Young leaves tend to be broad and have serrated edges, while older leaves show an elongated form and smooth edges. In order to avoid young

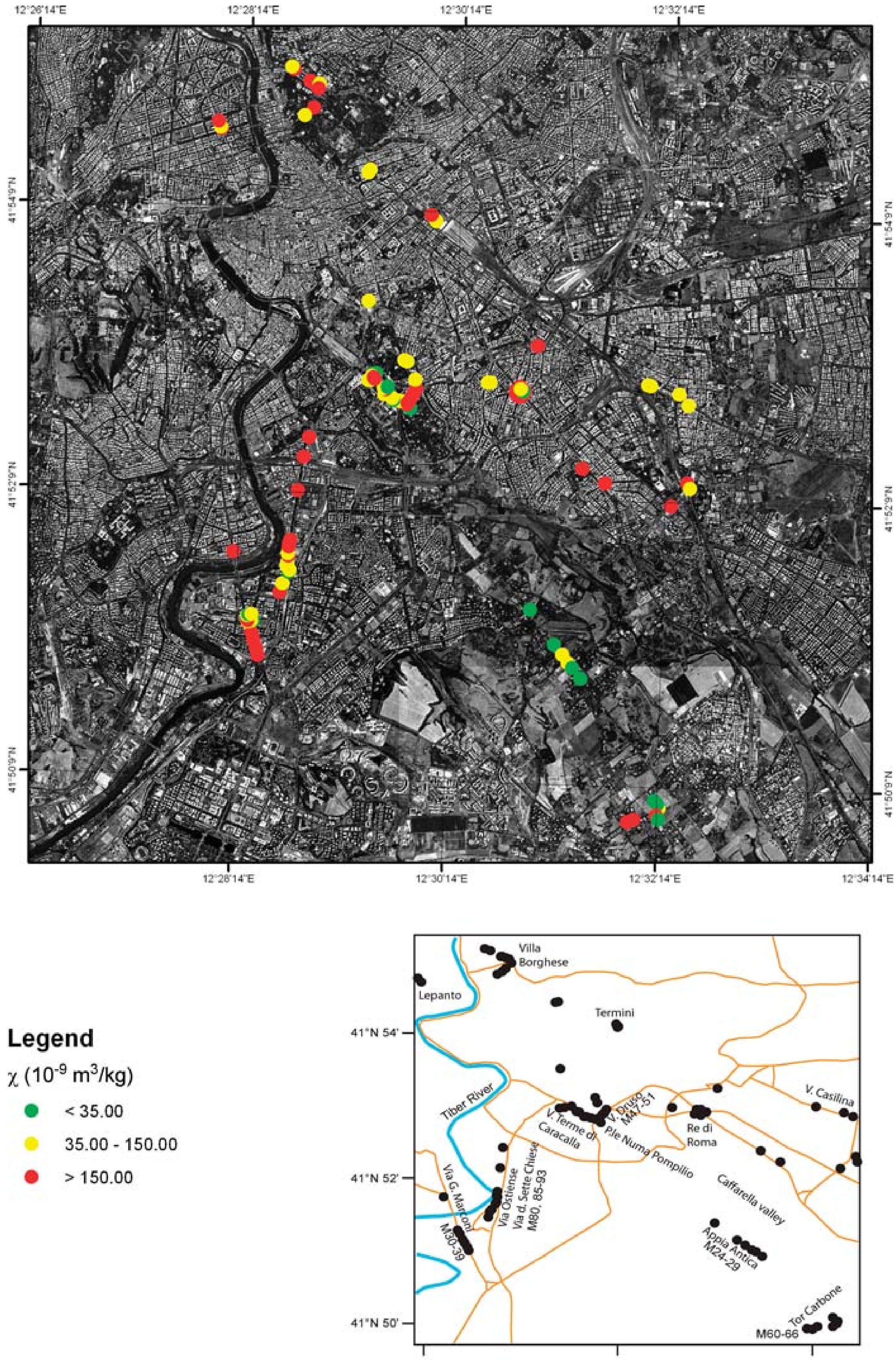

Figure 1. Location of the 112 *Q. ilex* trees sampled in the town of Rome (Italy) for this study. The sketch map shows the main localities that are discussed in the text and in Figs 2–4.

tree leaves for which the exposure time to the pollution source was not sufficient, leaf shape was considered for the selection of the samples.

All leaves are relatively thick, with a leathery surface, glossy and dark green in colour. Under natural conditions, *Q. ilex* has a leaf life-span of 2 yr on average, with a maximum up to 3 yr. The life span has also been correlated to pollution levels, where it may be reduced to about 1 yr in highly polluted city areas (Gratani *et al.* 2000).

2.3 Sampling and measurements

Six to eight leaves were cut with a small knife from the *Q. ilex* tree to exclude the leaf stem from the sample. Leaves were selected according to their age and exposure on each tree. The leaves were placed in a standard 5 g paper envelope. Magnetic measurements were mostly carried out in the palaeomagnetic laboratory of the INGV in Rome, Italy. All bulk susceptibility measurements took place 1 d after the sampling campaigns, and were later repeated after >10 d to check for changes in the magnetic properties of the leaves with respect to time. The low-field susceptibility measurements were performed on an AGICO KLY-3 Kappabridge. In comparison, Moreno *et al.* (2003) used an AGICO KLY-2 susceptibility bridge. While the KLY-2 tends to give slightly higher values than the KLY-3, cross-calibration of the two instruments showed that measurements were reproducible to within ± 1 per cent (Sagnotti *et al.* 2003). The plastic holder of the samples including an empty standard paper envelope had a low diamagnetic susceptibility (-4.6×10^{-9} m^3 kg^{-1}) that was compensated for in the measurement procedure. The low-field magnetic susceptibility provides a measure of the ease with which a material can be magnetized in a uniform external magnetic field and mostly depends from the concentration of ferrimagnetic particles. For a detailed description of the magnetic parameters used in this study we refer to the exhaustive textbooks of Dunlop & Ozdemir (1997) and Evans & Heller (2003).

Each sample was weighed before the measurements in order to normalize the magnetic susceptibility values relative to the leaf mass (χ, m^3 kg^{-1}). For repetitive measurements, the new weight values were used, to compensate for the water loss in the leaves. Normalization by wet or by dry mass was, therefore, possible at any time. With the purpose of testing how easily magnetic particles can be washed off from the surface of the leaves, selected leaves were cleaned either washing them manually with a wet tissue, or using a Cole-Parmer 8891 ultrasonic cleaner filled with distilled water.

Thermomagnetic curves, monitoring the changes of magnetic susceptibility during heating-cooling cycles, were measured with the AGICO Kappabridge KLY-3 instrument coupled with a CS-3 furnace. The analysis of thermomagnetic curves may allow the identification of the composition of the magnetic particles, by the recognition of their specific Curie/Neèl temperatures. Leaves were crushed to fine powder, passed through a fine sieve of 0.6 mm and placed in the CS-3 holder. A first sample was heated from room temperature (20 °C) to 700 °C and cooled down in one single cycle at a rate of 11 °C min^{-1}. A second sample was heated up to 430 °C, at a rate of 8.5°C min^{-1}, kept at 430 °C for 10 min and then cooled down to room temperature. Then, the same sample was heated again in a second cycle up to 700 °C at the same rate and cooled down.

Hysteresis cycles and measurements of isothermal remanent magnetization (IRM) acquisition and backfield remagnetization were carried out on a Princeton Measurements Corporation (PMC) MicroMag 2900 instrument with the Alternating Gradient Magnetometer (AGM) coil in magnetic fields up to 1 T. These measurements provide information on the coercive force (B_C), remanent coercive force (B_{CR}), saturation remanent magnetization (M_{RS}) and saturation magnetization (M_S). B_C and B_{CR} depend on composition and grain size; for given composition, M_{RS} depends more on grain size than on concentration. The ratios M_{RS}/M_S and B_{CR}/B_C can provide information on the magnetic grain size and domain state. Small squares of about 4×4 mm^2 each were cut from the leaf. It was not possible to weigh such small samples; therefore, the remanence values were normalized by area rather than by mass.

Some of the hysteresis loops did not appear to be saturated at 0.5 T, which is indicative that a higher coercivity phase may be present in the leaf samples. In order to analyse better the coercivity distribution of the magnetic particles on the tree leaves, and their interaction field strengths, First Order Reversal Curves (FORCs) were measured on selected samples. FORC measurements are obtained by cycling the sample from a positive saturation field to a preparation field, with subsequent measurement in a field sweeping from the preparation field to saturation (Pike *et al.* 1999; Roberts *et al.* 2000). 121 FORCs were measured for each sample in steps of 2.8 mT and an averaging time of 100–500 ms, depending on the magnetic intensity of the sample, using a 0.5 T saturating field. To better visualize the produced set of loops, they are transformed into contour plots (Winkelhofer & Zimanyi 2006) referred to as FORC diagrams. IRM acquisition curves were also measured, for selected samples, at the Laboratory for Natural Magnetism (LNM), ETH Zürich, at room temperature and at 77 K (liquid nitrogen) on a 2G three axis cryogenic magnetometer model 755. Samples were put into a Teflon standard cube and magnetized along the *x*-axis with an ASC pulse magnetizer, model IM 10–30, at –1 T, then rotated 180° and magnetized incrementally up to 1 T at both temperatures. Values were normalized by weight. In order to subtract the holder signal, the empty Teflon holder was measured before the samples were measured. Measurements were repeatable at 77 K which indicates that no temperature change occurred during measurement.

3 RESULTS

Location of sampling sites and results from susceptibility measurements in Rome are plotted onto a aerial photo map and shown in Fig. 1. The figure shows that within the city boundaries of Rome the magnetic susceptibility values show a high spatial variability linked to different pollution levels in different areas. Susceptibility values range from diamagnetic in green areas to low values around $\chi = 1 \times 10^{-8}$ m^3 kg^{-1} in areas which represent the background magnetic susceptibility signal in Rome and up to values as high as $\chi = 7 \times 10^{-7}$ m^3 kg^{-1} along roads with heavy traffic.

3.1 High traffic areas

Much of the sampling focused on trees growing along roads that are severely congested by daily traffic jams. Major roads leading out of the city centre are the *Viale G. Marconi* in the southwest, *Via Ostiense* east of *Viale G. Marconi*, and *Via Casilina* and *Via Appia Nuova* in the southeast of Rome. A central road in the city centre is the *Viale delle Terme di Caracalla*, which is cross cut by the *Via Druso*, intersecting at *Piazzale Numa Pompilio*, a large square with a system of traffic lights. The highest magnetic susceptibility values were obtained from trees located along these roads. The susceptibility data from high traffic areas are presented in Table 1.

Q. ilex line the medial green traffic divider on the *Viale Guglielmo Marconi* (Fig. 2a). The highest susceptibility magnetic values along

Table 1. Magnetic susceptibility for high traffic localities along Viale Guglielmo Marconi (M30–M33), Via Druso (M47–M51_p) and Via Ostiense (M80–M93).

Sample	Susceptibility ($m^3\ kg^{-1}$)
M30	3.40E-07
M31	3.47E-07
M32	3.03E-07
M33	5.31E-07
M47	3.61E-07
M48	6.75E-07
M49	6.96E-07
M50	4.56E-07
M51	3.70E-07
M51_p	5.83E-07
M80	1.99E-07
M84	1.25E-07
M85	1.40E-07
M86	2.46E-07
M87	6.21E-08
M88	2.15E-07
M89	2.03E-07
M90	2.20E-07
M91	1.72E-07
M92	2.99E-07
M93	1.87E-07
Mean	3.20E-07 ± 1.78E-07

this road were found at M33 and M35 trees, located right behind intersections, where circulating vehicles accelerate. In contrast, M34, positioned before the intersection, shows about half magnetic susceptibility intensity, compared to M33 and M35, suggesting that idling cars do not release an equally high amount of magnetic PM. The highest susceptibility values from all the sample campaigns were observed at the intersections along Via Druso (Fig. 2b). Traffic is generally congested along this road and the *Q. ilex* trees are standing very close to the curb, with some branches hanging above the lanes.

Via Ostiense shows also a generally high pollution level, with all χ values along the road exceeding 10^{-7} m^3 kg^{-1} (Fig. 2c). Locality M91 was reported by Moreno *et al.* (2003) to have the highest overall susceptibility value $\chi = 1 \times 10^{-7}$ m^3 kg^{-1}, with reference to a *Platanus* sp. survey carried out in 2001 October. Moreno *et al.* (2003) also indicated that the magnetic susceptibility of *Platanus* sp. leaves is always much lower than that of *Q. ilex* leaves at the same location. The magnetic susceptibility maximum of the M91 *Platanus* sp. leaves was linked by Moreno *et al.* (2003) to exposure to trucks that were transporting the daily deliveries to the *Mercati Generali* (General Markets), formerly the largest market area in Rome. The markets were closed in 2002 September and moved to another location. The site is now empty, with no systematic heavy vehicle traffic, and susceptibility values have returned to the 'normal' level along *Via Ostiense*. It can be assumed that all *Q. ilex* leaves have been replaced since 2002, so that the average magnetic susceptibility value

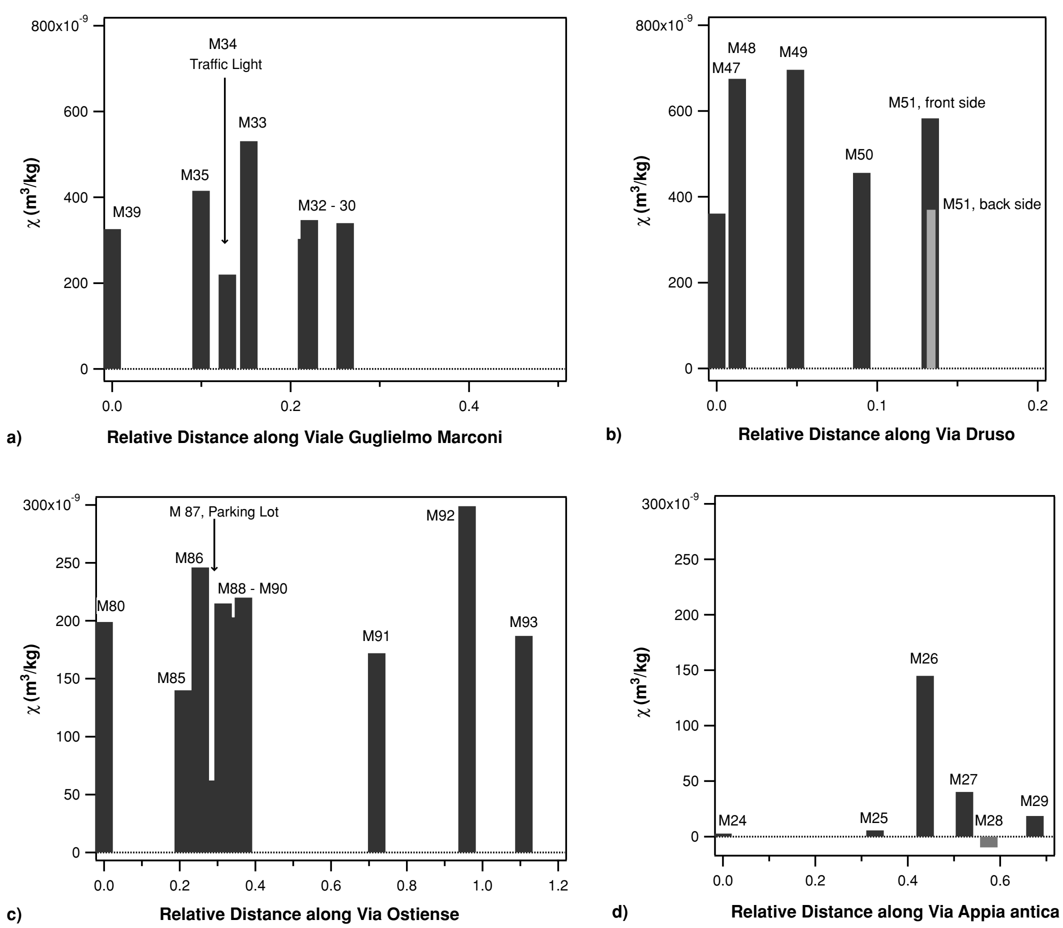

Figure 2. Distribution of mass magnetic susceptibility values along four selected roads in Rome. Viale Guglielmo Marconi (a), Via Druso (b) and Via Ostiense (c) represent three main high-traffic roads, Via Appia Antica (d) runs in a natural park in which vehicular traffic is very low and restricted to working days only.

Table 2. Magnetic susceptibility of the eleven trees sampled at three different locations in green areas. M26 was omitted from the statistical analysis.

Sample	Susceptibility ($m^3\ kg^{-1}$)
M24	2.69E-09
M25	5.65E-09
M27	4.03E-08
M28	−9.71E-09
M29	1.86E-08
M59	4.33E-08
M60	1.46E-09
M61	4.00E-09
M62	4.53E-08
M63	2.26E-09
M64	9.06E-10
Mean	1.41E-08 ± 1.97E-08

found in *Q. ilex* leaves at that location is representative of a better air quality.

3.2 Magnetic background signal

Three different large green areas were sampled. These were in the vicinity of the city centre (*Villa Borghese* park), along *Via Appia Antica* and in the Caffarella Valley. Susceptibility values are presented in Table 2. With respect to the high-traffic roads, the mean susceptibility is at least an order of magnitude lower at these localities, with a mean of $\chi = 1.4 \times 10^{-8}$ m^3 kg^{-1}. The sampling sites along *Via Appia Antica* (Fig. 2d) and in the Villa Borghese park show very low χ values, although some anthropogenic emissions (e.g. motorbikes, tractors on nearby agricultural land) occur. This may explain the occurrence of relatively high χ value along *Via Appia Antica* (i.e. tree M26). Absolute background magnetic susceptibility values may be diamagnetic away from any pollution source, since leaves consist of organic tissues and water. Very low susceptibility values were found in a line of *Q. ilex* trees in a field near *Via di Tor Carbone* in the south of Rome (Fig. 3). Here, trees a dozen meters away from the road have χ values close to zero. The four trees M60, M61, M63 and M64 have a mean value of 2.2×10^{-9} m^3 kg^{-1}, indicating the Roman background magnetic susceptibility value. The two trees more proximal to the road, M62 and M65, provided χ values of 4.5×10^{-8} and 1.5×10^{-7} m^3 kg^{-1}, respectively. The mean χ value of 1.4×10^{-8} m^3 kg^{-1} found in this study is consistent with the value formerly indicated by Moreno *et al.* (2003) for urban gardens and suburban parks of the southwestern sector of Rome (lower than 2×10^{-8} m^3 kg^{-1}); it may be, therefore, assumed as the typical background value for mass specific magnetic susceptibility of *Q. ilex* leaves in the metropolitan area of Rome.

3.3 Distance dependence

The data indicate a significant dependence of susceptibility as a function of the tree distance from the road. Green areas sampled at eleven different positions provided leaves with an average susceptibility of $\chi = 1.4 \times 10^{-8}$ m^3 kg^{-1}, whereas leaves along high traffic roads show an average of $\chi = 3.2 \times 10^{-7}$ m^3 kg^{-1}. In order to delineate such distance dependence, we sampled trees along profiles perpendicular to the main traffic road whenever possible. Beside the tree line perpendicular to *Via di Tor Carbone*, mentioned above, two other profiles could be sampled, and these were located at *Piazzale Numa Pompilio* (Fig. 4a) and at the intersection of *Via delle Sette Chiese*, a small side road, with *Via Ostiense* (Fig. 4b). All the data show a decrease in susceptibility as a function of distance from the road, with χ values decreasing to a 'magnetic background' level after as little as 20–30 m away from high-traffic roads.

3.4 Susceptibility changes within a leaf

The susceptibility of all samples was monitored as a function of time after their initial collection. Susceptibility values used for the interpretation were measured approximately 24 hr after sampling, the procedure used in Moreno *et al.* (2003). The susceptibility measurements were repeated at regular intervals, over a period of 27 d, to monitor magnetic changes as a function of time (Fig. 5). The samples lost most of their 'evaporable' water in the first 5–6 d after sampling and the volume magnetic susceptibility (k) of the three samples increased of about 5.6–7.2 $\times 10^{-6}$ SI during the same period. This corresponds to a percentage increase of 443 per cent for k of the weakest sample (M1 with original $k = 2.09 \times 10^{-6}$ SI), but of about 112 per cent for k of the strongest sample (M3 with original $k = 47.54 \times 10^{-6}$ SI). Therefore, the percentage increase is larger for the weakly magnetic samples and becomes less and less important for the highly magnetic samples. Considering the diamagnetic susceptibility of pure water ($k = -9 \times 10^{-6}$ SI), a simple loss of 1 g of water in a standard sample with a nominal volume of 10 cm^3 would produce a k increase of 9×10^{-6} SI. In our case, the observed k

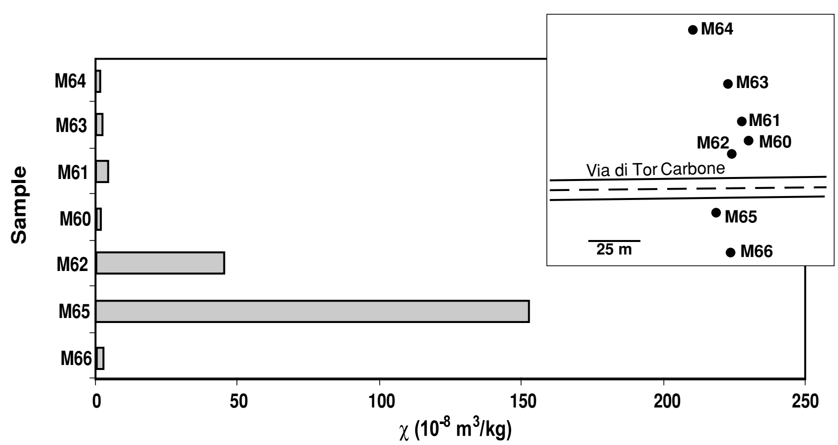

Figure 3. Distribution of mass magnetic susceptibility values along a profile of *Q. ilex* trees perpendicular to Via di Tor Carbone, a road in the southern margin of Rome characterized by heavy traffic during rush hours.

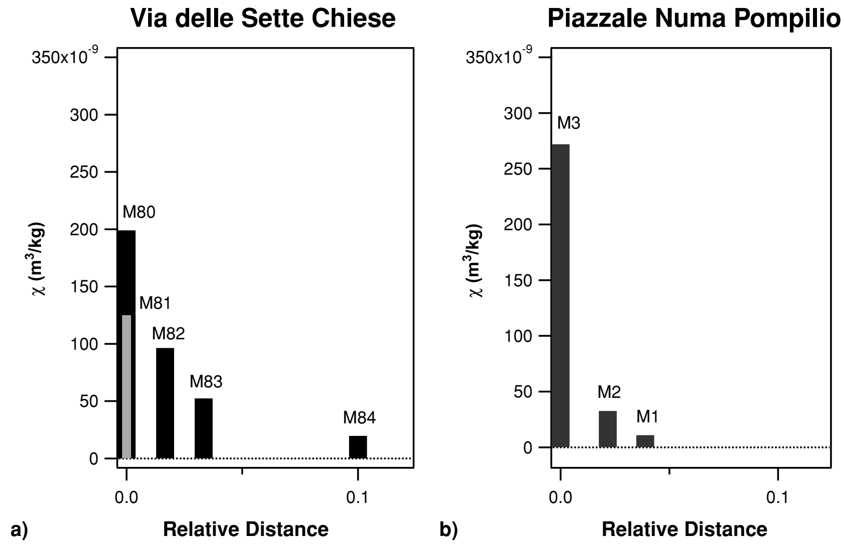

Figure 4. Distribution of mass magnetic susceptibility values along two profiles of *Q. ilex* trees perpendicular to Via delle Sette Chiese (a) and Piazzale Numa Pompilio (b), two high-traffic roads in the centre of Rome. The data show a substantial decrease of magnetic susceptibility values within a distance of about 20–30 m from the roads (see text).

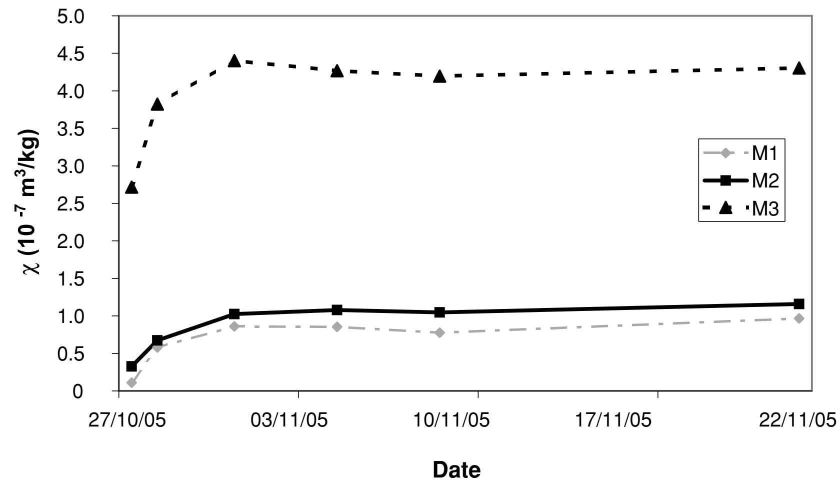

Figure 5. Time variation of magnetic susceptibility values in selected *Q. ilex* leaf specimens taken at Piazzale Numa Pompilio on 2005 October 26. The first measurement of the series was taken the day after the sampling. A distinct increase is observed in the first 3–4 d after sampling and can be related to the loss of diamagnetic water (see text).

increase of 6–7 $\times 10^{-6}$ SI during the first week after sampling would be accounted for by a loss of 0.7–0.8 g of water. And our leaves lost *ca.* 0.3–0.5 g of total weight after the first day. We therefore, conclude that all the observed changes in magnetic susceptibility through time may be due to the loss of water, producing both a reduction in weight and an increase in k and χ. We propose that a standard procedure be established that ensures that different magnetic susceptibility measurements could effectively be comparable each other. As different atmospheric conditions may yield different water content inside the leaves, the measurement of magnetic susceptibility directly after the sample collection, normalized by the sample natural weight, as executed until now, is considered inappropriate. A much better, although more labour-intensive procedure, would imply drying of leaves at 60 °C or higher temperatures, up to 100–120 °C (iron minerals should not go through chemical alteration up to 150 °C, see Hirt *et al.* 1993) until all the water has been lost followed by susceptibility measurements, with normalization by the dry weight.

Other authors have proposed that not all magnetic PM stays suspended on the leaf surface, but gets incorporated into the stomata cavities or within the wax coating (Urbat *et al.* 2004). Matzka and Maher (1999) found that, based on seven leaves from birch trees, an average of 75 per cent of the initial magnetization can be removed. In this study, we manually cleaned seven samples with detergent and towel and 59 per cent of the initial susceptibility remained on average (values spread in a range between 36 and 84 per cent, see Table 3). Five samples were cleaned in an ultrasonic bath, and 46 per cent of the initial magnetization remained on average (Table 3) This suggests that approximately half of the magnetic susceptibility is due to phases that are caught in the leaf structure.

3.5 Weather dependence

To address the concerns about the dependence of the magnetic susceptibility on the weather condition, repetitive measurements

Table 3. Susceptibility of tree leaf samples after cleaning.

	Susceptibility after cleaning the leaf samples				
	Uncleaned (m^3 kg^{-1})	Hand-cleaned (m^3 kg^{-1})	Ultrasonic-cleaned (us) (m^3 kg^{-1})	Per cent	Per cent us
M8	5.45E-08	1.95E-08	n/a	35.73 per cent	
M9	1.75E-07	1.48E-07	n/a	84.22 per cent	
M10	1.38E-07	8.63E-08	6.90E-08	62.30 per cent	49.86 per cent
M11	7.01E-08	5.87E-08	1.89E-08	83.73 per cent	26.89 per cent
M22	2.61E-07	1.17E-07	1.42E-07	44.67 per cent	54.36 per cent
M23	2.84E-07	1.27E-07	1.37E-07	44.61 per cent	48.23 per cent
M51	6.60E-07	3.94E-07	3.30E-07	59.69 per cent	50.01 per cent
Average of remaining magnetization (percentage)				59.28 per cent	45.87 per cent

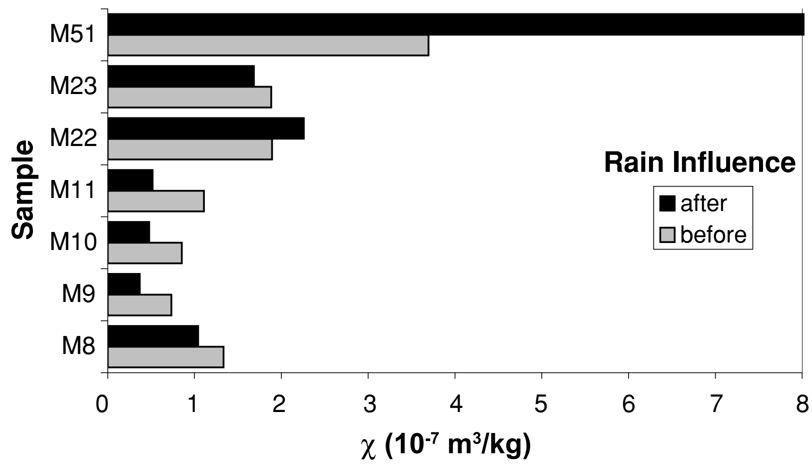

Figure 6. Comparison of mass specific magnetic susceptibility values for selected specimens before and after a major rain episode. Variations are not systematic and either increase or decrease were observed after the rainfall.

were made at different locations before and after major precipitation events. General climate information for the city of Rome and detailed rainfall and temperature data recorded during the sampling period are listed in Tables S1 and S2 in the electronic supplementary material. In this study, the variable weather conditions permitted an investigation of the influence of precipitation on the magnetic susceptibility values. Seven selected sites were resampled after rainy days on November 8 and on December 15 after an exceptional high-rate precipitation period (December 1–13). There is no clear indication that rain systematically reduced magnetic susceptibility due to washing off the magnetic PM particles. Of the seven repeatedly sampled locations, five show a decrease between 11 per cent (M23) and 53 per cent (M11), two show an increase (Fig. 6). During repeated sampling we could only collect different leaf batches from the same tree. Our results suggest that the measured data only reflects the natural variability of leaf-susceptibility values, which may be expected at each single tree, and that they are not heavily influenced by meteorological events.

3.6 Magnetic mineralogy and grain size

One laboratory method to define magnetic mineralogy in a material is by analysis of thermomagnetic curves (i.e. Petrovsky & Kapicka 2006). The problem with biologic samples is the organic content, which can strongly influence the atmosphere in the sample holder during the heating run. In this study, thermomagnetic heating-cooling cycles were made on a few samples collected from highly contaminated leaves from Via Druso and Piazza Re di Roma (Fig. 1). In full heating-cooling cycles the samples were heated up to 700 °C and then cooled down to room temperature, producing an irreversible thermomagnetic curve (Figs 7a and b). There is a distinct inflection between 300 and 400°C, more pronounced for the samples collected from Via Druso (Fig. 7a) than for the sample collected from Piazza Re di Roma (Fig. 7b), followed by a drastic drop in magnetic susceptibility values at ∼580 °C, after which the signal becomes very weak and noisy. The cooling curve shows a sharp increase of susceptibility after passing below 580 °C and flattening until reaching 400 °C, when the susceptibility begins to decrease.

To better understand the decrease in susceptibility during heating from 40 to 400 °C, a sample from Via Druso was subjected to a double thermomagnetic cycle (Fig. 7c). The sample was first heated to a temperature of 430 °C, at a slowest rate (8.5 °C min^{-1}) and kept at the maximum temperature for 10 min (in order to enhance the possible effects of thermal alteration), and subsequently cooled down to 45 °C. The inflection between 300 and 400 °C is markedly developed in both the heating and the cooling curves. The cooling curve is however lower than the heating curve. The sample was then subjected to a second full heating-cooling cycle to 700 °C (Fig. 7c), with a ‘normal’ rate of 11 °C min^{-1}. The data were similar to those measured on the first sample from Via Druso (Fig. 7a).

Hysteresis measurements were performed on all samples with $\chi > 2 \times 10^{-7}$ m^3 kg^{-1}, the required threshold to get a measurable and repeatable signal on the AGM. The values of all samples, normalized to their surface and given in SI units, are summarized in Table 4. The hysteresis loops of the different samples show very similar shapes and are compatible with a mixture of multidomain (MD) and superparamagnetic (SP) ferrimagnetic particles. We refer to the paper of Szönyi *et al.* (2007) for a detailed discussion of the hysteresis properties.

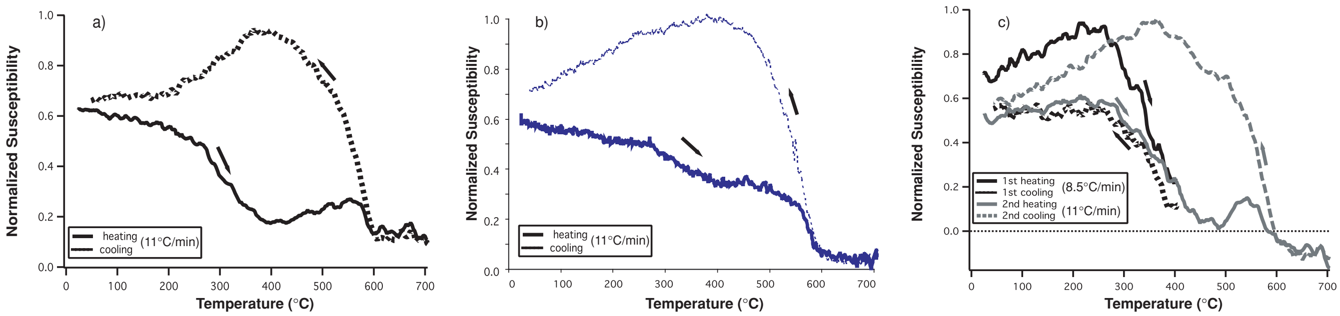

Figure 7. Thermomagnetic susceptibility curves for two selected specimens, showing the changes in volume magnetic susceptibility during heating-cooling cycles measured in air: (a) and (b) show full heating-cooling cycles from room temperature up to 700 °C for a sample collected in Via Druso (a) and in Piazza Re di Roma (b); (c) shows a double thermomagnetic run for a sample collected in Via Druso, with a first cycle limited to 430 °C followed, after the specimen was cooled to room temperature, by a subsequent full cycle up to 700 °C (see text for discussion).

Table 4. Hysteresis parameters.

Sample	Surface (m^2)	Bc (mT)	Mrs (A)	Ms (A)	Bcr (mT)
M47.1	2.00E-05	8.71	2.37E-04	2.41E-03	35.8
M47.2	2.00E-05	6.99	7.03E-04	7.70E-03	36.2
M47.3	1.50E-05	6.69	5.72E-04	6.11E-03	31.6
M48	1.05E-05	6.87	1.29E-03	1.43E-02	36.4
M49	1.69E-05	7.47	4.59E-04	4.83E-03	39.2
M98	1.80E-05	10.23	1.26E-03	1.04E-02	36.8
M51	1.66E-05	6.86	2.91E-04	3.84E-03	36.1
M3	1.40E-05	6.50	3.53E-04	4.39E-03	36.6
M5prox	1.35E-05	6.58	1.69E-04	2.00E-03	36.7
M5Dist	1.70E-05	6.76	4.29E-05	5.85E-04	33.7
M4Dist	2.25E-05	6.54	3.17E-05	3.29E-04	33.0
M30	1.38E-05	7.06	5.43E-04	6.21E-03	42.4
M31	1.49E-05	7.47	3.31E-04	3.60E-03	36.0
M32	1.66E-05	6.56	4.93E-04	5.82E-03	34.4
M33	1.20E-05	6.97	1.33E-03	1.49E-02	38.2
M34	1.40E-05	7.67	3.80E-04	3.87E-03	37.4
M80	1.70E-05	8.46	6.65E-04	6.05E-03	35.7
M86	1.80E-05	7.07	1.81E-04	1.78E-03	36.0
M88	1.70E-05	7.99	4.32E-04	4.31E-03	36.6
M90	2.14E-05	6.04	3.01E-04	3.82E-03	35.2
M92	1.80E-05	8.21	4.76E-04	4.42E-03	35.2
M96	2.25E-05	7.02	5.85E-04	5.63E-03	34.2
M58	2.25E-05	8.07	9.16E-04	8.88E-03	36.2
M35	2.25E-05	6.18	1.17E-03	1.23E-02	40.2
M39	2.49E-05	6.31	5.26E-04	6.43E-03	39.5
M68	2.14E-05	8.13	2.89E-04	2.71E-03	38.2
M55	1.75E-05	9.12	4.70E-04	4.32E-03	39.0
M57	2.25E-05	9.22	3.13E-04	2.49E-03	39.5
M97	1.88E-05	7.86	2.28E-04	2.24E-03	36.7
M103	1.80E-05	7.65	5.08E-04	4.95E-03	37.5
M43	2.26E-05	5.90	4.51E-04	5.93E-03	36.5
M46	2.30E-05	8.01	5.33E-04	5.60E-03	38.6
M97.2	1.88E-05	8.50	2.42E-04	2.26E-03	36.7
Mean	1.89E-05	7.44	5.08E-04	5.32E-03	36.72
SD	5.15E-06	1.01	3.39E-04	3.52E-03	2.16

Anhysteretic remanence magnetization (ARM) was measured on 21 selected samples. Since the ARM intensity is linearly proportional to the applied DC field, the anhysteretic susceptibility (χ_{ARM}) was computed by normalizing the ARM magnetic moment acquired along the sample *z*-axis by weight and the DC-bias field. A correction was also taken into account for the magnetization of the empty plastic boxes. The values of the ARM measurements are presented in Table 5. The plot of χ_{ARM} versus χ (King *et al.* 1982) shows a general linear trend of the data, indicating that the mineralogy and its grain size distribution are generally constant throughout the data set (Fig. 8).

Table 5. ARM and χARM values from 21 selected specimens.

Sample	Dry weight (g)	ARM ($Am^2\ kg^{-1}$)	χARM ($m^3\ kg^{-1}$)
foM1	1.16	1.76E-05	2.16E-07
foM2	1.70	1.06E-05	1.28E-07
foM3	1.21	3.44E-05	4.27E-07
foM92	1.33	4.07E-05	5.06E-07
foM96	1.65	5.33E-05	6.64E-07
foM97	1.22	4.54E-05	5.64E-07
foM98	1.70	2.57E-05	3.17E-07
foM80	1.32	3.94E-05	4.89E-07
foM81	1.46	2.84E-05	3.51E-07
foM82	1.77	8.13E-06	9.61E-08
foM83	1.08	1.90E-05	2.33E-07
foM84	1.21	2.62E-05	3.23E-07
foM29	0.92	2.24E-05	2.75E-07
foM60	1.50	8.69E-06	1.03E-07
foM36	1.04	1.29E-05	1.56E-07
foM37	1.74	2.86E-05	3.53E-07
foM38	1.30	1.39E-05	1.69E-07
foM39	1.26	5.65E-05	7.05E-07
foM40	1.48	1.65E-05	2.02E-07
foM41	1.30	1.31E-05	1.58E-07
foM42	1.75	2.43E-05	2.99E-07

Note: χARM values were computed taking into account that the ARM was imparted in a DC field of 0.1 mT and corrected for the mean χARM value of the empty holders ($6.02 \times 10^{-9}\ m^3\ kg^{-1}$).

The acquisition of an IRM is dependent on the coercivity distribution of the magnetic phases that are present in a material. The absolute IRM values acquired in a pulse-field of 1000 mT (IRM_{1T}) mostly depend on the concentration of ferrimagnetic particles. When an IRM is acquired in different temperatures it is also possible to gain information on the grain size of the magnetic fraction. In this study, stepwise IRM acquisition in pulse magnetic fields was measured at room temperature and at 77 K on representative samples. For all samples the IRM acquired at room temperature showed a rapid increase in low magnetic fields. In agreement with hysteresis data, IRM saturation was generally reached by 0.3–0.5 T, and B_{CR} was found to range from 39 to 50 mT. With regards to the IRM acquired at 77 K, samples were not saturated in the highest applied field of 1.0 T, and B_{CR} increased consistently with values in the range 50–71 mT (Fig. 9). The lack of saturation in low pulse magnetic field and the relatively high B_{CR} values indicate that the assumption that pure magnetite is the only magnetite phase on leaves is overly simplistic.

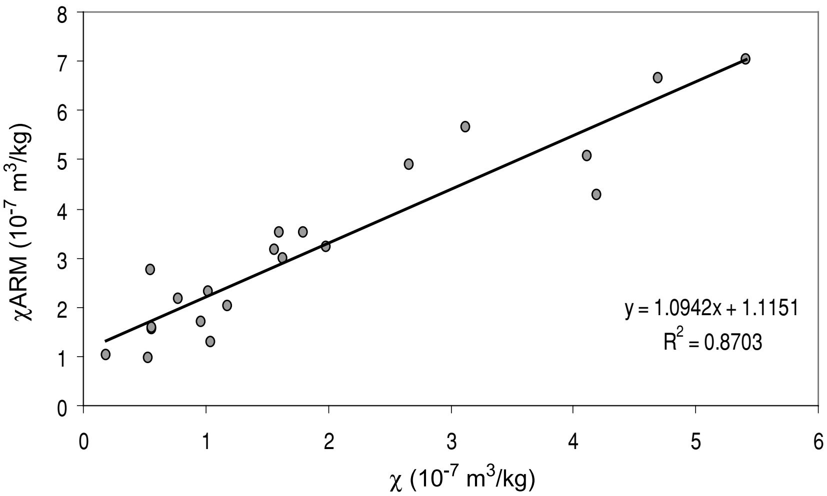

Figure 8. 'King' plot of anhysteretic magnetic susceptibility versus magnetic susceptibility (King *et al.* 1982) for 21 selected specimens representing variable distances from the sources (high-traffic roads and railways). The data plot along a linear trend (best-fit with $R^2 = 0.87$) which indicates a limited variation in grain size of the magnetic particles.

Measurements of seven different samples show a very good linear relationship ($R^2 = 0.99$) between susceptibility and IRM_{1T} values, and comparison of saturation remanent magnetization from the hysteresis data with susceptibility shows a linear correlation with a coefficient $R^2 = 0.76$ (Fig. 10). This result is similar to that found by Moreno *et al.* (2003), with $R^2 = 0.77$. The lower correlation coefficient for M_{RS} versus χ may be ascribed to the difficulties in defining precisely M_{RS} on these weakly magnetized samples, as shown in Szönyi *et al.* (2007).

An extensive Scanning Electron Microscope (SEM) and Energy Dispersive System (EDS) investigation on the origin of fine airborne powders in Rome is in progress (Sagnotti and Taddeucci, in preparation). As a representative example of the results, here we show a typical metallic particle found on the surface of a *Q. ilex* leaf (Fig. 11a). The morphology of these particles is mostly irregular, with a rough, moss-like, surface. Their chemical composition indicates that the metallic particles consist of variably oxidized iron grains (Fig. 11b), occasionally enriched by a variety of other elements (Si, S, Cr, Cu and Zn).

4 DISCUSSION AND INTERPRETATION

4.1 Pollution in the city of Rome

The susceptibility of tree leaf samples is a good proxy for estimating the ferromagnetic (*sensu lato*) content of PM accumulated on the surface of the leaves. Magnetic biomonitoring of tree leaves is an original experimental method to delineate the capillary distribution of PM in large urban areas. Results are however dependent on the tree species. In this study, which extends the work of Moreno *et al.* (2003), the sampling was restricted to *Quercus ilex*, a typical evergreen oak widespread in Rome, that proved to be a good accumulator of PM.

The magnetic survey, covering a large part of the city of Rome, showed that low and high magnetic susceptibility values were systematically associated with large green areas and high-traffic roads, respectively. Even along high-traffic roads magnetic susceptibility of tree leaves may indicate 'critical' points. Highest values correspond to locations with highest traffic volume and severe traffic jams, with peak susceptibility values as high as 7×10^{-7} m^3 kg^{-1}, that is about two orders of magnitude higher than the values measured in green areas and urban parks. A strong, exponential distance dependence with respect to the source along the streets in Rome was found and investigated in detail. The fact that susceptibility depends mostly on distance from roadsides has already been established in previous studies (i.e. Hoffmann *et al.* 1999; Matzka and Maher 1999; Moreno *et al.* 2003). Gautam *et al.* (2004) note that susceptibility decreases exponentially and monotonously with respect to distance and reaches the background values already after ~5 m from the roadside. Gramotnev *et al.* (2003) found a power-law decrease of particle numbers with respect to distance with both direct measurements and theoretical models.

The low magnetic susceptibility values obtained in green areas away from roads and vehicular traffic indicate that industrial or other general magnetic PM sources are negligible in Rome. Natural PM from distant sources was also proven to have insignificant magnetic properties in the Latium Region (Sagnotti *et al.* 2006). The magnetic PM found on tree leaves accumulated over the entire lifespan of the leaves. A location with a high truck traffic volume at the General Markets had a high susceptibility in 2001 but a low susceptibility in 2005, 3 yr after the location of the Markets was moved. This indicates that long-term PM pollution levels can be monitored with leaves. Magnetic PM pollution is also independent of the sampling location, as no spatial change in the magnetic mineralogy was found.

4.2 Mineralogy and grain size

Susceptibility versus temperature curves have indicated the magnetic susceptibility at room temperature is due magnetic phases that lose their magnetization between 300 and 400 °C and at ca. 580 °C. The latter is the Curie temperature for pure magnetite. The inflection between 300 and 400 °C may be due to a range of composition for magnetite solid solutions with other spinel phases (i.e. Yamanaka & Okita 2001) or to the progressive conversion of maghemite to hematite (Stacey & Banerjee 1974). Depressed Curie temperatures in iron oxides have been reported for some anthropogenic phases collected in Danube River sediments from Bulgaria (Jordanova *et al.* 2004). They found that these low Curie temperatures

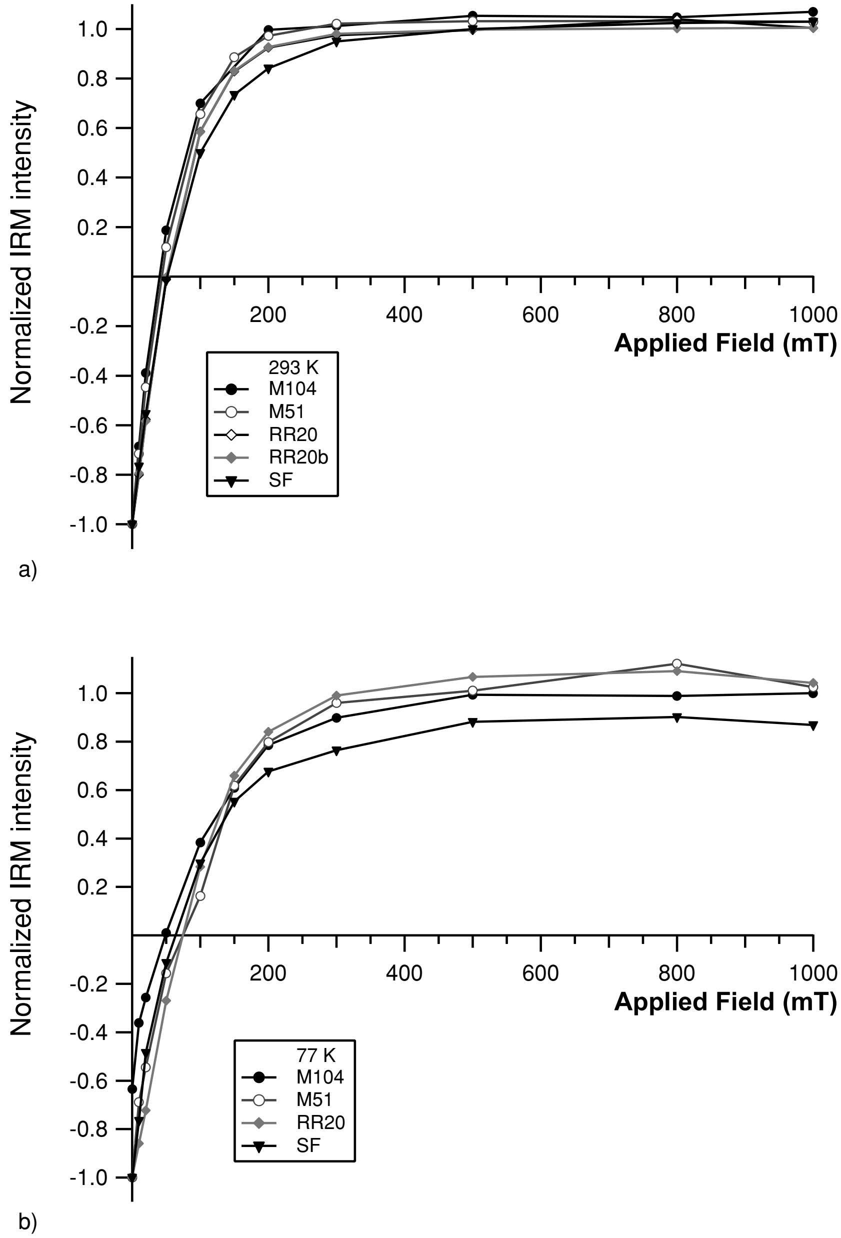

Figure 9. IRM acquisition curves at room (a, $T = 293$ K) and at liquid nitrogen (b, $T = 77$ K) temperatures for selected samples.

correlated with particles that had high Al content. One particle with an Al content of 44 per cent had a Curie temperature around 450 °C. Substitution of iron by other elements, such as in ferrites $M^{2+}Fe_2O_4$ employed in industrial alloys, may be responsible for the Curie temperature around 430 °C that is observed in our leaves. The thermomagnetic cycle limited to 430 °C (Fig. 7c) shows a sharp decrease of the magnetic susceptibility during heating. The fact that this cooling curve is slightly lower than heating curve (Fig. 7c) indicates that there was no production of new magnetic mineral phases at temperatures lower than 430 °C. Heating to higher temperature leads instead to the formation of magnetite, as indicated by the cooling curves showing much higher susceptibility values than the heating curves and a distinct Curie temperature around 580 °C. Dekkers *et al.* (2000) noted that the heating chamber of the CS-3 unit of the AGICO Kappabridge is very limited and oxygen depletion can lead to a reducing atmosphere, favouring the formation of magnetite. The irreversibility of the thermomagnetic curves has been seen in other investigations on PM (e.g. Gautam *et al.* 2004; Muxworthy *et al.* 2002). The decrease of magnetic susceptibility values on cooling below 400°C may be due to the presence of grain sizes in the range close to the threshold between superparamagnetic (SP) and single domain (SD) particles. As very small SP particles lose their SP behaviour while cooling down, they become magnetically ordered SD particles, which leads to a decrease of the total susceptibility.

The IRM acquisition shows a rapid increase in low fields with a gradual saturation by about 500 mT. At 77K there is an increase in the magnetization and in B_{cr}, which suggests the blocking of a phase with superparamagnetic particle size. Both the hysteresis loops and the IRM acquisition suggest that there is either a single phase that saturates between 300 and 500 mT or a combination of magnetic phases with high and low coercivities. The samples do not

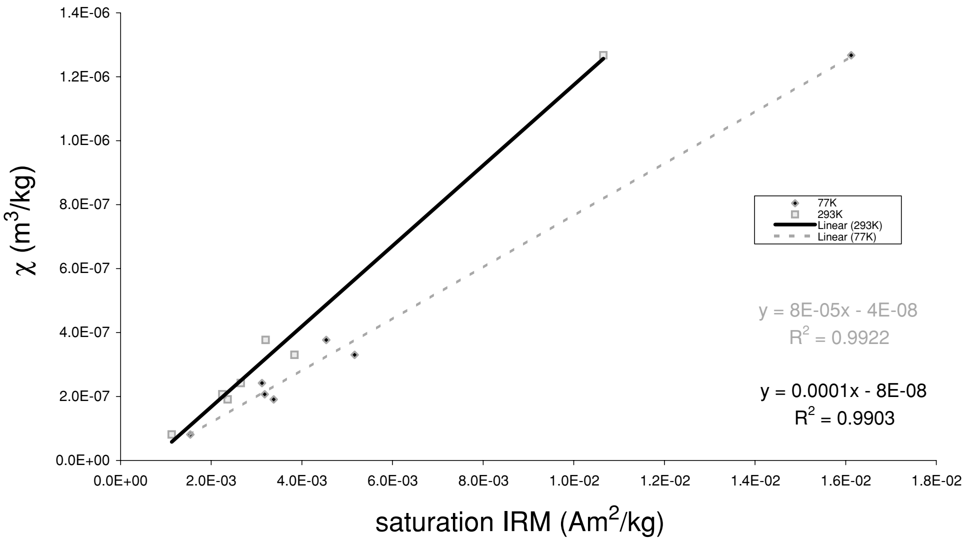

Figure 10. Plot of magnetic susceptibility versus saturation IRM values measured at 293 K and at 77 K for seven selected specimens. The data plot along a linear trend (best-fit with $R^2 > 0.99$). Though the goodness of the fit may be biased by the single high value of specimen M50, the exclusion of such specimen still gives a high correlation coefficient ($R^2 > 0.86$).

acquire an ARM easily and have a bulk coercivity that is too high for MD stoichiometric magnetite or maghemite. Hematite has been identified by Hoffmann *et al.* (1999) in an investigation of PM10 pollution on a top soil, related to road emissions. Muxworthy *et al.* (2002) used Mössbauer spectroscopy in a study on PM collected with filter trays and were not able to identify hematite. They state, however, that they would not be able to detect hematite if it had superparamagnetic grain size.

The hysteresis data and the χ_{ARM} versus χ ratios indicate that the overall grain size distribution of all specimens is remarkably similar, suggesting a uniform mixture mineralogy (*cf.* Szönyi *et al.* 2007). As a consequence, the particle size distribution with respect to distance from the source (i.e. high-traffic roads) is not easy to establish. Moreno *et al.* (2003) suggested that grain sizes decrease with increasing distance to the road. On the other hand, Urbat *et al.* (2004) suggested that the grain size is increasing with respect to the distance of the street, with smallest particle sizes originating from traffic emissions close to streets. This study rather points out that variations in grain size of the magnetic particles are limited, and no particular distinct trend with distance from the source was observed.

Treating the leaves to remove the organic compounds would leave all non-organic material that would be available for a characterization of both coercivity and thermal properties of the magnetic phases and of their geochemistry. While it is clear that the emissions originate from circulating vehicles and settle on the leaf surface, they can originate directly from improper combustion in the engines, or may be derived from abrasion of tires and brakes. Furthermore, oxidation processes on the magnetic particles may occur in ambient air before being deposited on the leaves. The formation processes, chemical/mineralogical composition and structure of anthropogenic ferrimagnetic particles are different from those of natural particles. All iron oxide phases, from nearly native iron in the core via wuestite–magnetite–maghemite phases to highly oxidized phases such as hematite on the rim, can be found within the same magnetic spherule (e.g. Jordanova *et al.* 2004, 2006). The net result implies that the magnetic properties of anthropogenic magnetic particles may not be easily compared with those of natural mineral systems.

5 CONCLUSIONS

Magnetic biomonitoring with *Q. ilex* tree leaves is a useful approach to delineate primary anthropogenic airborne PM pollution, which leads to the deterioration of ambient air quality and causes adverse effects to human health. Specific magnetic susceptibility shows good linear correlation coefficients with other concentration dependent magnetic parameters (e.g. intensity of artificial remanences). The rapidity and ease with which magnetic susceptibility can be measured makes it the key proxy for biomonitoring through magnetic surveys. A new protocol for magnetic susceptibility measurements is proposed here, in order to take into account changes with time after collection of the samples. Susceptibility measurements could monitor PM emission levels throughout an extensive area in a major city such as Rome. It would allow a quick assessment to identify locations where more rigorous monitoring should be made, also with respect to traffic bans in critical areas according to new PM10 regulations promulgated by the European Union. During this study, 112 different locations were repeatedly sampled. These repetitions and the comparison of young and old leaves from the same trees reveal that susceptibility values are the result of a time-accumulated exposure of the tree leaves during their lifespan and not just a point measurement in time. These findings are useful in proposing guidelines concerning human health and the exposure of the population to airborne PM, as well as for planning the location of a network of PM monitoring stations. It is emphasized that not only PM, but especially iron-bearing magnetic PM is dangerous to the human health due to its aggressively reacting iron radicals.

It was noted that the distance from the source (i.e. the vehicular traffic) is a crucial factor for strength of the magnetic signal, ranging from highest values closest to congested roads with stop-and-go traffic to low values within several meters. Three classes are proposed for the town of Rome. High traffic shows average values of $\chi = 3.2 \times 10^{-7}$ m^3 kg^{-1}, green areas with low traffic volume in the vicinity shows average values of $\chi = 1.4 \times 10^{-8}$ m^3 kg^{-1} and the background magnetic susceptibility is estimated at $\chi = 2.2 \times 10^{-9}$ m^3 kg^{-1}. Background signals in Rome are very weak,

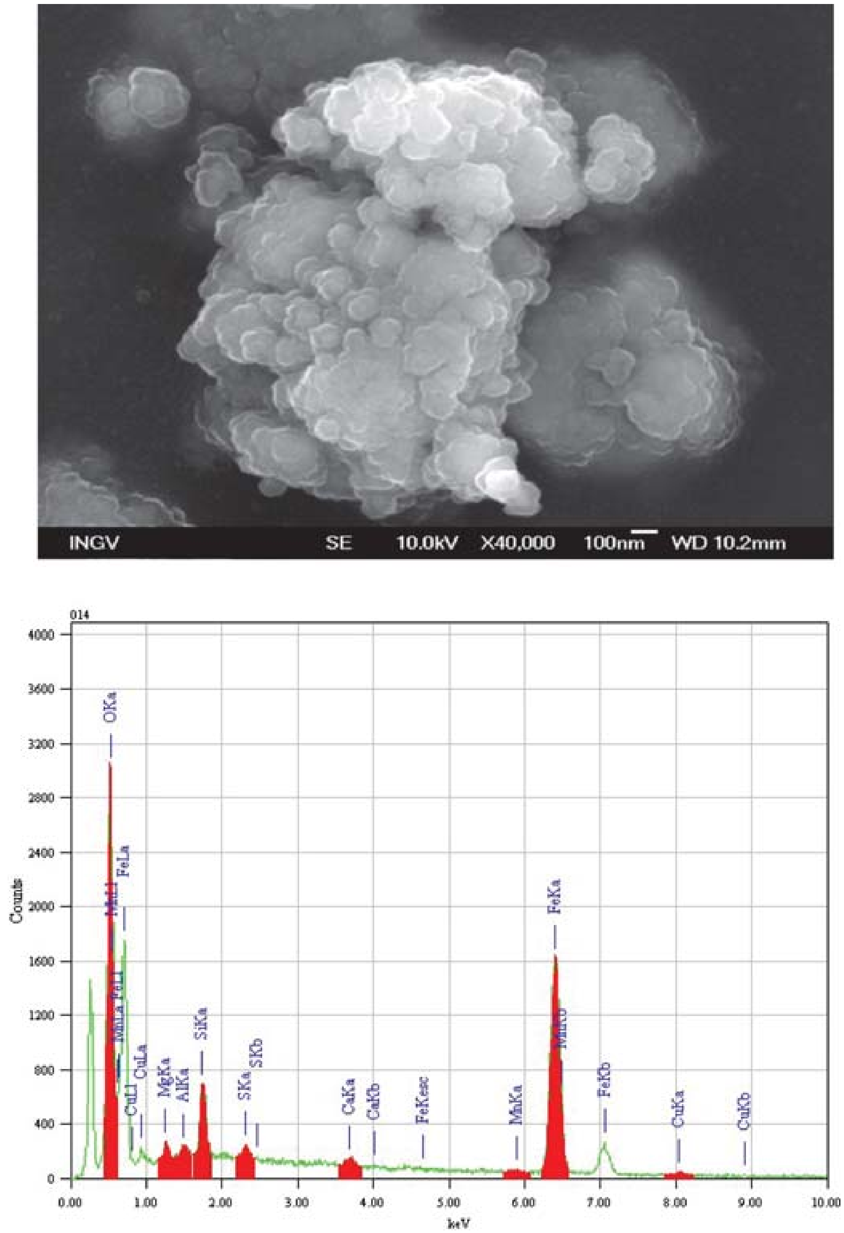

Figure 11. Representative SEM-EDS analysis of metallic particles found on *Q. ilex* leaves. (a) SEM microphotograph; (b) X-ray spectra showing a standardless chemical analysis.

confirming the absence of industrial PM emissions as opposed to other cities. As distance dependence is the most influential factor of the traffic related PM level, avoiding close contact with the pollution sources is helpful to reduce health hazards for the population. Keeping a distance of ∼10 m to major roads already reduces primary anthropogenic magnetic PM levels on the order of magnitudes.

Variations within the leaf surface as well as variations due to meteorological conditions are negligible in this study. Cleaning experiments confirm the hypothesis that not all PM can be washed off, supporting the suggestion that a large part of the magnetic PM is deeply caught within the leaf structure in the *Q. ilex* leaves (Szönyi *et al.* 2007). While rainfall has a net decrease effect on susceptibility of seven tested samples, no clear correlations can be found. Depending on location, position of the leaf within the tree and, therefore, the protection from or the exposure to precipitation, an increase or decrease of susceptibility is observed.

Hysteresis properties, temperature-dependence of magnetic susceptibility, ARM and IRM parameters reveal that various populations of magnetic particles accumulate on the tree leaves, suggesting a uniform compositions and grain size distributions. Concise and detailed reconstruction of the relative proportions and grain sizes of the various magnetic PM populations is still difficult, as well as the precise identification of their sources. More research is necessary in this context.

ACKNOWLEDGMENTS

We are grateful to Simone Atzori for his valuable help to prepare Fig. 1 and to Jacopo Taddeucci for the SEM-EDS analyses. We also acknowledge the constructive comments by Eduard Petrovský and an anonymous reviewer that were of substantial support in improving the manuscript. ETH Contribution Nr. 1531.

REFERENCES

Dekkers, M.J., Passier, H.F. & Schoonen, M.A.A., 2000. Magnetic properties of hydrothermally synthesized greigite (Fe_3S_4) – II. High- and low-temperature characteristics, *Geophys. J. Int.,* **141,** 809–819.

Dunlop, D.J. & Özdemir, Ö., 1997. *Rock Magnetism: Fundamentals and Frontiers,*, 573 pp., Cambridge Univ. Press, Cambridge.

Evans, M.E. & Heller, F., 2003. *Environmental Magnetism, Principles and Applications of Enviromagnetics,* 299 pp., Academic Press, London.

Flanders, P.J., 1999. Identifying fly ash at a distance from fossil fuel power stations, *Environ. Sci. Tech.,* **33,** 528–532.

Gautam, P., Blaha, U., Appel, E. & Neupane, G., 2004. Environmental magnetic approach towards the quantification of pollution in Kathmandu urban area, Nepal, *Phys. Chem. Earth.,* **29,** 973–984.

Gillies, J.A., Gertler, A.W., Sagebiel, J.C. & Dippel, W.A., 2001. On-road particulate matter PM2.5 and PM10 emissions in the Sepulveda Tunnel, Los Angeles, *Calif. Environ. Sci. Tech.,* **35,** 1054–1063.

Goddu, S.R., Appel, E., Jordanova, D. & Wehland, F., 2004. Magnetic properties of road dust from Visakhapatnam (India)—relationship to industrial pollution and road traffic, *Phys. Chem. Earth,* **29,** 985–995.

Gramotnev, G., Brown, R., Ristovski, Z., Hitchins, J. & Morawska, L., 2003. Determination of average emission factors for vehicles on a busy road, *Atmos. Environ.,* **37,** 465–474.

Gratani, L., Crescente, M.F. & Petruzzi, M., 2000. Relationship between leaf life-span and photosynthetic activity of Quercus Ilex in polluted urban areas (Rome), *Environ. Poll.,* **110,** 19–28.

Hirt, A.M., Banin, A. & Gehring, A.U., 1993. Thermal generation of ferromagnetic minerals from iron-enriched smectites, *Geophys. J. Int.,* **115,** 1161–1168.

Hoffmann, V., Knab, M. & Appel, E., 1999. Magnetic susceptibility mapping of roadside pollution, *J. Geochem. Expl.,* **66,** 313–326.

Jordanova, D., Hoffmann, V. & Fehr, K.T., 2004. Mineral magnetic characterization of anthropogenic magnetic phases in the Danube river sediments (Bulgarian parts), *Earth planet. Sci. Lett.,* **221,** 71–89.

Jordanova, D., Jordanova, N. & Hoffmann, V., 2006. magnetic mineralogy and grain-size dependance of hysteresis parameters of single spherules from industrial waste products, *Phys. Earth planet. Int.,* **154,** 255–265.

King, J.W., Banerjee, S.K., Marvin, J.A. & Özdemir, Ö., 1982. A comparison of different magnetic methods for determining the relative grain size of magnetite in natural materials: some results from lake sediments, *Earth Planet. Sci. Lett.,* **59,** 404–419.

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 fuzzy c-means cluster analysis, *Eur. J. Environ. Eng. Geophys.,* **6,** 125–140.

Magiera, T., Strzyszcz, Z., Kapicka, A. & Petrovský, E., 2006. Discrimination of lithogenic and anthropogenic influences on topsoils magnetic susceptibility in Central Europe, *Geoderma,* **130,** 299–311.

Matzka, J. & Maher, B.A., 1999. Magnetic biomonitoring of roadside tree leaves: identification of spatial and temporal variations in vehicle-derived particles, *Atmos. Environ.,* **33,** 4565–4569.

Morawska, L., Thomas, S., Bofinger, N., Wainwright, D. & Neale, D., 1998. Comprehensive characterization of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants, *Atmos. Environ.,* **32,** 2467–2478.

Moreno, E., Sagnotti, L., Dinarès-Turell, J., Winkler, A. & Cascella, A., 2003. Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves, *Atmos. Environ.,* **37,** 2967–2977.

Morris, W.A., Versteeg, J.K., Bryant, D.W., Legzdins, A.E., McCarry, B.E. & Marvin, C., 1995. H. Preliminary comparisons between mutagenic and magnetic susceptibility of respirable airborne particle, *Atmos. Environ.,* **29,** 3441–3450.

Muxworthy, A.R., Matzka, J. & Petersen, N., 2001. Comparison of magnetic parameters of urban atmospheric particulate matter with pollution and meteorological data, *Atmos. Environ.,* **35,** 4379–4386.

Muxworthy, A.R., Schmidbauer, E. & Petersen, N., 2002. Magnetic properties and Mössbauer spectra of urban atmospheric particulate matter: a case study from Munich, *Germany, Geophys. J. Int.,* **150,** 558–570.

Petrovský, E. & Elwood, B., 1999. Magnetic monitoring of air-, land- and water pollution, in *Quaternary Climates, Environments and Magnetism,* pp. 279–322, eds Maher, B. & Thompson, R., Cambridge University Press, Cambridge.

Petrovský, E. & Kapička, A., 2006. On determination of the Curie point from thermomagnetic curves, *J. Geophys. Res.,* **111,** B12S27, doi:10.1029/2006JB004507.

Petrovský, E., Kapicka, A., Jordanova, N., Knab, M. & Hoffmann, V., 2000. Low-field magnetic susceptibility: a proxy method of estimating increased pollution of different environmental systems, *Environ. Geol.,* **39,** 312–318.

Petrovský, E., Kapicka, A., Jordanova, N. & Boruvka, L., 2001. Magnetic properties of alluvial soils contaminated with lead, zinc and cadmium, *J. Appl. Geophys.,* **48,** 127–136.

Pike, C.R., Roberts, A.P. & Verosub, K.L., 1999. Characterizing interactions in fine magnetic particle systems using first order reversal curves, *J. Appl. Phys.,* **85,** 6660–6667.

Pope, III C.A. & Dockery, D.W., 1999. Epidemiology of particle effects, in *Air Pollution and Health,* pp. 673–705, eds Holgate, S.T., Samet, J.M., Koren, H.S. & Maynard, R.L., Academic Press, London.

Roberts, A.P., Pike, C.R. & Verosub, K.L., 2000. First-order reversal curve diagrams: a new tool for characterizing the magnetic properties of natural samples, *J. Geophys. Res,* **B105,** 28 461–28 475.

Sagnotti, L., Rochette, P., Jackson, M., Vadeboin, F., Dinarès-Turell, J., Winkler, A. & the Mag-Net Science Team, 2003. Inter-laboratory calibration of low-field magnetic and anhysteretic susceptibility measurements, *Phys. Earth Planet. Int.,* **138,** 25–38.

Sagnotti, L., Macrì, P., Egli, R. & Mondino, M., 2006. Magnetic properties of atmospheric particulate matter from automatic air sampler stations in Latium (Italy): toward a definition of magnetic fingerprints for natural and anthropogenic PM10 sources, *J. geophys. Res.,* **111,** B12S22, doi:10.1029/2006JB004508.

Spiteri, C., Kalinski, V., Rösler, W., Hoffmann, V. & Appel, E., MAGPROX team, 2005. Magnetic screening of a pollution hotspot in the Lausitz area, Eastern Germany: correlation analysis between magnetic proxies and heavy metal contamination in soils, *Environ. Geol.,* **49,** 1–9.

Spassov, S., Egli, R., Heller, F., Nourgaliev, D.K. & Hannam, J., 2004. Magnetic quantification of urban pollution sources in atmospheric particulate matter, *Geophys J. Int.,* **159,** 555–564.

Stacey, F.D. & Banerjee, S.K., 1974. *The Physical Principles of Rock Magnetism*. Elsevier, New York, 195 pp.

Szönyi, M., Sagnotti, L. & Hirt, A.M., 2007. On leaf magnetic homogeneity in particulate matter biomonitoring studies, *Geophys. Res. Lett.,* **34,** L06306, doi:10.1029/2006GL029076.

Tuch, T.M., Wehner, B., Pitz, M., Cyrys, J., Heinrich, J., Kreyling, W.G., Wichmann, H.E. & Wiedensohler, A., 2003. Long-term measurements of size-segregated ambient aerosol in two German cities located 100 km apart, *Atmos. Environ.,* **37,** 4687–4700.

Urbat, M., Lehndorff, E. & Schwark, L., 2004. Biomonitoring of air quality in Cologne conurbation using pine needles as a passive sampler. Part I: magnetic properties, *Atmos. Environ.,* **38,** 3781–3792.

Veneva, L., Hoffmann, V., Jordanova, D., Jordanova, N. & Fehr, Th., 2004. Rock magnetic, mineralogical and microstructural characterization of fly ashes from Bulgarian power plants and the nearby anthropogenic soils, *Phys. Chem. Earth,* **29,** 1011–1023.

Wichmann, H.E. & Peters, A., 2000. Epidemiological evidence of the effects of ultrafine particle exposure, *Philos. Trans. Roy. Soc. Lond.,* **A358,** 2751–2769.

Winkelhofer, M. & Zimanyi, G.T., 2006. Extracting the intrinsic switching field distribution in perpendicular media: a comparative analysis, *J. Appl. Phys.,* **99,** 08E710.

Xie, S., Dearing, J.A. & Bloemendal, J., 2000. The organic content of street dust in Liverpool, UK, and its association with dust magnetic properties, *Atmos. Environ.,* **34,** 269–275.
Yamanaka, T. & Okita, M., 2001. Magnetic properties of the Fe_2SiO_4-Fe_3O_4 spinel solid solutions, *Phys. Chem. Miner.,* **28,** 102–109.

SUPPLEMENTARY MATERIAL

The following supplementary material is available for this article:

Table S1. Temperature and precipitation data for Rome, Italy, recorded at 41°51′48″ N, 12° 25′ 15″ E.

Table S2. Temperature and precipitation data for sampling period in November and December 2005, recorded at 41°51′48″ N, 12° 25′ 15″ E. Shaded areas show days when leave samples were taken.

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