How does the amount and composition of PM deposited on *Platanus acerifolia* leaves change across different cities in Europe?

Chiara Baldacchini,[1] Ana Castanheiro,[2] Nairuhi Maghakyan,[3] Gregorio Sgrigna,[1] Jolien Verhelst,[2] Rocío Alonso,[4] Jorge H. Amorim,[5,+] Patrick Bellan,[6] Danijela Djunisijevic Bojović,[7] Jürgen Breuste,[8] Oliver Bühler,[9] Ilie C. Cântar,[10] Paloma Cariñanos,[11] Giulia Carriero,[12] Galina Churkina,[13] Lucian Dinca,[10] Raffaela Esposito,[1] Stanisław W. Gawroński,[14] Maren Kern,[15] Didier Le Thiec,[16] Marco Moretti,[17] Tine Ningal,[18] Eleni C. Rantzoudi,[19] Iztok Sinjur,[20] Biljana Stojanova,[21] Mira Aničić Urošević,[22] Violeta Velikova,[23] Ivana Živojinović,[24] Lilit Sahakyan,[3] Carlo Calfapietra,[1,*] Roeland Samson[2]

(1) Institute of Agro Environmental and Forest Biology, National Research Council (IBAF–CNR), Via Marconi 2, Porano 05010, & Via Castellino 111, Napoli 80131, Italy

(2) Laboratory of Environmental and Urban Ecology, Dept. of Bioscience Engineering, University of Antwerp, Groenenborgerlaan 171, Antwerp 2020, Belgium

(3) Center for Ecological-Noosphere Studies of National Academy of Sciences of Armenia, Yerevan, Armenia

(4) Ecotoxicology of Air Pollution, CIEMAT, Avda. Complutense 22, edif. 70, Madrid 28040, Spain

(5) CESAM & Dept. of Environment and Planning, University of Aveiro, Aveiro 3810-193, Portugal

(6) Vegetation consultant/Landscape engineer, Båstadsgatan 6a, Malmö, Sweden

(7) University of Belgrade, Faculty of Forestry, Chair of Landscape Horticulture, Kneza Višeslava, Belgrade 11000, Serbia

(8) Dept. Geography and Geology, University Salzburg, Hellbrunnerstr. 34, Salzburg 5020, Austria

(9) Dept. of Geosciences and Natural Resource Management, University of Copenhagen, Rolighedsvej 23, Frederiksberg 1958, Denmark

(10) National Institute for Research and Development for Forestry "Marin Dracea", Padurea Verde Alley 8, Timisoara 300310, & B-dul Eroilor 128, Bucharest 077190, Romania

(11) Dept. of Botany, University of Granada & IISTA-CEAMA, Andalusian Institute for Earth System Research, Av. Mediterraneo, Granada 18071, Spain

(12) IPSP-CNR, Via Madonna del piano 10, Sesto Fiorentino 50019, Italy

(13) Institute for Advanced Sustainability Studies (IASS), Berlinerstr 130, Potsdam 14467, Germany

[14] Laboratory of Basic Research in Horticulture, Faculty of Horticulture, Biotechnology and Landscape Architecture, Warsaw University of Life Sciences, Ul. Nowoursynowska 159, Warsaw 02-776, Poland

[15] Bern University of Applied Sciences, School of Agricultural, Forest and Food Sciences HAFL, division of Forest Science, Länggasse 85, Zollikofen 3052, Switzerland

[16] UMR EEF, INRA, Université de Lorraine, Champenoux 54280, France

[17] Swiss Federal Research Institute WSL, Biodiversity and Conservation Biology, Zürcherstrasse 111, Birmensdorf 8903, Switzerland

[18] School of Geography, University College Dublin, Belfield, Dublin 4, Ireland

[19] Laboratory Teaching Staff, Silviculture Laboratory, Forestry and Environmental Management and Natural Resources Dept., Dimocritus University of Thrace, Pantazidou 193, Orestiada, Greece

[20] Slovenian Forestry Institute, Večna pot 2, Ljubljana 1000, Slovenia

[21] Urban Greenery Dept., PE Parks and Greenery, Bul. Ilinden 104, Skopje 1000, Macedonia

[22] Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, Belgrade 11080, Serbia

[23] Institute of Plant Physiology and Genetics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[24] European Forest Institute Central-East and South-East European Regional Office (EFICEEC-EFISEE), University of Natural Resources and Life Sciences, Vienna, Feistmantelstrasse 4, Vienna 1180, Austria

[+] Current address: Swedish Meteorological and Hydrological Institute (SMHI), Air quality research unit, Norrköping 60176, Sweden

[*] Corresponding author. Address: IBAF-CNR, Via Marconi 2, 05010 Porano (TR), Italy. Telephone: +39 0763 374929. Fax: +39 0763 374980. Email address: carlo.calfapietra@ibaf.cnr.it

Abstract

Particulate matter (PM) deposited on *Platanus acerifolia* tree leaves has been sampled in the urban areas of 28 European cities, over 20 countries, with the aim of testing leaf deposited particles as indicator of atmospheric PM concentration and composition. Leaves have been collected close to streets characterised by heavy traffic and within urban parks. Leaf surface density, dimensions, and elemental composition of leaf deposited particles have been compared with leaf magnetic content, and discussed in connection with air quality data. The PM quantity and size were mainly dependent on the regional background concentration of particles, while the

percentage of iron-based particles emerged as a clear marker of traffic-related pollution in most of the sites. This indicates that *Platanus acerifolia* is highly suitable to be used in atmospheric PM monitoring studies and that morphological and elemental characteristics of leaf deposited particles, joined with the leaf magnetic content, may successfully allow urban PM source apportionment.

I. Introduction

From the 1970s, higher plants have emerged as suitable bioindicators in urban and industrial areas.[1] In particular, tree leaves efficiently accumulate particulate matter (PM), mainly due to gravitational and/or inertial deposition on lamina and tips.[2,3] Different tree species have shown different PM accumulation rates, and the ability of leaves to act as PM receptors depends upon height and canopy structure, leaf surface characteristics including leaf pubescence and wettability, as well as meteorological conditions.[4–11] This has further led to the conception of trees as potential PM pollution mitigation actors,[12–14] with the consequent development of new urban tree planting programs, prioritizing specific tree species selection, alongside choosing strategic locations for their optimal outcomes.[15,16]

Particulate matter is known to produce adverse effects on humans, and PM removal is a major health concern.[17] For instance, particles with a diameter smaller than 10 µm (PM10) may enter human lungs and cause cardiovascular diseases, decrease lung function and even cause lung cancer.[18] PM is also a carrier of toxic substances, especially heavy metals,[19,20] which can cause negative health effects, such as disorders in hematogenesis, and in the central nervous, cardio-vascular and urogenital systems.[21] Moreover, individual heavy metals are known to trigger specific diseases such as Alzheimer`s and Parkinson`s diseases.[22] Despite the imposition of PM concentration limit values from the European Community (EC),[23] PM concentrations in many European countries often exceed these limits.[24] Within this context, a full comprehension of the features and mechanisms of PM deposition on urban tree leaves under real conditions emerges as highly required, since it may greatly help in facing and solving the PM pollution problem in urban environments, through both PM monitoring and mitigation strategies.

The deposition of PM on tree leaves in European urban environments has been investigated by studying different deciduous tree species, such as: *Acer campestre, Acer negundo*, *Acer* *pseudoplatanus, Aesculus hippocastanum*, *Carpinus betulus, Celtis occidentalis, Corylus colurna, Fraxinus pennsylvanica*, *Padus serotina, Pinus nigra, Platanus acerifolia, Platanus orientalis*, *Quercus ilex, Quercus robur*, *Salix alba, Tilia europaea,* and *Tilia tomentosa*.[2–7,10,11,25–31]

Different analytical techniques have been used for leaf deposited PM10 characterisation, such as atomic absorption spectrometry (AAS),[5,27] gas chromatography–mass spectrometry (GC-MS),[27] inductively coupled plasma mass spectrometry (ICP/MS),[7] saturation isothermal remanent magnetization (SIRM),[3,4,25,26,29–31] and scanning electron microscopy (SEM), also implemented with x-ray spectroscopy (EDX).[2,5,31,32] In particular, magnetic analysis of leaf material has been pointed as a rapid, easy and relatively cheap strategy for identifying pollution hot spots, especially those related with traffic and industrial activities.[3,4,25,26,29–31] In order to separate leaf deposited PM from the rest of the leaf material, washing procedures, and subsequent filtering of the obtained solution, have been introduced.[3,6,10,11,28,32] However, only SEM/EDX analyses have allowed a full characterisation of individual, leaf deposited PM10 particles, both upon collection on filters[32] and, most important, on "as it is" leaves.[2,5,31] Thus, the coupling of single particle techniques, such as SEM/EDX, with macroscopic leaf material analysis, such as SIRM, is emerging as a highly promising method for obtaining a full quanti-qualitative characterisation of leaf deposited PM.[31,33]

In July 2014, within the context of the COST Action FP1204 "Greeninurbs" (www.greeninurbs.com), a call for leaf collection in urban environments was launched among European scientists working on urban green infrastructure and urban forests, for comparing leaf deposited PM10 particles across European cities, as indicator of atmospheric PM concentration and composition. Some large-scale air quality monitoring experiments have been set up before, e.g. the "*European Network for the Assessment of Air Quality by the Use of Bioindicator Plants Cooperative*" (EuroBionet, involving 12 cities in 8 countries[34]) and the "*European Survey of Atmospheric Heavy Metal Deposition"* (involving 30 European countries[35]). Moreover, the source apportionment of PM in Europe, as obtained by sampling PM through gravimetric techniques and analyzing it with a variety of analytical methodologies, has been recently reviewed within the context of the COST Action 633 (by analysing data from 33 cities over 12 countries[36]). However, the present study describes and analyses the largest dataset ever collected on leaf deposited PM within European urban environments. The leaves of *Platanus acerifolia* trees were used as passive air filters, and the leaf deposited PM10 particles have been characterised by performing SEM/EDX analysis on untreated collected leaves, also discriminating adaxial from abaxial leaf surface adsorbed particles. The results obtained are discussed in comparison with leaf magnetic content, as determined by SIRM on the same samples, and with air quality data and environmental/urban metadata.

II. Experimental

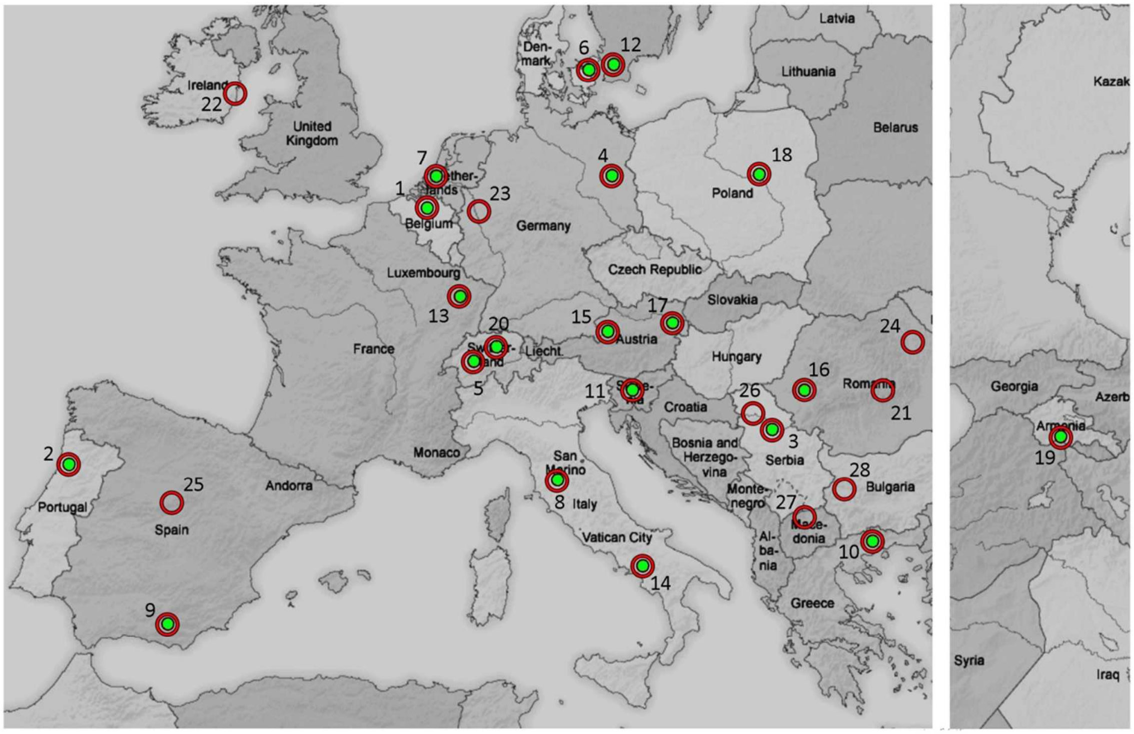
Test species and sampling

Leaves have been collected at 56 sites, in 28 cities over 20 countries (Figure 1). Participants were asked to collect leaf samples according to a specific protocol, together with supporting background data (see Table S1 for sampling information and metadata).The campaign has been carried out at the end of the summer (between August 25th, 2014 and September 7th, 2014), and leaves have been sampled after a rainless period of at least three days, to reduce the influence of the meteorological variability among the cities.

A single species has been sampled, to minimize possible differences in particle deposition due to differences in leaf surface characteristics.[9] *Platanus acerifolia* was selected as test species, due to the poor effect of rainfall on the accumulation of metal particles on its leaves,[29] and to its high capability in PM capturing, in general.[5,6,8,9] Indeed, *P. acerifolia* has been shown to have significantly higher leaf PM retention amount than *S. japonica* and *C. deodara*, likely due to its ridged leaf surface[8], while *P. occidentalis* (same genus as *P. acerifolia*) showed the second highest amounts of leaf accumulated PM both in-wax and on surface, when compared with 23 other tree species.[9] Only leaves of *Quercus variabilis* captured higher amounts of PM due to its great quantity of pubescence and rough surface.[9] However, this species is only poorly distributed in Europe, while *Platanus acerifolia*, is very abundant in all the European countries, thank to its wide hardiness range, which is from 5 to 9 according to USDA zone.[37]

Leaves were sampled at two contrasting urban environments, *e.g.* in a park area and near a street characterised by heavy traffic – further named park and street sites, respectively. At each sampling location, five full grown and undamaged leaves were sampled from the outer canopy of the same tree. A sampling height between three and five meters was requested by the protocol, as the best compromise to avoid data contamination by very local sources at the ground level, while ensuring a feasible procedure during sampling and the absence of leaf contamination by citizens. Street site trees were sampled at the traffic-exposed side.

After collection, leaves were stored between clean paper sheets and enclosed in paper envelopes, avoiding mechanical stresses. The dried leaves were sent to the organising laboratories for analysis. There, each leaf was manually cut over its main vein, to obtain two similar halves to be used in SEM/EDX (conducted in Italy, at the IBAF CNR unit in Naples) and SIRM (performed in Belgium, at the Laboratory of Environmental and Urban Ecology of Antwerp University) analyses. A full characterisation of the samples and a wide gathering of background metadata were obtained for 20 cities, while only SIRM investigation was performed for the remaining 8, due to damages of the leaves during transport and missing information (Figure 1, Table S1).



1	Antwerp	5	Bern	9	Granada	13	Nancy	17	Vienna	21	Brasov	25	Madrid
2	Aveiro	6	Copenhagen	10	Kavala	14	Naples	18	Warsaw	22	Dublin	26	Novi Sad
3	Belgrade	7	Den Haag	11	Ljubljana	15	Salzburg	19	Yerevan	23	Düsseldorf	27	Skopje
4	Berlin	8	Florence	12	Malmö	16	Timisoara	20	Zurich	24	Iasi	28	Sofia

Figure 1: Map of cities participating in the European sampling campaign. Samples from cities listed as 1-20 (red-green spots; green labels in the table) have been analysed by both SEM/EDX and SIRM, and corresponding metadata are listed in Table S1. Samples from cities listed as 21-28 (red circles; red labels in the table) have been analysed only using SIRM.

Morphological and elemental characterisation

The characterisation of deposited PM by means of SEM provides a quantification in terms of particles' number and size.[38] Conversely, PM levels are most often reported in terms of mass per unit volume (e.g. mg m^{-3}), determined either gravimetrically or computed from a mean particle abundance measurement using a mean density of background materials,[24,36] or of mass per leaf area (e.g. mg m^{-2}), when leaf deposited PM is collected by a washing/filtration procedure.[3,6,10,11,28]

Electron microscopy analyses were performed on two different leaves – randomly chosen from the five available - for each sampling site. For each leaf, two portions of 1 cm^2 were cut from the leaf part above the left main rib, and separately used for the analysis of the abaxial and adaxial leaf surfaces (Figure S1). A Phenom ProX™ (Phenom-World™, The Netherlands) scanning electron microscope was used, equipped with X-ray analyser and charge-reduction sample holder suited for biological samples. Leaf portions were mounted within the sample holder by using double coated carbon conductive PELCO Tabs™ (Ted Pella™, Inc., USA), after having fluxed them with compressed air.

Imaging was performed in backscattered electron configuration, with an incident electron energy of 5 keV, in order to limit the surface charging. The sample surface was randomly imaged by 150 µm wide scans, at a resolution of 1024 x 1024 pixels. For each leaf, five images were acquired at each leaf surface (Figure S2). On these images, PM can be easily distinguished as bright particles, with the colour contrast of SEM features being proportional to the atomic number of the elemental components (*i.e.* the brighter the particle, the heavier the components). SEM images were analysed with Gwyddion software,[39] in order to obtain the number and the dimensions of the leaf deposited particles. In particular, the diameter of the equivalent sphere (or particle equivalent diameter, d_{eq}) was obtained for each imaged particle, with a cut-off value of 300 nm (which corresponds to the dimension of two image pixels). Particles with a d_{eq} larger than 10 µm (which accounted for less than 0.1 % of the total detected particles) were excluded from the analysis. The final dataset was composed by PM0.3-10 particles.

Elemental analysis of selected particles was performed through dedicated Phenom Pro Suite™ software. The leaf surfaces were scanned at 150 µm scan size, with an incident electron energy of 15 keV (Figure S2d). Approximately 200 particles were investigated per sampling site: 50 randomly selected particles on each surface of the two leaves. The equivalent sphere diameter d_{eq} of such particles was obtained by averaging their two main Feret diameters,[40] as measured by ImageJ software (Figure S2d).[41] The corresponding EDX spectra (Figure S2e) were obtained by positioning the laser beam in the particles' centre. The elements identified in the particles were C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Sn, and Sb. The comparison of the particles' composition was based on those elements detected with a mean concentration higher than 0.1% over the whole dataset (e.g., Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe), while trace metals (Ti, Cr, Mn, Ni, Cu, Zn, Mo, Sn, Sb) were grouped in a single residual variable ("Res"). Fluorine was excluded from the analysis since it is present just in trace concentration and it cannot be included in the "Res" variable, being not a metal. C, N, and O were also excluded due to several reasons:[32,38] (a) they can be related to biogenic factors; (b) EDX is known to fail in the correct determination of light elements; and (c) the high values and variability of C and O concentrations as obtained by EDX could hinder the variability of the other elements' concentration, which are the more relevant in terms of pollution.

Semi-quantitative estimation of the amount of the selected elements was obtained by calculating the weighted volume percentage ($W_{\%}$) occupied by each element x over the N particles selected.[32] To do this, the composition percentage (C) of each element x on each particle i (C_{xi}, as obtained by the EDX software) was multiplied by the corresponding particle volume (V_i), calculated as $V_i = 4/3\ \pi\ (d_{eq}/2)^3$. For each element, such volume percentages were summed together, and the sum was then normalized by using the total volume of all the N analysed particles, obtaining the weighted volume percentage ($W_{\%}$) for each element x, by following Eqn. 1:

$$W_{\%_x} = \frac{\sum_{i=1}^{N} C_{x_i} \times V_i}{\sum_{i=1}^{N} V_i} \qquad \text{Eqn. 1}$$

SIRM determination

SIRM mainly quantifies the fraction of ferro(i)magnetic particles,[42–44] such as the Fe-based particles coming from combustion and metallic wear/abrasion events. Therefore, leaf SIRM has been extensively used as indicator of anthropogenic activity and air pollution,[3,4,25,30,31,33,44–46] enabling the identification of different urban conditions, e.g. as between street and park sites.

Each half leaf was digitally scanned (HP Scanjet G3110), and its surface area was measured using ImageJ software.[41] Then, each half leaf was tightly packed in cling film and pressed into a 10 cm^3

plastic container, which was magnetized with a pulsed field of 1 T using a Molspin pulse magnetizer (Molspin Ltd., UK). For each magnetized sample, the SIRM was measured using a calibrated Molspin Minispin magnetometer (Molspin Ltd., UK). The magnetometer was calibrated using a magnetically-stable rock specimen at the beginning of every session and after every 15 measurements. Each sample was measured twice, to reduce measurement errors, and the mean of the two measured values was considered. The SIRM value of empty containers was considered as blank signal, therefore subtracted from all measured values. The SIRM values (expressed in mA m^{-1}) were normalized for the sample container volume (10 cm^3) and leaf surface area (in cm^2),[4] which leads to SIRM values normalized per area, expressed in Ampere (A).

Statistical Analysis

Statistical analysis of data distributions was performed using Origin 8.1 software (OriginLab, Northampton, MA). The particle surface density was analysed by calculating, for each site, the mean value and the standard deviation, as obtained by averaging the particle surface densities obtained from the 20 corresponding SEM images. On the other side, the mean particle equivalent diameter values (and the corresponding standard deviations) were calculated, for each site, by averaging over the whole particle dataset. A mean SIRM value per site was obtained, by averaging the SIRM values of the correspondent leaf samples, and the standard error (SE) was calculated in order to account for the uncertainty around the mean estimate.

Correlation, variance (ANOVA) and principal component (PCA) analyses were performed by using Statistica 7.0 (StatSoft, Inc. 2004 US). Correlation analysis was used to check the relation among experimental data and metadata (R^2 and p values are provided). ANOVA (performed by using Fisher’s test, with post-hoc Wilks test for the multivariate analysis) allowed to verify the relation among experimental parameters and both the location of the sampling site and the leaf surface side (p and Wilks’ λ values are provided). PCA based on correlation was applied, after suitable data variable standardization, in order to discriminate the sampling sites on the basis of the experimental variables. Sixteen new space variables (principal components, PCs) were determined, on the basis of the least square criterion, as those maximizing the description of the sites’ variability.

III. Results & Discussion

Particle leaf surface density and morphology

The number of leaf deposited particles observed in a single SEM image (150 x 150 µm^2) ranged from 0 (Salzburg, park site) to 4414 (Yerevan, street site) particles. The mean PM0.3-10 surface density values, as obtained at the 40 sites, were mostly within the same order of magnitude (10^4 particles per mm^2; Table S2), with few exceptions. The mean particle density at the Yerevan street site was about 10^5 particles per mm^2, likely due to the dry continental climate and arid steppe native landscape, while the Florence street site mean particle density was ca. 5 x 10^3 particles per mm^2, probably because of the relatively high sampling height (12 m; Table S1).[45] The mean particle density measured at the park and street sites of the same city were not significantly different (within the standard variation range), except for Warsaw (1.2 ± 0.6 particles per mm^2 and 3.7 ± 1.4 particles per mm^2, respectively for park and street sites).

At every sampling location, the distribution of the PM0.3-10 particles as a function of their equivalent diameter d_{eq} was monotonically decreasing (Figure S2), as previously observed in similar experiments.[38] This is consistent with the typical distribution observed in urban areas for the aerosol particle concentration as a function of the particle size: a lognormal behaviour is expected, with the main distribution peak centred at a particle diameter value of about 0.1 µm or below, and monotonically decreasing in our region of interest.[47–52] Thus, the majority of the measured particles (ranging between 52.7 % for Timisoara street site and 67.1% for Naples street site; Table S2) was related to fine PM (d_{eq} in the 0.3-0.6 µm range), while coarse particles (d_{eq} > 2.5 µm) represented less than 5% (from 0.6% for Ljubljana park site to 4.6% for Granada park site; Table S2). The mean values of the leaf deposited particles' d_{eq} ranged between 0.6 µm (Aveiro, Belgrade and Ljubljana park sites; Salzburg street site) and 0.9 µm (Granada park site; Timisoara street site) and are statistically equivalent across all sites (Table S2).

When the particles deposited on the adaxial and abaxial leaf surfaces were analysed separately, clear differences emerged in terms of both mean particle density and equivalent diameter d_{eq} (Table S3). At every sampled site, the adaxial leaf surfaces were characterised by higher densities of leaf deposited particles as compared to the abaxial ones, resulting in an almost doubled mean particle leaf surface density value (3.4 x 10^4 particles per mm^2 vs. 1.7 x 10^4 particles per mm^2), throughout the sites. Moreover, the particles observed at the adaxial leaf surfaces had a larger mean d_{eq} with respect to those at the abaxial ones, with the mean values over the sampled sites being (0.75 ± 0.07) µm and (0.67 ± 0.04) µm, respectively. These results are in line with previous observations: variations in leaf surface microstructure and wind turbulence may lead to a difference in the quantity and composition of particles accumulated at the adaxial and abaxial leaf surfaces.[9,53]

Univariate ANOVA determined that both the mean particle density and the mean d_{eq} correlate with the leaf surface side ($p < 0.0001$ for both parameters) but not with the site location ($p = 0.18$ for the mean particle density, and $p = 0.38$ for the mean d_{eq}). Multivariate ANOVA performed by using particle density and mean d_{eq} as dependent variables and leaf surface and site location as independent categorical predictor factors showed still a correlation with the leaf surface (Wilks' $\lambda = 0.67$, $p < 0.0001$) but not with the sampling site (Wilks' $\lambda = 0.97$, $p = 0.34$).

The almost homogeneous mean values obtained for both the particle density and the equivalent diameter of leaf deposited particles at the 40 sampling sites are consistent with the mean daily atmospheric PM10 concentration values measured by the closest air quality monitoring stations in the in-leaf period. Indeed, all the provided atmospheric PM10 concentrations were in the (20 ± 10 µg m^{-3}) range (Table S1), as also previously observed in different European cities.[24,54] However, by comparing the mean PM0.3-10 leaf deposited particle density (Tables S2) with the corresponding mean daily atmospheric PM10 concentration (Table S1), no significant correlation was obtained (Figure 2a). A significant, positive correlation ($R^2 = 0.3$, $p < 0.05$) was observed, instead, if only the coarse particle fraction (PM2.5-10) was taken into account (Table S2; Figure 2b). This indicates that PM10 concentration data, as obtained by air quality monitoring stations, is strongly biased towards coarse particles (*i.e.* larger particles contribute more than smaller particles), while our approach is a powerful tool for the detection of fine PM,[55] which represents the majority (and the most harmful part[18]) of leaf deposited particles. In particular, in our data, the PM0.3-1 fraction accounts for about the 80%-90% of the total PM0.3-10 fraction. Moreover, local pollution variations could be hidden by monitoring urban air quality through few, disperse stations, which provide very low spatial resolution data. Conversely, the use of urban vegetation as monitoring tool could enable the study of local PM in a more comprehensive way, without the need of on-site apparatus, contributing particularly for the simplification of future research.

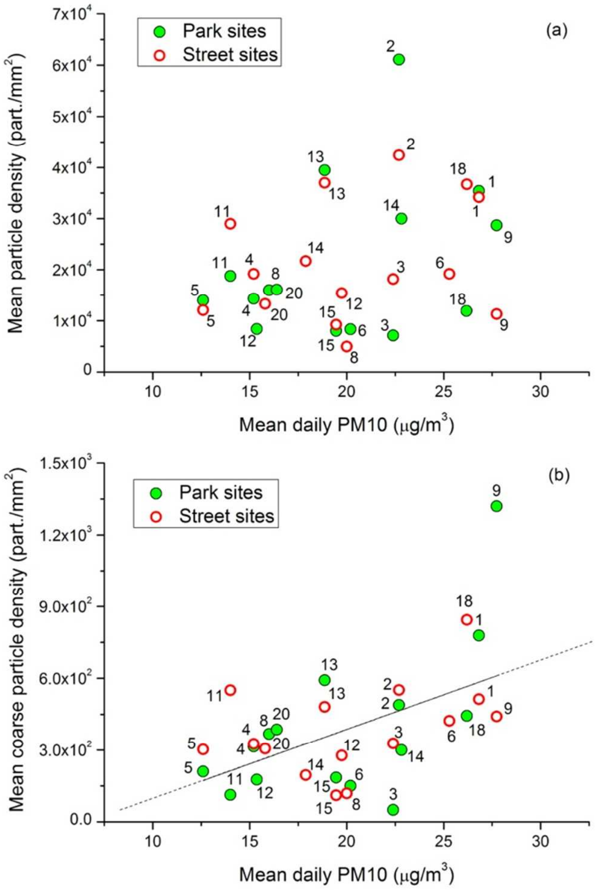


Figure 2. Relationship between the PM0.3-10 (a) and the PM2.5-10 (b) mean particle leaf surface density and the corresponding mean daily atmospheric PM10 concentration, as measured by the air quality monitoring station closest to the sampled tree. No correlation is obtained when the total of the PM0.3-10 particles is taken into account (a), while a good linear correlation is obtained between PM2.5-10 density and PM10 concentration data (black line in panel b; $R^2 = 0.3$, $p < 0.05$). For corresponding city numbers, see Figure 1.

Particle composition and leaf magnetic response

The sum of the weighted volume percentage $W_{\%}$ of the elements selected for the elemental analysis represented between 12.3% (Den Haag park site) and 31.3% (Warsaw street site) of the selected particles' total volume (Table S4). For five cities (Belgrade, Bern, Granada, Nancy, Naples), the percentages obtained at the park and street sites differ less than 1%. For Antwerp, the park site has a summed $W_{\%}$ (18.4%) that is higher than that observed at the street site (17.1%), while for all the other cities higher summed $W_{\%}$ values were found for the street compared to the park sites. As a result, mean summed $W_{\%}$ values of 20.4% and 23.6% were obtained by averaging all park and street sites, respectively (Table S4). This difference is mainly due to the more than double mean $W_{\%}$ of Fe at the street (3.4%) compared to the park (1.4%) sites (Table S4). Although Fe is an indicator of crustal soil resuspension, as well as *e.g.* Al, Ca, and Si,[56] combustion processes derived from *e.g.* vehicle traffic are a known source of small Fe-bearing spherules, as Fe often occurs as an impurity in fossil fuels.[31] In addition to combustion sources, Fe enriched particles can be generated also via exhaust emissions and metallic wear/abrasion, such as from tire and brake wear, and road pavement abrasion.[42,46]

From the total of the 28 participating cities, the individual leaf SIRM values measured on *Platanus acerifolia* leaves ranged from 7.2 µA (Copenhagen) to 202.1 µA (Düsseldorf) in park sites, and from 9.2 µA (Kavala) to 1192.2 µA (Warsaw) in street sites (mean values and SE for each site are reported in Table S5). For the 20 cities that were analysed by both SEM/EDX and SIRM (Figure 1), the park leaves showed a mean SIRM value of (30.2 ± 2.4) µA, while a mean SIRM value of (152.8 ± 21.7) µA was obtained for the street leaves.

The park sites showed lower leaf SIRM values than those observed for the corresponding street sites, with exception of the city of Granada, whose park site SIRM value is almost double than that at the street site ((61.1 ± 6.9) µA and (25.3 ± 6.8) µA, respectively; Table S5). This could be due to the fact that Granada park site tree is very close to a high traffic density street (10 m; Table S1), as well as to a railway track (ca. 480 m; Table S1). However, it is worth noting that also the Fe $W\%$ is doubled between Granada park and street site (2.6% and 1.3%, respectively; Table S4) and that Granada leaves are characterised, at both park and street sites, by the highest coarse particle densities (4.6% and 3.9%, respectively), resulting in the highest mean particle d_{eq} (about 0.9 µm at both sites) observed throughout our campaign. Thus, both the street and the park sampling sites seem to be affected by analogous PM10 levels, and the most probable reason is that, only in this city, leaves have been sampled after 60 days without rain (Table S1).[57]

Almost 90% of the analysed leaves presented SIRM < 300 µA, while the city of Warsaw showed SIRM values that are more than threefold higher, at the street site (Table S5). The same site presented also the highest Fe (11.1%) and trace metals (“Res” is 2.1%) content from all analysed cities. Moreover, the Warsaw street site had a significantly higher particle density with respect to the corresponding park site. Because the particle surface density and composition, and the leaf SIRM value of the Warsaw park site were comparable to those of the other cities’ park sites, it is plausible to assume that, at the Warsaw street site, the PM level is mainly due to local emission sources, in this case traffic. Indeed, the highest traffic intensity (ca. 41200 vehicles h^{-1}) was registered at the street site of Warsaw, from all studied sites. Moreover, air quality in Warsaw is known to be greatly affected by traffic, due to both the city conformation,[58] and the massive use of old diesel cars that characterizes the transition economies of Eastern Europe.[59]

When comparing SIRM data with the leaf deposited particles' Fe content as analysed by SEM/EDX, most of the street sites revealed both leaf SIRM and Fe content values higher than those observed at the park sites, suggesting a rather clear distinction between the two urban conditions (Figure 3). Street sites showed large ranges of both leaf SIRM and Fe $W_{\%}$ values (with mean values from about 20 µA to almost 1000 µA, and from less than 1% to almost 11%, respectively), and a good correlation is obtained between Fe *W%* and SIRM values over the entire street sites' dataset ($R^2 = 0.4$, $p < 0.05$). On the other side, the park sites showed low SIRM (< 40 µA) and Fe $W_{\%}$ (< 2%) values, but with few exceptions: parks in Ljubljana and Yerevan showed a high SIRM value but a low Fe $W_{\%}$, Zurich and Berlin had a Fe $W_{\%}$ > 2% but a low SIRM value, while Antwerp and Granada revealed both Fe $W_{\%}$ > 2% and SIRM value > 40 µA. As a consequence, no correlation is obtained between Fe *W%* and SIRM values on the park sites' dataset.

Although the magnetic signature of urban polluted sources is mainly due to ferro(i)magnetic minerals (such as Fe-oxides, Fe-sulfides, or more rarely native Fe), magnetic parameters such as SIRM reflect the presence of magnetic particles in terms of their composition, concentration and grain size.[43,44] Thus, while SEM/EDX provides the elemental composition of leaf deposited PM, leaf SIRM values account for the particle chemical structure (crystal lattice and magnetic moments). Therefore, different PM sources may induce different leaf SIRM values at comparable Fe content, or *vice versa* (Figure 3). Those sites revealing similar leaf SIRM and Fe content, such as Ljubljana and Zurich street sites, or Den Haag and Salzburg park sites, are likely exposed to similar urban PM sources. However, the street sites of *e.g.* Salzburg and Yerevan, which revealed similar leaf SIRM values but different Fe content, or of *e.g.* Aveiro and Yerevan, with similar Fe content but different leaf SIRM, suggest the presence of different PM sources within the compared cities. Nonetheless, significant correlations are usually observed between leaf SIRM and Fe content close to high traffic density streets,[31,33] as corroborated also by our magnetic and particle analyses (Figure 3), suggesting similar sources across the different street sites. On the contrary, when the city background aerosol becomes more important, *i.e.* at park sites, the differences among the urban PM composition emerge.

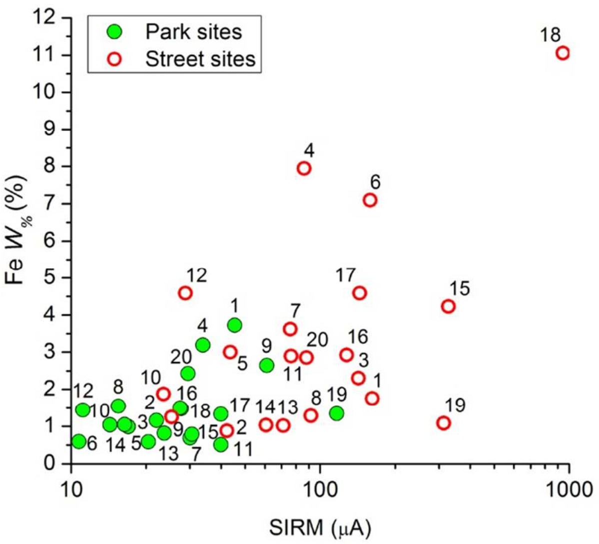


Figure 3. Relationship between the Fe weighted volume percentage $W_{\%}$ of PM0.3-10 particles deposited on *Platanus acerifolia* leaves sampled over 20 different cities across Europe, both at a street and a park site, and the logarithm of the SIRM value as measured from the same leaves. For corresponding city numbers, see Figure 1.

Site discrimination through Principal Component Analysis

A PCA was performed, by considering as input variables the particles' surface density and morphological characteristics (namely, percentage of fine PM0.3-0.6 and of coarse PM2.5-10 particles, and the mean particle equivalent diameter d_{eq}), the weighted volume percentage $W_{\%}$ of the main elements represented in the leaf deposited particles (Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and trace metals grouped in the "Res" variable), and the logarithm of the SIRM value. The PCA generated 16 principal components (PCs). The loadings, eigenvalues and percentages of explained variance of the 10 most representative PCs are reported in the Supporting Information (Table S6). The most discriminant component (PC1), which accounts for the 27.0% of the total variance, mainly differentiates the sites with a high percentage of fine particles (positive PC1 values) from those showing a relatively high concentration of coarse particles (negative PC1 value) (Figure 4a). The PC2 (which accounts for the 16.3% of the total variance) separates the sampling sites on the basis of the composition of the leaf deposited particles: negative PC2 values indicate high percentage of Na, Ca, Cl, Fe, trace metals ("Res" variable) and SIRM value, while positive PC2 values characterise sites with relatively high percentage of Si, Al and Mg (Figure 4a).

The projection of the 40 analysed cases in the PC1-PC2 plane shows that the majority of the park sites are clustered in the plot region with positive PC2 values (Figure 4b), showing high concentrations of the elements belonging to the "crustal component" aerosol group,[36,60,61] This suggests that resuspension is the major PM source contributor within park sites, while traffic pollution, usually located away from parks, seems to be of less importance. Consistently, the centroid of the park site group is placed towards the region with a high fine particle density.[52] Also some street sites (such as Belgrade, Den Haag, Ljubljana, Kavala, Nancy, Naples, and Zurich) falls in the positive PC2 region, showing low levels of source specific pollution. However, most of the street sites are spread in the negative PC2 region (Figure 4b), mainly divided in three groups.

One group (negative PC1 values) shows a high content of Fe and trace metals (Ti, Cr, Mn, Ni, Cu, Zn, Mo, Sn, Sb) and high leaf SIRM values, and it is characterised by coarser particles and higher particle densities (Granada and Yerevan park and street sites, Timisoara, Warsaw and Vienna street sites). This reveals the presence of PM mostly generated by mechanical actions such as material abrasion and/or dust resuspension, which are largely associated with anthropogenic activities and, in particular, with traffic.[32,36,48,52] In addition to Granada park site (discussed previously), also Yerevan park site belongs to this group, likely due to the extremely dry continental climate, joined with the high background urban pollution levels,[62] and with the many streets with moderate and high traffic loads surrounding the sampled park.[57]

The group at positive PC1 values is characterised by high percentages of fine particles and with high concentrations of Na and Cl (Salzburg and Malmö street sites), Ca (Bern and Florence street sites), or of these three elements together with S (Aveiro park and street sites), and low metal content, suggesting that natural sources should be invoked.[32,48] High concentrations of Na and Cl together are likely due to the presence of salt sources, which could be the marine aerosol (such as for Malmö), salt mines (Salzburg), or salines (Aveiro).[36] The high Ca and S concentrations observed at Aveiro sites are likely to originate from salines as well.[63] Resuspension may induce high concentration of salt particles at street sites,[64] and the similarity between the park and the street sites of Aveiro could be due to the proximity of the park site to the closest street (37 m; Table S1).[57] On the other side, geomorphology of the area could partially explain the high Ca concentrations observed at the Bern and Florence street sites, and also the erosion of calcareous buildings present in these cities could be invoked.[65]

Finally, Berlin and Copenhagen street sites fall in between the previous two groups, being mostly characterised by the presence of fine particles with high levels of both Na and Fe levels, which could be linked to anthropogenic sources that involve high-temperature processes.[32,48]

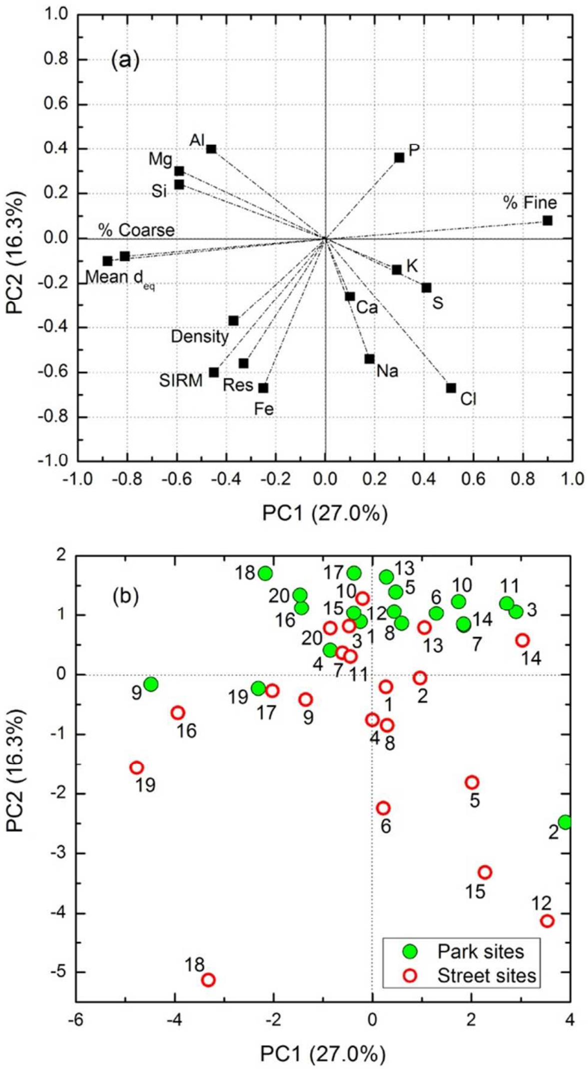


Figure 4. Outputs of the PCA performed by considering as input variables the particle leaf surface density ("Density") and morphological characteristics (namely, percentage of fine PM0.3-0.6 – "% Fine" - and coarse PM2.5-10 – "% Coarse" - particles and the mean particle equivalent diameter – "Mean d_{eq}"), the weighted volume percentage $W_{\%}$ of the main elements composing the leaf deposited particles (Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and trace metals grouped in the "Res" variable), and the logarithm of leaf SIRM value. The parameters have been obtained from *Platanus acerifolia* leaves sampled at 20 different cities across Europe, both at a street and a park site. (a) Projection in the PC1-PC2 plane of the input variables contributions. (b) Projection in the PC1-PC2 plane of the coordinates of the analysed cases. For corresponding city numbers see Figure 1.

The combination of the morphological characteristics and elemental data of leaf deposited particles, which can be used as indicators for atmospheric PM concentration and composition,[32,38] and leaf SIRM, which can be interpreted as pointer of anthropogenic PM pollution,[33,42,43] allowed, then, to characterise PM source apportionment for most of the explored cities across Europe, without the need of on-site apparatus or sample preparation. Interestingly, the main PM sources identified in this study are in line with those previously obtained by sampling PM with gravimetric techniques and analyzing it with a wide range of analytical methodologies[36]. A common regional background PM composition and concentration was observed across the 20 investigated cities, while certain local conditions such as the influence of *e.g.* marine/sea salt aerosols (Malmö, Salzburg, Aveiro), or a dry continental climate and arid steppe landscape (Yerevan), were clearly recognized. A clear distinction between street and park sites was generally registered and, given the lower metal content observed on park leaves in comparison to street leaves, the promotion and implementation of urban parks and other green infrastructures (*e.g.* green walls) will contribute positively to human health in cities. In this connection, this study is pertinent to urban planners and other stakeholders, since it revealed how local urban conditions can vary within the same city, or neighbourhood.

Acknowledgements

This paper has been realised within the context of the COST Action FP1204 "Greeninurbs", supported by the EC. We acknowledge project PON infrastructure Amica (High Technology Infrastructure for Climate and Environmental Monitoring; PONa3_00363) for the availability of the SEM-EDX facility. Thanks are due to Leo Slingerland (previously at Wageningen UR, The Netherland) and Lars Christensen (Municipal Tree Officer of Copenhagen, Denmark) for participating in the campaign.

Supporting Information

Further information on the sampling techniques, sample site locations, and sample descriptions; additional figures and tables.

References

(1) Ristić, M.; Perić-Grujić, A.; Antanasijević, D.; Ristić, M.; Aničić Urošević, M.; Tomašević, M. Plants as Monitors of Lead Air Pollution. In *Pollutant Diseases, Remediation and Recycling*; Lichtfouse, E., Schwarzbauer, J., Robert, D., Eds.; Springer, 2013; Vol. 4, pp 390–431.

(2) Tomašević, M.; Vukmirović, Z.; Rajšić, S.; Tasić, M.; Stevanović, B. Characterization of trace metal particles deposited on some deciduous tree leaves in an urban area. *Chemosphere* **2005**, *61* (6), 753–760 DOI: 10.1016/j.chemosphere.2005.03.077.

(3) Hofman, J.; Wuyts, K.; Van Wittenberghe, S.; Brackx, M.; Samson, R. Reprint of On the link between biomagnetic monitoring and leaf-deposited dust load of urban trees: Relationships and spatial variability of different particle size fractions. *Environ. Pollut.* **2014**, *192*, 285–294 DOI: 10.1016/j.envpol.2014.05.006.

(4) Kardel, F.; Wuyts, K.; Maher, B. A.; Hansard, R.; Samson, R. Leaf saturation isothermal remanent magnetization (SIRM) as a proxy for particulate matter monitoring: Inter-species differences and in-season variation. *Atmos. Environ.* **2011**, *45* (29), 5164–5171 DOI: 10.1016/j.atmosenv.2011.06.025.

(5) Sawidis, T.; Breuste, J.; Mitrovic, M.; Pavlovic, P.; Tsigaridas, K. Trees as bioindicator of heavy metal pollution in three European cities. *Environ. Pollut.* **2011**, *159* (12), 3560–3570 DOI: 10.1016/j.envpol.2011.08.008.

(6) Popek, R.; Gawrońska, H.; Wrochna, M.; Gawroński, S. W.; Sæbø, A. Particulate Matter on Foliage of 13 Woody Species: Deposition on Surfaces and Phytostabilisation in Waxes – a 3-Year Study. *Int. J. Phytoremediation* **2013**, *15* (3), 245–256 DOI: 10.1080/15226514.2012.694498.

(7) Simon, E.; Baranyai, E.; Braun, M.; Cserháti, C.; Fábián, I.; Tóthmérész, B. Elemental concentrations in deposited dust on leaves along an urbanization gradient. *Sci. Total Environ.* **2014**, *490*, 514–520 DOI: 10.1016/j.scitotenv.2014.05.028.

(8) Wang, H.; Shi, H.; Li, Y.; Yu, Y.; Zhang, J. Seasonal variations in leaf capturing of particulate matter, surface wettability and micromorphology in urban tree species. *Front. Environ. Sci. Eng.* **2013**, *7* (4), 579–588 DOI: 10.1007/s11783-013-0524-1.

(9) Mo, L.; Ma, Z.; Xu, Y.; Sun, F.; Lun, X.; Liu, X.; Chen, J. Assessing the Capacity of Plant Species to Accumulate Particulate Matter in Beijing, China. *PLoS One* **2015**, *10* (10), e0140664 DOI: 10.1371/journal.pone.0140664.

(10) Sæbø, A.; Popek, R.; Nawrot, B.; Hanslin, H. M.; Gawrońska, H.; Gawroński, S. W. Plant species differences in particulate matter accumulation on leaf surfaces. *Sci. Total Environ.* **2012**, *427–428*, 347–354 DOI: 10.1016/j.scitotenv.2012.03.084.

(11) Sæbø, A.; Hanslin, H. M.; Baraldi, R.; Rapparini, F.; Gawrońska, H.; Gawroński, S. W. Characterization of Urban Trees and Shrubs for Particulate Deposition, Carbon Sequestration and Bvoc Emissions. *Acta Hortic.* **2013**, No. 990, 509–517 DOI: 10.17660/ActaHortic.2013.990.66.

(12) Beckett, K. P.; Freer-Smith, P. H.; Taylor, G. Urban woodlands: their role in reducing the effects of particulate pollution. *Environ. Pollut.* **1998**, *99*, 347–360 DOI: doi:10.1016/S0269-7491(98)00016-5.

(13) Tiwary, A.; Sinnett, D.; Peachey, C.; Chalabi, Z.; Vardoulakis, S.; Fletcher, T.; Leonardi, G.; Grundy, C.; Azapagic, A.; Hutchings, T. R. An integrated tool to assess the role of new planting in PM10 capture and the human health benefits: A case study in London. *Environ. Pollut.* **2009**, *157* (10), 2645–2653 DOI: 10.1016/j.envpol.2009.05.005.

(14) Escobedo, F. J.; Kroeger, T.; Wagner, J. E. Urban forests and pollution mitigation: Analyzing ecosystem services and disservices. *Environ. Pollut.* **2011**, *159*, 2078–2087 DOI: 10.1016/j.envpol.2011.01.010.

(15) Llausàs, A.; Roe, M. Green Infrastructure Planning: Cross-National Analysis between the North East of England (UK) and Catalonia (Spain). *Eur. Plan. Stud.* **2012**, *20* (4), 641–663 DOI: 10.1080/09654313.2012.665032.

(16) Morani, A.; Nowak, D. J.; Hirabayashi, S.; Calfapietra, C. How to select the best tree planting locations to enhance air pollution removal in the MillionTreesNYC initiative. *Environ. Pollut.* **2011**, *159* (5), 1040–1047 DOI: 10.1016/j.envpol.2010.11.022.

(17) Anderson, J. O.; Thundiyil, J. G.; Stolbach, A. Clearing the Air : A Review of the Effects of Particulate Matter Air Pollution on Human Health. *J. Med. Toxicol.* **2012**, *8* (2), 166–175 DOI: 10.1007/s13181-011-0203-1.

(18) Pope, C. A.; Burnett, R. T.; Thun, M. J.; Calle, E. E.; Krewski, D.; Ito, K.; Thurston, G. D. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *J. Am. Med. Assoc.* **2002**, *287* (9), 1132–1141 DOI: 10.1016/j.scitotenv.2011.03.017.

(19) Duzgoren-Aydin, N. S.; Wong, C. S. C.; Aydin, A.; Song, Z.; You, M.; Li, X. D. Heavy Metal Contamination and Distribution in the Urban Environment of Guangzhou, SE China. *Environ. Geochem. Health* **2006**, *28* (4), 375–391 DOI: 10.1007/s10653-005-9036-7.

(20) Chaudhari, P. R.; Gupta, R.; Gajghate, D. G.; Wate, S. R. Heavy metal pollution of ambient air in Nagpur City. *Environ. Monit. Assess.* **2012**, *184* (4), 2487–2496 DOI: 10.1007/s10661-011-2133-4.

(21) Li, H.; Qian, X.; Hu, W.; Wang, Y.; Gao, H. Chemical speciation and human health risk of trace metals in urban street dusts from a metropolitan city, Nanjing, SE China. *Sci. Total Environ.* **2013**, *456–457*, 212–221 DOI: 10.1016/j.scitotenv.2013.03.094.

(22) Oves, M.; Khan, M. S.; Zaidi, A.; Ahmad, E. Soil Contamination, Nutritive Value, and Human Health Risk Assessment of Heavy Metals: An Overview. In *Toxicity of Heavy Metals to Legumes and Bioremediation*; Zaidi, A., Wani, P. A., Khan, M. S., Eds.; Springer Vienna, 2012; pp 1–27.

(23) EC. http://ec.europa.eu/environment/air/quality/standards.htm.

(24) Harrison, R. M.; Stedman, J.; Derwent, D. New directions: why are PM10 concentrations in Europe not falling? *Atmos. Environ.* **2008**, *42*, 603–606 DOI: 10.1016/j.atmosenv.2007.11.023.

(25) Power, A. L.; Worsley, A. T.; Booth, C. Magneto-biomonitoring of intra-urban spatial variations of particulate matter using tree leaves. *Environ. Geochem. Health* **2009**, *31* (2), 315–325 DOI: 10.1007/s10653-008-9217-2.

(26) Wuytack, T.; Verheyen, K.; Wuyts, K.; Kardel, F.; Adriaenssens, S.; Samson, R. The potential of biomonitoring of air quality using leaf characteristics of white willow (Salix alba L.). *Environ. Monit. Assess.* **2010**, *171*, 197–204 DOI: 10.1007/s10661-009-1271-4.

(27) De Nicola, F.; Maisto, G.; Prati, M. V.; Alfani, A. Leaf accumulation of trace elements and polycyclic aromatic hydrocarbons (PAHs) in Quercus ilex L. *Environ. Pollut.* **2008**, *153* (2), 376–383 DOI: 10.1016/j.envpol.2007.08.008.

(28) Sgrigna, G.; Sæbø, A.; Gawroński, S. W.; Popek, R.; Calfapietra, C. Particulate Matter deposition on Quercus ilex leaves in an industrial city of central Italy. *Environ. Pollut.* **2015**, *197*, 187–194 DOI: 10.1016/j.envpol.2014.11.030.

(29) Hofman, J.; Wuyts, K.; Van Wittenberghe, S.; Samson, R. On the temporal variation of leaf magnetic parameters: Seasonal accumulation of leaf-deposited and leaf-encapsulated particles of a roadside tree crown. *Sci. Total Environ.* **2014**, *493* (June 2016), 766–772 DOI: 10.1016/j.scitotenv.2014.06.074.

(30) Moreno, E.; Sagnotti, L.; Dinarès-Turell, J.; Winkler, A.; Cascella, A. Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves. *Atmos. Environ.* **2003**, *37*, 2967–2977 DOI: 10.1016/S1352-2310(03)00244-9.

(31) Davila, A. F.; Rey, D.; Mohamed, K.; Rubio, B.; Guerra, A. P. Mapping the Sources of Urban Dust in a Coastal Environment by Measuring Magnetic Parameters of Platanus hispanica Leaves. *Environ. Sci. Technol.* **2006**, *40*, 3922–3928 DOI: 10.1021/es0525049.

(32) Sgrigna, G.; Baldacchini, C.; Esposito, R.; Calandrelli, R.; Tiwary, A.; Calfapietra, C. Characterization of leaf-level particulate matter for an industrial city using electron microscopy and X-ray microanalysis. *Sci. Total Environ.* **2016**, *548–549*, 91–99 DOI: 10.1016/j.scitotenv.2016.01.057.

(33) Castanheiro, A.; Samson, R.; De Wael, K. Magnetic- and particle- based techniques to investigate metal deposition on urban green. *Sci. Total Environ.* **2016**, *571*, 594–602 DOI: doi:10.1016/j.scitotenv.2016.07.026.

(34) Klumpp, A.; Ansel, W.; Klumpp, G.; Belluzzo, N.; Calatayud, V.; Chaplin, N.; Garrec, J. P.; Gutsche, H.-J. J.; Hayes, M.; Hentze, H.-W. W.; et al. EuroBionet: a pan-European biomonitoring network for urban air quality assessment. *Environ. Sci. Pollut. Res. Int.* **2002**, *9* (3), 199–203 DOI: 10.1007/BF02987489.

(35) Schröder, W.; Nickel, S.; Schönrock, S.; Meyer, M.; Wosniok, W.; Harmens, H.; Frontasyeva, M. V; Alber, R.; Aleksiayenak, J.; Barandovski, L.; et al. Spatially valid data of atmospheric deposition of heavy metals and nitrogen derived by moss surveys for pollution risk assessments of ecosystems. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 10457–10476 DOI: 10.1007/s11356-016-6577-5.

(36) Viana, M.; Kuhlbusch, T. A. J.; Querol, X.; Alastuey, A.; Harrison, R. M.; Hopke, P. K.; Winiwarter, W.; Vallius, M.; Szidat, S.; Prévôt, A. S. H.; et al. Source apportionment of particulate matter in Europe: A review of methods and results. *Aerosol Sci.* **2008**, *39*, 827–849 DOI: 10.1016/j.jaerosci.2008.05.007.

(37) www.usna.usda.gov/Newintro/platanus.

(38) Wilkinson, K. E.; Lundkvist, J.; Netrval, J.; Eriksson, M.; Seisenbaeva, G. A.; Kessler, V. G. Space and time resolved monitoring of airborne particulate matter in proximity of a traffic roundabout in Sweden. *Environ. Pollut.* **2013**, *182*, 364–370 DOI: 10.1016/j.envpol.2013.07.043.

(39) Nečas, D.; Klapetek, P. Gwyddion: an open-source software for SPM data analysis. *Cent. Eur. J. Phys.* **2012**, *10* (1), 181–188 DOI: 10.2478/s11534-011-0096-2.

(40) Merkus, H. G. *Particle Size Measurements: Fundamentals, Practice, Quality.*; Springer Science + Business Media B.V., 2009.

(41) Rasband, W. S. S. ImageJ. U. S. National Institutes of Health: Bethesda, Maryland, USA.

(42) Matzka, J.; Maher, B. A. Magnetic biomonitoring of roadside tree leaves: identification of spatial and temporal variations in vehicle-derived particulates. *Atmos. Environ.* **1999**, *33*, 4565–4569 DOI: doi:10.1016/S1352-2310(99)00229-0.

(43) Lu, S. G.; Wang, H. Y.; Guo, J. L. Magnetic enhancement of urban roadside soils as a proxy of degree of pollution by traffic-related activities. *Environ. Earth Sci.* **2011**, *64*, 359–371 DOI: doi: 10.1007/s12665-010-0859-x.

(44) Evans, M. E.; Heller, F. Environmental magnetism: Principles and applications of enviromagnetics. In *International Geophysics*; 2003; Vol. 86, pp 1–299.

(45) Hofman, J.; Stokkaer, I.; Snauwaert, L.; Samson, R. Spatial distribution assessment of particulate matter in an urban street canyon using biomagnetic leaf monitoring of tree crown deposited particles. *Environ. Pollut.* **2013**, *183*, 123–132 DOI: 10.1016/j.envpol.2012.09.015.

(46) McIntosh, G.; Gómez-Paccard, M.; Osete, M. L. The magnetic properties of particles deposited on Platanus x hispanica leaves in Madrid, Spain, and their temporal and spatial variations. *Sci. Total Environ.* **2007**, *382* (1), 135–146 DOI: 10.1016/j.scitotenv.2007.03.020.

(47) Hussein, T.; Hameri, K.; Aalto, P. P.; Paatero, P.; Kulmala, M. Modal structure and spatial – temporal variations of urban and suburban aerosols in Helsinki — Finland. *Atmos. Environ.* **2005**, *39*, 1655–1668 DOI: 10.1016/j.atmosenv.2004.11.031.

(48) Pugatshova, A.; Reinart, A.; Tamm, E. Features of the multimodal aerosol size distribution depending on the air mass origin in the Baltic region. *Atmos. Environ.* **2007**, *41* (21), 4408–4422 DOI: 10.1016/j.atmosenv.2007.01.044.

(49) Wu, Z.; Hu, M.; Lin, P.; Liu, S.; Wehner, B.; Wiedensohler, A. Particle number size distribution in the urban atmosphere of Beijing, China. *Atmos. Environ.* **2008**, *42* (34), 7967–7980 DOI: 10.1016/j.atmosenv.2008.06.022.

(50) Gómez-Moreno, F. J.; Pujadas, M.; Plaza, J.; Rodríguez-Maroto, J. J.; Martínez-Lozano, P.; Artíñano, B. Influence of seasonal factors on the atmospheric particle number concentration and size distribution in Madrid. *Atmos. Environ.* **2011**, *45* (18), 3169–3180 DOI: 10.1016/j.atmosenv.2011.02.041.

(51) Lonati, G.; Crippa, M.; Gianelle, V.; Van Dingenen, R. Daily patterns of the multi-modal structure of the particle number size distribution in Milan, Italy. *Atmos. Environ.* **2011**, *45* (14), 2434–2442 DOI: 10.1016/j.atmosenv.2011.02.003.

(52) Pant, P.; Harrison, R. M. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. *Atmos. Environ.* **2013**, *77*, 78–97 DOI: 10.1016/j.atmosenv.2013.04.028.

(53) Ottelé, M.; van Bohemen, H. D.; Fraaij, A. L. A. Quantifying the deposition of particulate matter on climber vegetation on living walls. *Ecol. Eng.* **2010**, *36*, 154–162 DOI: 10.1016/j.ecoleng.2009.02.007.

(54) Barmpadimos, I.; Keller, J.; Oderbolz, D.; Hueglin, C.; Prévôt, A. S. H.; Pr, A. S. H. One decade of parallel fine (PM2.5) and coarse (PM10-PM2.5) particulate matter measurements in Europe: trends and variability. *Atmos. Chem. Phys.* **2012**, *12*, 3189–3203 DOI: 10.5194/acp-12-3189-2012.

(55) Tittarelli, A.; Borgini, A.; Bertoldi, M.; De Saeger, E.; Ruprecht, A.; Stefanoni, R.; Tagliabue, G.; Contiero, P.; Crosignani, P. Estimation of particle mass concentration in ambient air using a particle counter. *Atmos. Environ.* **2008**, *42* (36), 8543–8548 DOI:

10.1016/j.atmosenv.2008.07.056.

(56) Jancsek-Turoczi, B.; Hoffer, A.; Nyiro-Kosa, I.; Gelencser, A. Sampling and characterization of resuspended and respirable road dust. *J. Aerosol Sci.* **2013**, *65*, 69–76 DOI: 10.1016/j.jaerosci.2013.07.006.

(57) Karner, A. A.; Eisinger, D. S.; Niemeier, D. A. Near-Roadway Air Quality: Synthesizing the Findings from Real-World Data. *Environ. Sci. Technol.* **2010**, *44* (14), 5334–5344.

(58) Reizer, M.; Juda-Rezler, K. Explaining the high PM10 concentrations observed in Polish urban areas. *Air Qual. Atmos. Heal.* **2015**, *1*, 1–15 DOI: 10.1007/s11869-015-0358-z.

(59) Kronenberg, J.; Bergier, T. Sustainable development in a transition economy: Business case studies from Poland. *J. Clean. Prod.* **2012**, *26*, 18–27 DOI: 10.1016/j.jclepro.2011.12.010.

(60) Lorenzini, G.; Grassi, C.; Nali, C.; Petiti, A.; Loppi, S.; Tognotti, L. Leaves of Pittosporum tobira as indicators of airborne trace element and PM10 distribution in central Italy. *Atmos. Environ.* **2006**, *40* (22), 4025–4036 DOI: 10.1016/j.atmosenv.2006.03.032.

(61) Amato, F.; Pandolfi, M.; Viana, M.; Querol, X.; Alastuey, A.; Moreno, T. Spatial and chemical patterns of PM 10 in road dust deposited in urban environment. *Atmos. Environ.* **2009**, *43* (9), 1650–1659 DOI: 10.1016/j.atmosenv.2008.12.009.

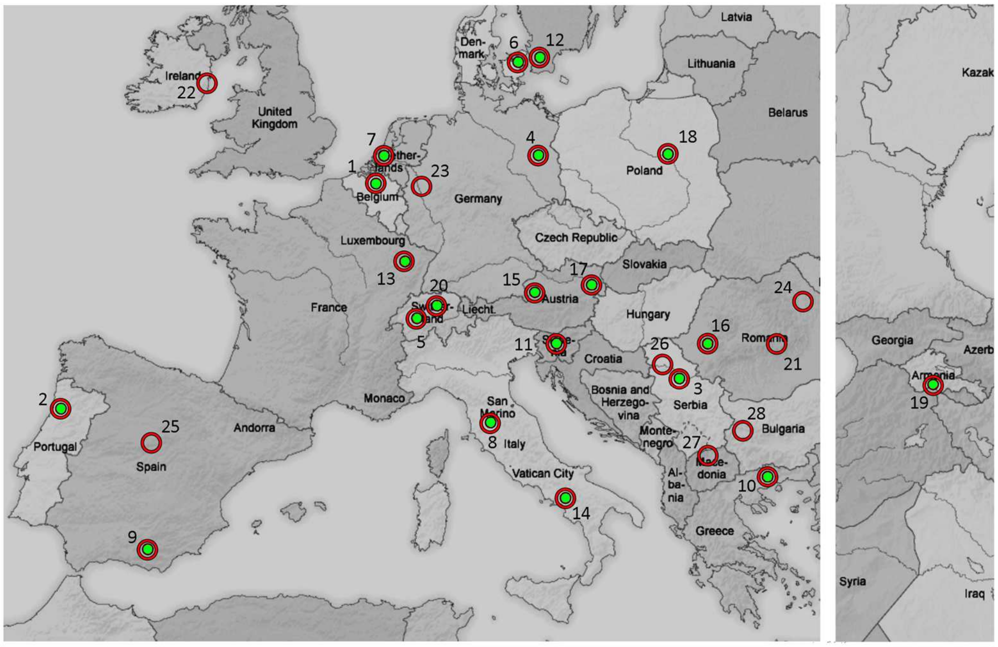
(62) Tepanosyan, G.; Sahakyan, L.; Belyaeva, O.; Saghatelyan, A. Origin identification and potential ecological risk assessment of potentially toxic inorganic elements in the topsoil of the city of Yerevan, Armenia. *Geochemical Explor.* **2016**, *167*, 1–11 DOI: 10.1016/j.gexplo.2016.04.006.

(63) Rodrigues, C. M.; Bio, A.; Amat, F.; Vieira, N. Artisanal salt production in Aveiro/Portugal - an ecofriendly process. *Saline Systems* **2011**, *7* (1), 3 DOI: 10.1186/1746-1448-7-3.

(64) Amato, F.; Nava, S.; Lucarelli, F.; Querol, X.; Alastuey, A.; Baldasano, J. M.; Pandolfi, M. A comprehensive assessment of PM emissions from paved roads: Real-world Emission Factors and intense street cleaning trials. *Sci. Total Environ.* **2010**, *408* (20), 4309–4318 DOI: 10.1016/j.scitotenv.2010.06.008.

(65) Cuccia, E.; Piazzalunga, A.; Bernardoni, V.; Brambilla, L.; Fermo, P.; Massabò, D.; Molteni, U.; Prati, P.; Valli, G.; Vecchi, R. Carbonate measurements in PM10 near the marble quarries of Carrara (Italy) by infrared spectroscopy (FT-IR) and source apportionment by positive matrix

factorization (PMF). *Atmos. Environ.* **2011**, *45* (35), 6481–6487 DOI: 10.1016/j.atmosenv.2011.08.004.



1	Antwerp	5	Bern	9	Granada	13	Nancy	17	Vienna	21	Brasov	25	Madrid
2	Aveiro	6	Copenhagen	10	Kavala	14	Naples	18	Warsaw	22	Dublin	26	Novi Sad
3	Belgrade	7	Den Haag	11	Ljubljana	15	Salzburg	19	Yerevan	23	Düsseldorf	27	Skopje
4	Berlin	8	Florence	12	Malmö	16	Timisoara	20	Zurich	24	Iasi	28	Sofia

Figure 1: Map of cities participating in the European sampling campaign. Samples from cities listed as 1-20 (red-green spots; green labels in the table) have been analysed by both SEM/EDX and SIRM, and corresponding metadata are listed in Table S1. Samples from cities listed as 21-28 (red circles; red labels in the table) have been analysed only using SIRM.

160x122mm (300 x 300 DPI)

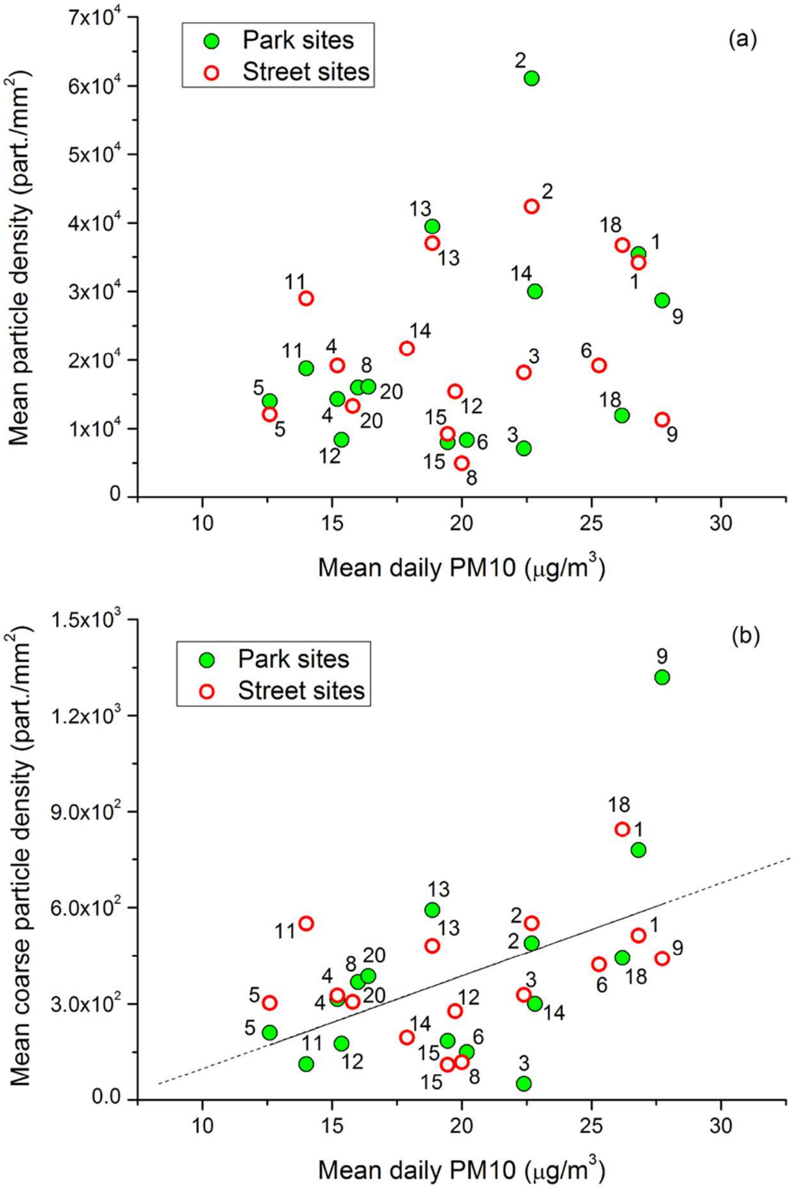


Figure 2. Relationship between the PM0.3-10 (a) and the PM2.5-10 (b) mean particle leaf surface density and the corresponding mean daily atmospheric PM10 concentration, as measured by the air quality monitoring station closest to the sampled tree. No correlation is obtained when the total of the PM0.3-10 particles is taken into account (a), while a good linear correlation is obtained between PM2.5-10 density and PM10 concentration data (black line in panel b; R2 = 0.3, $p < 0.05$). For corresponding city numbers, see Figure 1.

85x125mm (300 x 300 DPI)

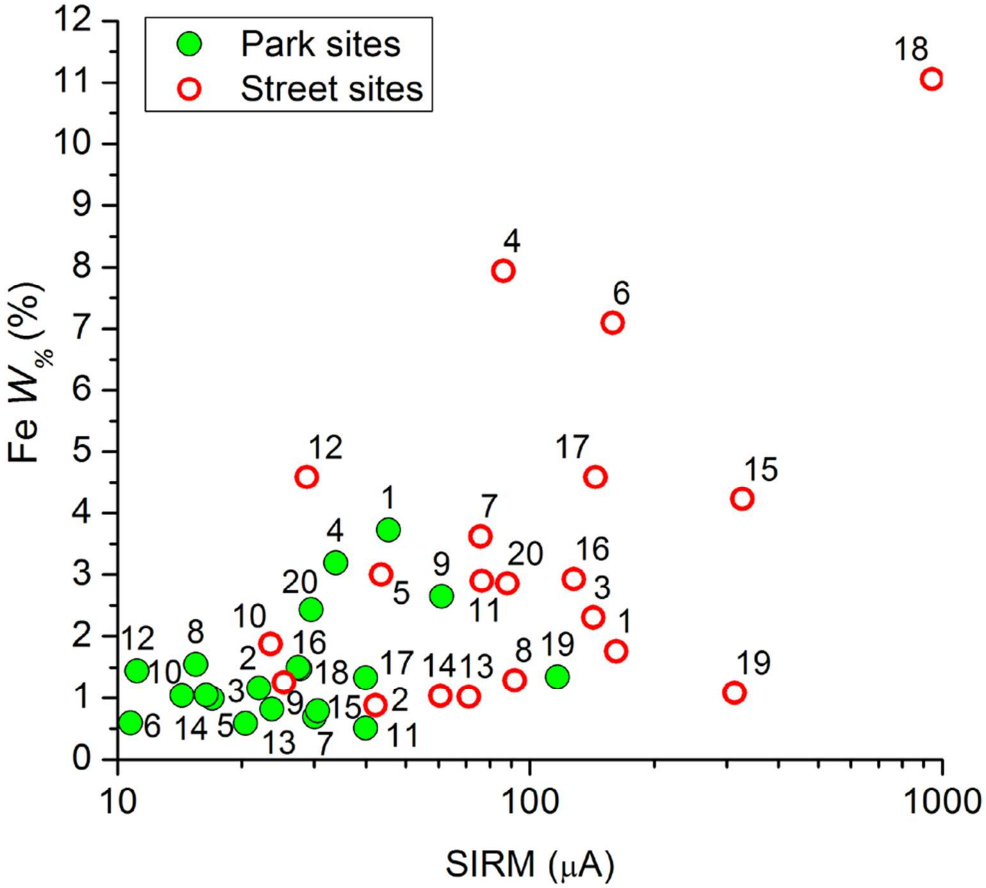


Figure 3. Relationship between the Fe weighted volume percentage W% of PM0.3-10 particles deposited on Platanus acerifolia leaves sampled over 20 different cities across Europe, both at a street and a park site, and the logarithm of the SIRM value as measured from the same leaves. For corresponding city numbers, see Figure 1.

85x77mm (300 x 300 DPI)

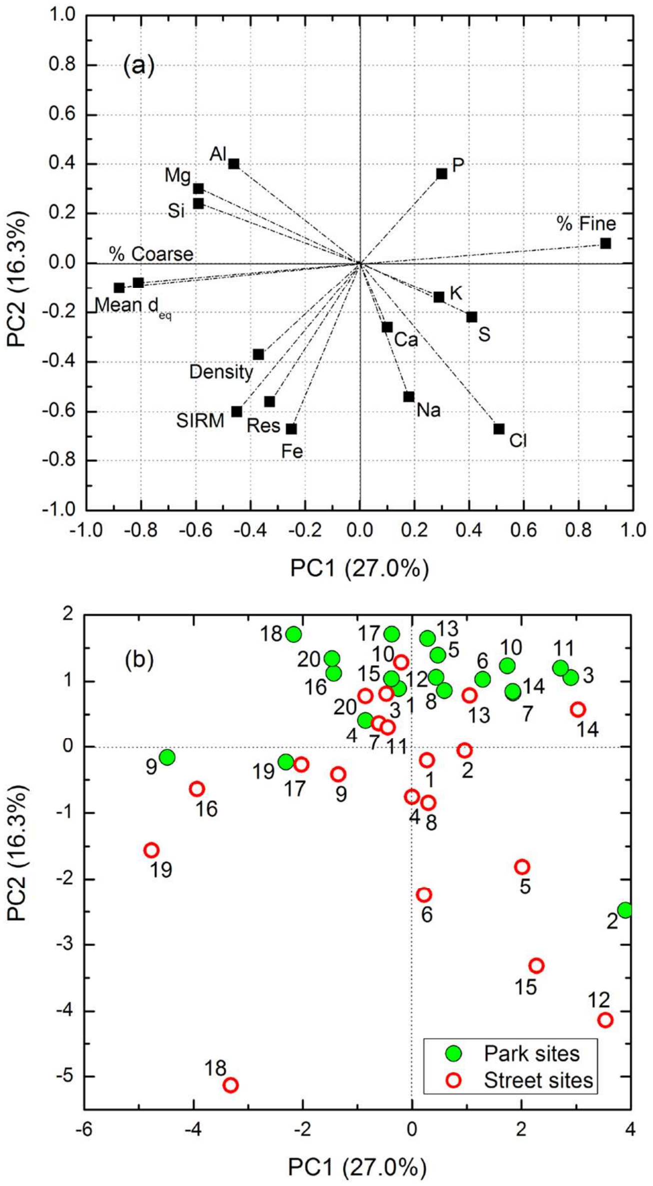
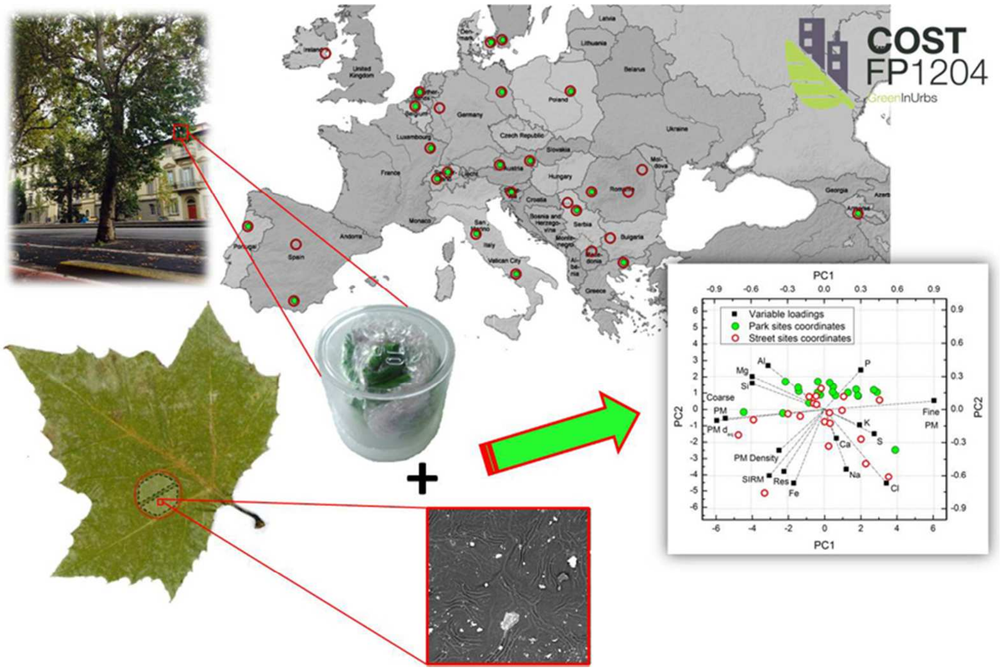


Figure 4. Outputs of the PCA performed by considering as input variables the particle leaf surface density ("Density") and morphological characteristics (namely, percentage of fine PM0.3-0.6 – "% Fine" - and coarse PM2.5-10 – "% Coarse" - particles and the mean particle equivalent diameter – "Mean deq"), the weighted volume percentage W% of the main elements composing the leaf deposited particles (Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and trace metals grouped in the "Res" variable), and the logarithm of leaf SIRM value. The parameters have been obtained from Platanus acerifolia leaves sampled at 20 different cities across Europe, both at a street and a park site. (a) Projection in the PC1-PC2 plane of the input variables contributions. (b) Projection in the PC1-PC2 plane of the coordinates of the analysed cases. For corresponding city numbers see Figure 1.

85x152mm (300 x 300 DPI)



71x47mm (300 x 300 DPI)