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

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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

63 *Platanus acerifolia* is highly suitable to be used in atmospheric PM monitoring studies and that
64 morphological and elemental characteristics of leaf deposited particles, joined with the leaf
65 magnetic content, may successfully allow urban PM source apportionment.

66

67 ## I. Introduction

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

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

89 The deposition of PM on tree leaves in European urban environments has been investigated by
90 studying different deciduous tree species, such as: *Acer campestre, Acer negundo*, *Acer*
91 *pseudoplatanus, Aesculus hippocastanum*, *Carpinus betulus, Celtis occidentalis, Corylus colurna,*

92 *Fraxinus pennsylvanica*, *Padus serotina, Pinus nigra, Platanus acerifolia, Platanus orientalis*, *Quercus*
93 *ilex, Quercus robur*, *Salix alba, Tilia europaea,* and *Tilia tomentosa*.[2–7,10,11,25–31]

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

107 In July 2014, within the context of the COST Action FP1204 "Greeninurbs" (www.greeninurbs.com),
108 a call for leaf collection in urban environments was launched among European scientists working on
109 urban green infrastructure and urban forests, for comparing leaf deposited PM10 particles across
110 European cities, as indicator of atmospheric PM concentration and composition. Some large-scale
111 air quality monitoring experiments have been set up before, e.g. the "*European Network for the*
112 *Assessment of Air Quality by the Use of Bioindicator Plants Cooperative*" (EuroBionet, involving 12
113 cities in 8 countries[34]) and the "*European Survey of Atmospheric Heavy Metal Deposition"* (involving
114 30 European countries[35]). Moreover, the source apportionment of PM in Europe, as obtained by
115 sampling PM through gravimetric techniques and analyzing it with a variety of analytical
116 methodologies, has been recently reviewed within the context of the COST Action 633 (by analysing
117 data from 33 cities over 12 countries[36]). However, the present study describes and analyses the
118 largest dataset ever collected on leaf deposited PM within European urban environments. The
119 leaves of *Platanus acerifolia* trees were used as passive air filters, and the leaf deposited PM10
120 particles have been characterised by performing SEM/EDX analysis on untreated collected leaves,
121 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

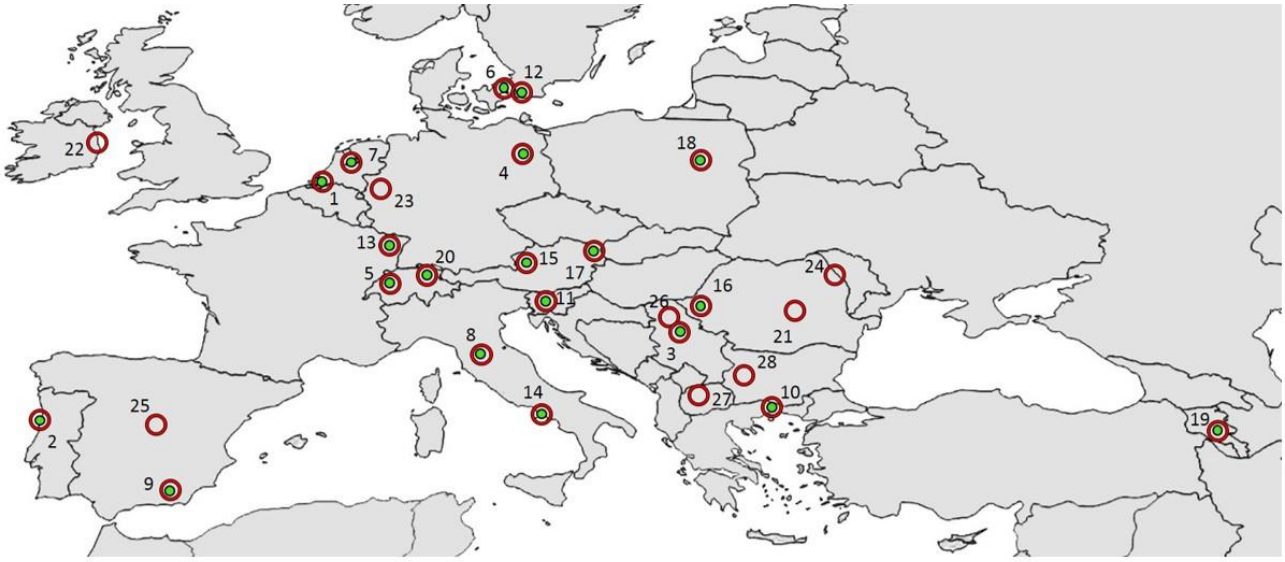
Leaves have been collected at 56 sites, in 28 cities over 20 countries (Figure 1). Participants were asked to collect leaf samples according to a specific protocol, together with supporting background data (see Table S1 for sampling information and metadata).The campaign has been carried out at the end 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, thanks 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. The underlying map is taken from Natural Earth database.

168 *Morphological and elemental characterisation*

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

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

182 Imaging was performed in backscattered electron configuration, with an incident electron energy
183 of 5 keV, in order to limit the surface charging. The sample surface was randomly imaged by 150
184 µm wide scans, at a resolution of 1024 x 1024 pixels. For each leaf, five images were acquired at
185 each leaf surface (Figure S2). On these images, PM can be easily distinguished as bright particles,
186 with the colour contrast of SEM features being proportional to the atomic number of the elemental
187 components (*i.e.* the brighter the particle, the heavier the components). SEM images were analysed
188 with Gwyddion software,[39] in order to obtain the number and the dimensions of the leaf deposited
189 particles. In particular, the diameter of the equivalent sphere (or particle equivalent diameter, d_{eq})
190 was obtained for each imaged particle, with a cut-off value of 300 nm (which corresponds to the
191 dimension of two image pixels). Particles with a d_{eq} larger than 10 µm (which accounted for less than
192 0.1 % of the total detected particles) were excluded from the analysis. The final dataset was
193 composed by PM0.3-10 particles.

194 Elemental analysis of selected particles was performed through dedicated Phenom Pro Suite™
195 software. The leaf surfaces were scanned at 150 µm scan size, with an incident electron energy of
196 15 keV (Figure S2d). Approximately 200 particles were investigated per sampling site: 50 randomly
197 selected particles on each surface of the two leaves. The equivalent sphere diameter d_{eq} of such

198 particles was obtained by averaging their two main Feret diameters,[40] as measured by ImageJ
199 software (Figure S2d).[41] The corresponding EDX spectra (Figure S2e) were obtained by positioning
200 the laser beam in the particles' centre. The elements identified in the particles were C, N, O, F, Na,
201 Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Sn, and Sb. The comparison of the particles'
202 composition was based on those elements detected with a mean concentration higher than 0.1%
203 over the whole dataset (e.g., Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe), while trace metals (Ti, Cr, Mn, Ni, Cu,
204 Zn, Mo, Sn, Sb) were grouped in a single residual variable ("Res"). Fluorine was excluded from the
205 analysis since it is present just in trace concentration and it cannot be included in the "Res" variable,
206 being not a metal. C, N, and O were also excluded due to several reasons:[32,38] (a) they can be related
207 to biogenic factors; (b) EDX is known to fail in the correct determination of light elements; and (c)
208 the high values and variability of C and O concentrations as obtained by EDX could hinder the
209 variability of the other elements' concentration, which are the more relevant in terms of pollution.

210 Semi-quantitative estimation of the amount of the selected elements was obtained by calculating
211 the weighted volume percentage ($W_{\%}$) occupied by each element x over the N particles selected.[32]
212 To do this, the composition percentage (C) of each element x on each particle i (C_{xi}, as obtained by
213 the EDX software) was multiplied by the corresponding particle volume (V_i), calculated as $V_i = 4/3\ \pi$
214 $(d_{eq}/2)^3$. For each element, such volume percentages were summed together, and the sum was then
215 normalized by using the total volume of all the N analysed particles, obtaining the weighted volume
216 percentage ($W_{\%}$) for each element x, by following Eqn. 1:

217 $$W_{\%_x} = \frac{\sum_{i=1}^{N} C_{x_i} \times V_i}{\sum_{i=1}^{N} V_i} \qquad \text{Eqn. 1}$$

218

219 *SIRM determination*

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

224 Each half leaf was digitally scanned (HP Scanjet G3110), and its surface area was measured using
225 ImageJ software.[41] Then, each half leaf was tightly packed in cling film and pressed into a 10 cm^3
226 plastic container, which was magnetized with a pulsed field of 1 T using a Molspin pulse magnetizer

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

235

236 *Statistical Analysis*

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

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

254

255 **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:

287 variations in leaf surface microstructure and wind turbulence may lead to a difference in the
288 quantity and composition of particles accumulated at the adaxial and abaxial leaf surfaces.[9,53]

289 Univariate ANOVA determined that both the mean particle density and the mean d_{eq} correlate with
290 the leaf surface side ($p < 0.0001$ for both parameters) but not with the site location ($p = 0.18$ for the
291 mean particle density, and $p = 0.38$ for the mean d_{eq}). Multivariate ANOVA performed by using
292 particle density and mean d_{eq} as dependent variables and leaf surface and site location as
293 independent categorical predictor factors showed still a correlation with the leaf surface (Wilks' λ =
294 0.67, $p < 0.0001$) but not with the sampling site (Wilks' $\lambda = 0.97$, $p = 0.34$).

295 The almost homogeneous mean values obtained for both the particle density and the equivalent
296 diameter of leaf deposited particles at the 40 sampling sites are consistent with the mean daily
297 atmospheric PM10 concentration values measured by the closest air quality monitoring stations in
298 the in-leaf period. Indeed, all the provided atmospheric PM10 concentrations were in the (20 ± 10
299 $\mu g\ m^{-3}$) range (Table S1), as also previously observed in different European cities.[24,54] However, by
300 comparing the mean PM0.3-10 leaf deposited particle density (Tables S2) with the corresponding
301 mean daily atmospheric PM10 concentration (Table S1), no significant correlation was obtained
302 (Figure 2a). A significant, positive correlation ($R^2 = 0.3$, $p < 0.05$) was observed, instead, if only the
303 coarse particle fraction (PM2.5-10) was taken into account (Table S2; Figure 2b). This indicates that
304 PM10 concentration data, as obtained by air quality monitoring stations, is strongly biased towards
305 coarse particles (*i.e.* larger particles contribute more than smaller particles), while our approach is
306 a powerful tool for the detection of fine PM,[55] which represents the majority (and the most harmful
307 part[18]) of leaf deposited particles. In particular, in our data, the PM0.3-1 fraction accounts for about
308 the 80%-90% of the total PM0.3-10 fraction. Moreover, local pollution variations could be hidden
309 by monitoring urban air quality through few, disperse stations, which provide very low spatial
310 resolution data. Conversely, the use of urban vegetation as monitoring tool could enable the study
311 of local PM in a more comprehensive way, without the need of on-site apparatus, contributing
312 particularly for the simplification of future research.

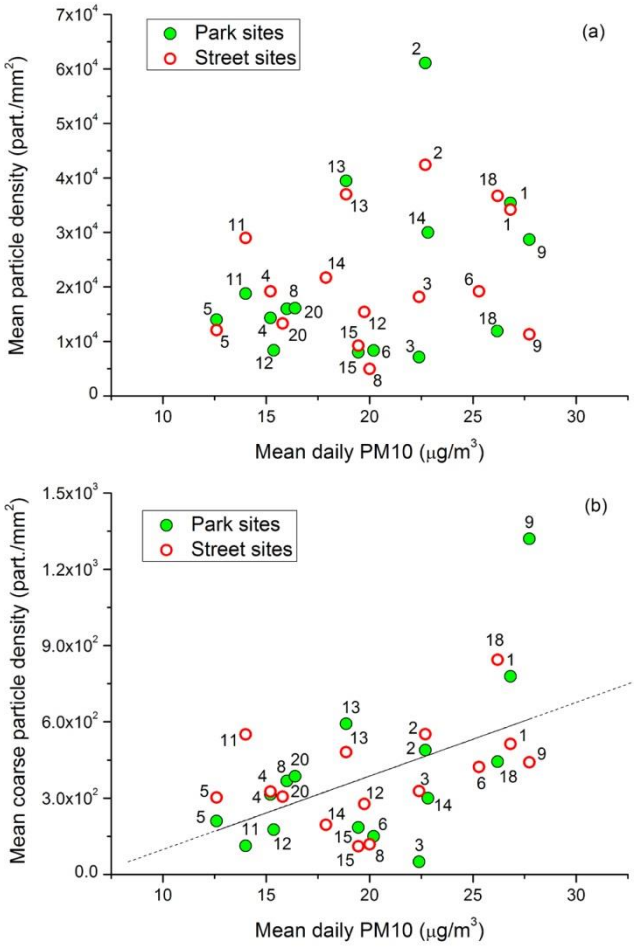


Figure 2. Relationship between the PM0.3-10 (a) and the PM2.5-10 (b) mean particle leaf surface density and the corresponding mean daily atmospheric PM10 concentration, as measured by the air quality monitoring station closest to the sampled tree. No correlation is obtained when the total of the PM0.3-10 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

328 result, mean summed $W_{\%}$ values of 20.4% and 23.6% were obtained by averaging all park and street
329 sites, respectively (Table S4). This difference is mainly due to the more than double mean $W_{\%}$ of Fe
330 at the street (3.4%) compared to the park (1.4%) sites (Table S4). Although Fe is an indicator of
331 crustal soil resuspension, as well as *e.g.* Al, Ca, and Si,[56] combustion processes derived from *e.g.*
332 vehicle traffic are a known source of small Fe-bearing spherules, as Fe often occurs as an impurity
333 in fossil fuels.[31] In addition to combustion sources, Fe enriched particles can be generated also via
334 exhaust emissions and metallic wear/abrasion, such as from tire and brake wear, and road
335 pavement abrasion.[42,46]

336 From the total of the 28 participating cities, the individual leaf SIRM values measured on *Platanus*
337 *acerifolia* leaves ranged from 7.2 µA (Copenhagen) to 202.1 µA (Düsseldorf) in park sites, and from
338 9.2 µA (Kavala) to 1192.2 µA (Warsaw) in street sites (mean values and SE for each site are reported
339 in Table S5). For the 20 cities that were analysed by both SEM/EDX and SIRM (Figure 1), the park
340 leaves showed a mean SIRM value of (30.2 ± 2.4) µA, while a mean SIRM value of (152.8 ± 21.7) µA
341 was obtained for the street leaves.

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

353 Almost 90% of the analysed leaves presented SIRM < 300 µA, while the city of Warsaw showed SIRM
354 values that are more than threefold higher, at the street site (Table S5). The same site presented
355 also the highest Fe (11.1%) and trace metals ("Res" is 2.1%) content from all analysed cities.
356 Moreover, the Warsaw street site had a significantly higher particle density with respect to the
357 corresponding park site. Because the particle surface density and composition, and the leaf SIRM
358 value of the Warsaw park site were comparable to those of the other cities' park sites, it is plausible

359 to assume that, at the Warsaw street site, the PM level is mainly due to local emission sources, in
360 this case traffic. Indeed, the highest traffic intensity (ca. 41200 vehicles h^{-1}) was registered at the
361 street site of Warsaw, from all studied sites. Moreover, air quality in Warsaw is known to be greatly
362 affected by traffic, due to both the city conformation,[58] and the massive use of old diesel cars that
363 characterizes the transition economies of Eastern Europe.[59]

364 When comparing SIRM data with the leaf deposited particles' Fe content as analysed by SEM/EDX,
365 most of the street sites revealed both leaf SIRM and Fe content values higher than those observed
366 at the park sites, suggesting a rather clear distinction between the two urban conditions (Figure 3).
367 Street sites showed large ranges of both leaf SIRM and Fe $W_{\%}$ values (with mean values from about
368 20 µA to almost 1000 µA, and from less than 1% to almost 11%, respectively), and a good correlation
369 is obtained between Fe *W%* and SIRM values over the entire street sites' dataset ($R^2 = 0.4$, $p < 0.05$).
370 On the other side, the park sites showed low SIRM (< 40 µA) and Fe $W_{\%}$ (< 2%) values, but with few
371 exceptions: parks in Ljubljana and Yerevan showed a high SIRM value but a low Fe $W_{\%}$, Zurich and
372 Berlin had a Fe $W_{\%}$ > 2% but a low SIRM value, while Antwerp and Granada revealed both Fe $W_{\%}$ >
373 2% and SIRM value > 40 µA. As a consequence, no correlation is obtained between Fe *W%* and SIRM
374 values on the park sites' dataset.

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

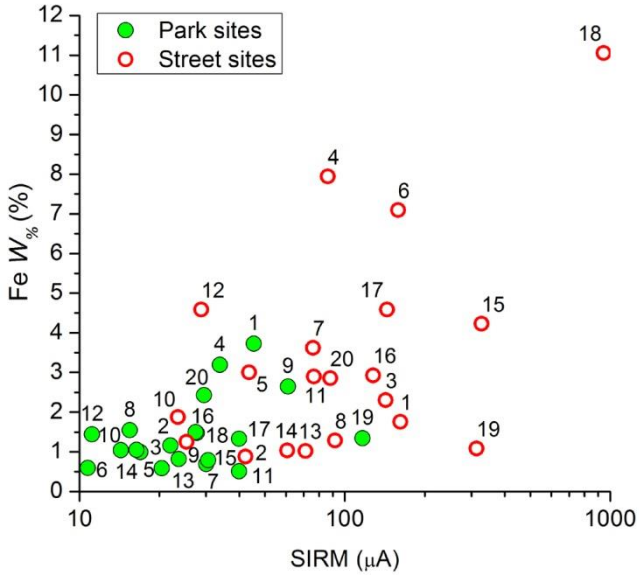


Figure 3. Relationship between the Fe weighted volume percentage $W_{\%}$ of PM0.3-10 particles deposited on *Platanus acerifolia* leaves sampled over 20 different cities across Europe, both at a street and a park site, and the logarithm of the SIRM value as measured from the same leaves. For corresponding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

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

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

430 The group at positive PC1 values is characterised by high percentages of fine particles and with high
431 concentrations of Na and Cl (Salzburg and Malmö street sites), Ca (Bern and Florence street sites),
432 or of these three elements together with S (Aveiro park and street sites), and low metal content,
433 suggesting that natural sources should be invoked.[32,48] High concentrations of Na and Cl together
434 are likely due to the presence of salt sources, which could be the marine aerosol (such as for Malmö),
435 salt mines (Salzburg), or salines (Aveiro).[36] The high Ca and S concentrations observed at Aveiro sites
436 are likely to originate from salines as well.[63] Resuspension may induce high concentration of salt
437 particles at street sites,[64] and the similarity between the park and the street sites of Aveiro could be
438 due to the proximity of the park site to the closest street (37 m; Table S1).[57] On the other side,
439 geomorphology of the area could partially explain the high Ca concentrations observed at the Bern
440 and Florence street sites, and also the erosion of calcareous buildings present in these cities could
441 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]

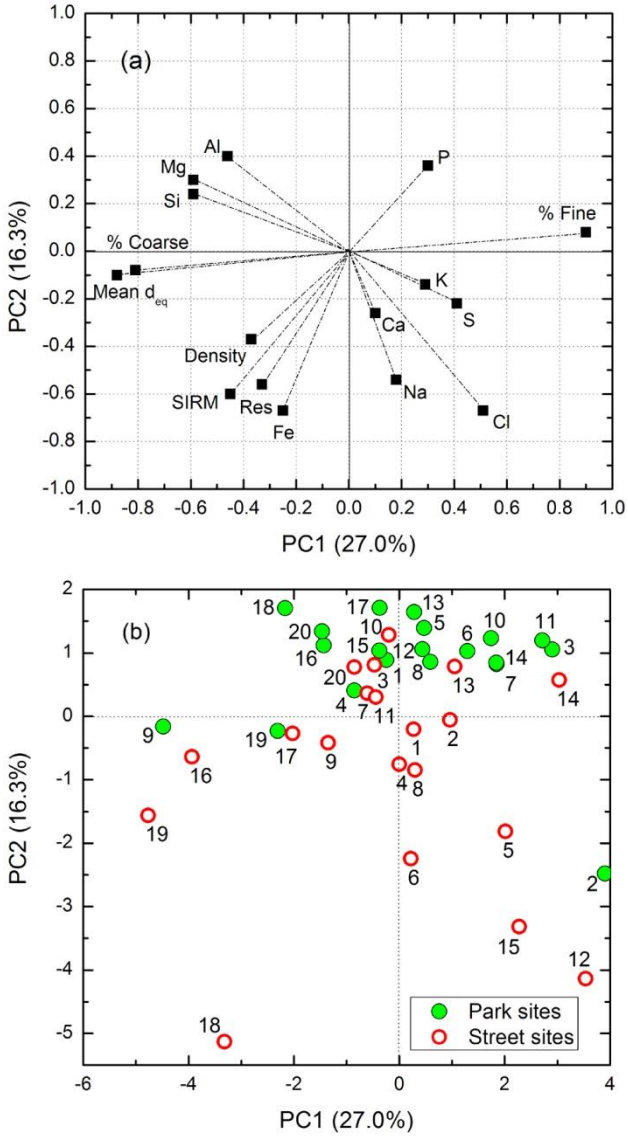


Figure 4. Outputs of the PCA performed by considering as input variables the particle leaf surface density ("Density") and morphological characteristics (namely, percentage of fine PM0.3-0.6 – "% Fine" - and coarse PM2.5-10 – "% Coarse" - particles and the mean particle equivalent diameter – "Mean d_{eq}"), 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 morphological characteristics and elemental composition 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 at least some major PM sources for most of the explored cities across Europe. Common regional background PM composition and concentration were observed, across the 20 investigated cities, while certain local conditions, such as the influence of *e.g.* salt aerosol sources (Malmö, Salzburg, Aveiro) or a dry continental climate and arid steppe landscape (Yerevan), were clearly recognized.

The main PM sources identified in this study are in line with those previously obtained by sampling PM with gravimetric-based techniques and analysing it with a wide range of analytical methodologies.[36] Thus, although leaf monitoring is, as a methodology, not as uniform as gravimetric ones, the use of tree leaves as natural passive air filters has been demonstrated to be a good approach for comparing PM deposition in cities along a wide geographical distribution, without the need for expensive, similar and calibrated equipment in the different cities. However, a strict, common leaf sampling protocol is required, to prevent variability due to *e.g.* sampling procedure and meteorological differences among sites.

In particular, the proposed methodology is highly suitable to investigate the presence in the atmosphere of inorganic, non-soluble, metallic particles, whose leaf deposition rate is strongly depending on the leaf surface characteristics (the sampling of a single tree species is thus required), while it is only slightly affected by the meteorological conditions, such as precipitations. Hence, such methodology allows to distinguish between different land use/polluted environments within a city, as a clear distinction between street and park sites was generally registered. In this regard, similar studies are pertinent to urban planners and other stakeholders, since they can reveal how local urban conditions vary within the same city, or neighbourhood, and may drive the implementation of urban parks and other green infrastructures (*e.g.* green walls) at critically polluted urban sites, positively contributing to human health in cities.

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Supporting Information

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

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