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## Analysis of particulate matter (PM) trapped by four different plant species in an urban forest: Quantification and characterization

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#### ABSTRACT

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Urban forests provide a series of ecosystem services, as recognized from the European 2030 Forestry Strategy; among them, they have the ability to capture particulate matter (PM) from the atmosphere, retaining it on leaves surface. This study analyses the efficiency in PM capturing of four broadleaved species: Celtis australis, Fraxinus ornus, Morus alba and Tilia cordata, set in an experimental urban forest in the city of Reggio Emilia (Italy). The airborne particles have been quantitatively and qualitatively analysed through SEM/x-EDS. Furthermore, the role played by leaf micromorphology in the efficiency of these four species to intercept PM has been assessed. Considering the total average number of particles trapped and collected by leaves for three years (from 2019 to 2021), F. ornus showed the highest capture-capacity (5.0  $\pm$  3.1  $\times$  10<sup>3</sup> particles/mm<sup>2</sup>), collecting 49 % more particles than Celtis australis, 86 % more than Tilia cordata and 135 % more than Morus alba. Qualitative analyses on PM have found that the majority (from 68 % to 74 %) of total particles show a diameter lower than 2,5  $\mu$ m. Leaf micromorphology proved to be important, however it was no possible to identify a micromorphological trait more influential than others in determining the ability of the species to capture PM. The particles trapped by leaves were mainly rich in non-toxic or low-toxic elements, but some of them can be considered potentially dangerous for human health and the environment for the presence of Ni, Cr and Ba. The PCA highlights as the principal source of pollution in this study seems to be the erosion soil, followed by vehicle traffic. These results can give useful knowledge to understand what the contribution of different plants species in PMs retention ability is, also identified as a regulation ecosystem service.

#### 1. Introduction

Urban and peri-urban forests have been defined as "*tree dominated ecosystems in and near human settlements, with an important role for a healthy and liveable cities*" (Endreny, 2018). As our world becomes progressively urbanized, urban forests assume a key role in improving good ecological relationships in urban areas, enhancing the overall welfare of individuals residing in and around the cities, which host the majority of the population today (FAO, 2017). The presence of trees, set into urban forests or other green infrastructures, provides a long series of ecosystem services, categorized as cultural (e.g., recreational), provisioning (e.g., food, fibers, water), regulating (e.g., climate and flood control) and supporting (e.g., pollination, soil formation) (Endreny, 2018). Among regulating services, plants are important allies in reducing air pollution, improving urban air quality. Regards to polluting gases, plants can absorb them through the stomata and then these elements spread into intercellular spaces (Lorenzini, 2005). Considering airborne particles, also defined as particulate matter (PM), some of them can be absorbed into the plant tissues (Lee et al., 2022), but many others are trapped by leaf surface. According to the World Health Organization (WHO), PM is one of the main pollutants with the greatest impact on human health, next to ozone (O<sub>3</sub>), carbon monoxide (CO), sulphur dioxide (SO<sub>2</sub>) and nitrogen dioxides (NO<sub>x</sub>) (OMS, 2021). PM is a mixture of solid and liquid particles, that remain suspended in the air, because their microscopic size. These particles are split into three main categories by aerodynamic diameter: PM<sub>10</sub>, which is a fraction of particulate matter comprising particles of 10  $\mu$ m in diameter or less; PM<sub>2.5</sub> which includes particles of  $2.5 \ \mu m$  in diameter or less and UFP (Ultrafine Particles), which comprises particles of 0.1 µm in diameter or less (Schraufnagel, 2020). Particulate matter can comprise heavy metals (for example lead, copper or zinc), chemical elements typical of soil, like aluminium (Al) or silicium (Si) and organic compounds, biogenic volatile organic compounds (BVOCs), (Zare et al., 2014). There are a lot of sources who can emits particles of different nature and size:

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- Natural sources, like soil dust, wildfires, marine aerosol, volcanic eruptions (Elbert et al., 2007) and biogenic aerosol (Thorpe and Harrison, 2008);
- Anthropogenic sources, as vehicle traffic, which may include emission from road vehicles (cars, trucks, etc.) and emit also "exhaust PM". Other vehicles like planes or boats can contribute to PM emissions. Industrial activities, like mining and building industries, power plants (Azarov et al., 2017) and agro-zootechnical industries represent other anthropogenic sources (Sun et al., 2017).

According to Karagulian et al. (2015), the contributions of pollution sources to overall PM emissions differ globally, and these variations occur within the same continent, among different countries and even within the boundaries of a single country. USA domestic fuel burning contributes to total  $PM_{10}$  emissions for 15 %, but it doesn't contribute to total  $PM_{10}$  emissions in the rest of Americas, while in Northern China and Southern China the pollution sources contributions to total  $PM_{10}$  are similar but not the same. PM exposure is associated with several negative health outcomes: a study conducted as part of European project Agency for Public Health Education Accreditation (APHEA) has calculated an increase in daily deaths of 0.52 % for all causes of death and 0.76 % and 0.71 % respectively for cardiovascular and pulmonary diseases for every 10  $\mu$ g/m<sup>3</sup> increase of PM (Katsouyanni, 2006).

Given the risks related to presence and the increasing rate of PM in the urban air, it is necessary to find strategies to reduce its concentration. Beyond the emissions reduction plans, reducing the quantity of already present PM in the atmosphere represents a valiant strategy. In this view, plants can offer an important contribution since they can act as a filter for airborne particles, reducing their concentration (Nowak, 2002).

The abatement of PM by plants can be analysed from two perspectives: deposition and dispersion. The primary mechanism could be referred to the "dry deposition", which is the exchange of substances between the atmosphere and Earth's surface through direct contact, in the absence of precipitation, as defined by Pryor et al. (2008). In contrast, "wet deposition" depends on a wide range of meteorological parameters (Janhäll, 2015). The mechanism of dry deposition can be influenced by different factors, as the size of airborne particles. Ultrafine particles of 10  $\mu$ m in diameter are deposited by impact with leaf surface, and the coarser ones (>10  $\mu$ m) settle by sedimentation.

A high air humidity can significantly influence the process, since PM with hygroscopic properties may absorb moisture from surroundings. As a result, the particle diameter can vary over time, leading to changes in their deposition features (Litschike and Kuttler, 2008). Winds also impact dry deposition, since there is a negative correlation between wind speed and the concentration of PM particles on vegetation cover (He et al., 2020; Liu et al., 2016). The dispersion of pollutants is strongly affected by several factors as urban topographic features which involve the presence of buildings, streets, and vegetation (Choi et al., 2023). The dispersion of pollutants relies also on a system of winds, which facilitate their transport and dilution across various scales. This process can also be influenced by variations in airflow resulting from buildings and vegetation (Janhäll, 2015): in the urban context, PM dispersion is greatly limited by urban canopy. The dispersion of airborne PM and its deposition on leaves surface are also deeply influenced by precipitation phenomena (Xu et al., 2017). Specifically, rainfall has an important PM removal effect, playing an integral part in the plant dust retention process (Xu et al., 2017; Zhou et al., 2021). Rainfall drops contribute to wash away part of PM from the leaf surface into the soil. The efficiency of this process depends on several characteristics such as the rainfall intensity, duration, the drops dimension and direction. However, few studies have investigated the relationship between rainfall features and its efficiency of PM wash-off from foliage (Xu et al., 2017). Several models have been studied and proposed to describe the dispersion of pollutants: the computational fluid dynamics (CFD) simulations try to

describe the PM dispersion phenomenon in a complex urban region (Fernández-Pacheco et al., 2023). However, it is difficult to predict PM distribution with accuracy (Blocken et al., 2016).

Dry deposition of the particulate matter is influenced by the characteristic of plants and the leaves morphology. Both macroscopic, linked to the height of the plants, the organization of the canopy and leaf area, and microscopic features, linked to the micromorphology of the leaf, can play a role in PM capture (Wang et al., 2013). Different heights allow the plants to catch different fractions of particles, coming from the upper areas of the biosphere, or the ones close to the ground (Mo et al., 2015). Moreover, deciduous and evergreen species show different capacity to capture and retain PM: evergreen plants and particularly the coniferous, have proven to be more efficient thanks to the needle-like leaves which easily intercept PM (Mo et al., 2015), despite being less pollution tolerant (Janhäll, 2015; Sæbø et al., 2012). Leaf shape can modify flows of air, so it has a great influence on the PM deposition (Weerakkody et al., 2018).

Leonard et al. (2016) have highlighted different concentrations of PM trapped by different shaped leaves: leaf adaxial surface gives greater contribution than abaxial one to capture all PM fractions, probably because of the gravity and wind turbulence, whereas only 17 % of total PM is deposited on the abaxial surface (Wang et al., 2006).

At the same time, leaves micromorphological features can affect the ability of plant species to capture airborne particles (Mo et al., 2015). Leaf micromorphology consists of different micro configurations present on leaf surfaces, such as grooves, ridges, hairs and stomata, which contribute to the roughness, and the presence of epicuticular waxes, which can affect the hydrophobicity of leaf surface (Cai et al., 2017; Leonard et al., 2016). There is a positive correlation between the hairiness and deposition rate (Dzierzanowski et al., 2011). The roughness of the leaf surface can also promote the retention of particulate matter by the leaf blades (Zhang et al., 2018): in this case, grooves of different depth and width can capture different fractions of airborne particles (Redondo-Bermúdez et al., 2021). The chemical composition and the thickness of the epicuticular wax layer are among the main factors that affect the wettability of leaf surface, as it determines the value of DCA (drop contact angle,  $\theta$ ): the larger DCA, the more repulsive the surface and the lower the wettability. According to previous studies (Muhammad et al., 2020), six main epicuticular waxes structures (EWS) could be observed on plants leaves: 'thin film', 'granules', 'tubules', 'platelets', 'rodlets' and 'filaments'. Functional plant types and families were significantly associated with distinct EWS types, possibly due to the phylogeny of the respective plant members. Consequently, it has been demonstrated that the DCA does not solely depend on EWS. Other leaf traits such as trichome density also influence the wettability of a leaf surface (Muhammad et al., 2020). Not-wettable surfaces provide effective non-stick properties, allowing the liquid drops to bounce on them, preventing the adhesion of particulate matter (Tyowua and Targema, 2017; Aryal and Neuner, 2010). Considering the available scientific literature, seems that there is no agreement on which micro- or macro feature has the greatest influence on the capture of the particulate by plants. The efficiency in PM retention by plant species should be evaluated in each specific case, with a qualitative and quantitative approach. According with one of the objectives of the Strategy for Biodiversity EU2030 "to build our societies' resilience to future threats such as the impacts of climate change" the present research aims to investigate the ability of four plants species to capture atmospheric particulate matter, evaluating the micro-morphological structure of leaves surface. The study is part of the 3-years "Urban Proof" Life Project placed in the city of Reggio Emilia and founded by European Union to increase the resilience of municipalities to climate change.

In detail, this study wants to 1) carry out a quantitative evaluation of PM collected by leaves of four tree species used to create an urban forest, 2) analyse the chemical composition of PM and 3) investigate the relationship between the micromorphology of the leaf and the ability of the plant species to retain particulate matter.

#### 2. Materials and methods

#### 2.1. Area of the study

The area of the study (also called "experimental forest") is located in the "Acque Chiare" park, in the city of Reggio Emilia (44°40′33''N, 10°39′01''E). This is an urban green area of 193,000 m<sup>2</sup>, located in the southeast zone of the city, placed in the Po Valley, in the North of Italy. Here, the experimental forest was planted in 2018, involving four different woody plant species, chosen according to Guidelines identified by REBUS project of Emilia-Romagna Region. The species selection criteria to create an urban forest comprises plant habitus, growth rate, resistance, adaptability, origin and leaf morphology. The four selected species are *Celtis australis* L., *Fraxinus ornus* L., *Morus alba* L. and *Tilia cordata* Mill. The study area is divided in four plots, each containing three rows of nine individuals for each single species for a total of 108 trees.

As shown in Fig. 1 on the southwest side of study area, there are residential buildings: the closest to the experimental forest was built between 2019 and 2020, whilst on the northern zone there are green open areas. To the west, the study area is bordered by a closed road (Via Giuseppe Mercalli), which is used only by residents.

#### 2.2. Samples collection and preparation

Quantitative evaluation and chemical analysis of PM were performed on leaves samples for each species, collected twice a year, at the end of April and at the end of September, during the period 2019 and 2021. Each sampling was performed choosing 4 or 5 leaves per species from different individuals, then carefully wrapped on wet paper and placed in a thermal box until the transport to the laboratory. About twenty explants per species with dimensions of  $0.25 - 0.5 \text{ cm}^2$  were obtained from each species samples. Explants were immediately treated to observation and analysis through Scanning Electron Microscopy (SEM). This procedure involves different stages:

- Fixing the samples in 3 % glutaraldehyde (GA) in phosphate buffer (0.1 M, pH 6.9) and let them rest overnight in the fridge at 0–5 °C;
  Washing through a series of 15-minute steps (6 7) in the same phosphate buffer used for GA solution and finally let them rest overnight in the refrigerator at 0–5 °C;
- Dehydration using acetone/water solutions at increasing acetone concentrations, followed by critical point dehydration using  $CO_2$  as the transition liquid (CPD 010 Balzers Union). Finally, samples were mounted on stubs, provided with small disks of conductive and adhesive layer.

For each plant species, each season and each year of the study, 2 stubs showing the adaxial surface and 2 stubs showing the abaxial one, were prepared. Two samples were put on each stub and the SEM analysis was performed on 24 different areas on each stub. Any area was randomly chosen, moving from time to time on the sample.

#### 2.3. Quantitative analysis and chemical composition of PM

All the samples were observed under the Nova NanoSEM 450 (SEM/ FEG) (FEI), in collaboration with the Interdepartmental Center Large Instruments (CIGS) of the University of Modena and Reggio Emilia.

The quantification of PM trapped by the leaves was performed, setting the instrument in Low Vacuum mode using BSED (GAD) detector; the chamber pressure was maintained at 50 Pa and the electron beam energy was 20 keV. 24 images from each sample were taken at 2000X magnification, considering only the adaxial explants. This means that for each year and for each species considered, 48 areas have been evaluated, comprising both spring and autumn samples. Each image was subsequently analysed through ImageJ software to count the number and to measure the size of the particles adherent to leaf surface. Each image corresponds to an area of 0,0075 mm<sup>2</sup>. PM was further analysed through Energy Dispersive X-ray Spectroscopy (X-EDS, Bruker QUANTAX-200) with the aim to get a semi-quantitative analysis of its chemical composition. In detail, 5 particles on 8 areas for each sample were analysed. In this way, 40 EDS-spectra were obtained and evaluated for each sample. A particulate-free area has always been analysed and identified as "control area" to determine leaf chemical composition. Energy spectra obtained were analysed through Esprit 2.1 software to calculate atomic mass percentage (Atom.%) of each element contained into the particulate.

#### 2.4. Leaf micromorphology analysis

Further leaves samples were performed in July 2022 and used for leaf micromorphology analysis. The samples were prepared according to same procedure described in Section 2.2; dried samples were gold-coated (10 nm thick) by an automatic metallizer (K550, Emitech). The samples were then observed with Nova NanoSEM 450 (FEI) in High Vacuum mode. The adaxial surfaces were observed at 500x, 2000x and 4000x magnifications, while the abaxial ones were viewed at 1000x and 2000x magnifications.

#### 2.5. Meteorological data

Regional Agency of Environmental Protection and Energy of Emilia-Romagna Region (ARPAE) has gathered data on daily precipitation in



Fig. 1. a) Satellite image of the "experimental forest" (identified within the red rectangle) and the study area in the southern of "Acque Chiare" park, in Reggio Emilia, Italy; b) a plants group of experimental urban forest.

the urban area of Reggio Emilia. This information is publicly available through its meteorological dataset provided on website: https://dati.arpae.it/dataset/dati-meteoclimatici-comunali.

#### 2.6. Statistical analysis

Statistical analysis was performed running ANOVA test and Tukey (HSD) test through Past 3.15 software to verify seasonal and annual intraspecific and interspecific variations. Past3.15 was released by Hammer, Ø., Harper, D.A.T. Ryan P.D. 2001. The values of the dimensions of particles were calculated using ImageJ functions; then, the relative frequencies of fractions of PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>10</sub> and of the coarser fraction (diameter >10  $\mu$ m) were calculated. The average and standard deviation of percent atomic mass and relative frequency of the elements was calculated. The data for each year were subjected to Principal Components Analysis (PCA), after normalization of data.

#### 3. Results

#### 3.1. Rainfall data

The total rainfall recorded from April 1st to September 30th for the years 2019, 2020, and 2021 amounted to 566.1 mm, 443.7 mm, and 218.9 mm, respectively. Daily rainfall data have been reported in Fig. 2.

#### 3.2. Quantitative evaluation of PM trapped by leaves

Quantitative analyses of PM showed that the distribution of airborne particles is not homogeneous on leaf surface, but there are areas very rich in PM and other areas almost free. This is supported by the presence of outlier values and the high standard deviation values, as shown in Fig. 3.

The amount of particulate captured by all four species varied over the three-year period considered. In general, the quantities of particulate matter trapped by plants were higher during 2020 than in the other two years. The average number of particles captured in the spring of 2020 tended to almost double compared to that collected in 2019 and 2021, in which low PM values were found. Considering only the autumn of the three years, the highest values of average particles captured by the leaves was found for the year 2020, except for *Tilia cordata*, which had the highest average autumn number in 2019. In Autumn 2021 all four species had captured the lowest amounts of particulate matter (Fig. 4).

If the interspecific variations were considered within any year, there was no significant differences among the amounts of PM trapped by the four species during the spring season. Differently, the number of particles on samples collected in autumn was significantly higher only in *Fraxinus ornus* and in *Tilia cordata*, but for this last species only in 2019 (Fig. 4).

Considering the total average number of particles trapped and collected by leaves during three years (Fig. 5), *F. ornus* showed the highest capture-capacity  $(5.0 \pm 3.1 \times 10^3 \text{ particles/mm}^2)$ , followed by

*Celtis australis*  $(3.3 \pm 2.3 \times 10^3 \text{ particles/mm}^2)$ , *Morus alba*  $(2.1 \pm 1.5 \times 10^3 \text{ particles/mm}^2)$  and *Tilia cordata*  $(2.7 \pm 1.9 \times 10^3 \text{ particles/mm}^2)$ .

Indeed, *Fraxinus ornus* was the only species which showed significant seasonal variations (p-value <0.05) for each year (Fig. 6). Its leaves captured and retained more particles when collected in autumn than in spring: this was more evident during the Autumn 2020, when PM trapped by *Fraxinus* is three times as much as it did in spring ( $216\pm104$  in 2020 *vs*  $121\pm44$  in 2019 and  $86\pm51$  n° particles/area in 2021). In *C. australis* significant seasonal variations emerged during the year 2020, since a higher number of particles has been counted on leaf surfaces in autumn in comparison with spring ones. *T. cordata* had collected more particles during the autumn 2019, while *M. alba* did not show significant differences in the quantities of airborne particles captured though the different seasons along three years.

Regarding the size of the PM captured it is mostly in fine fraction (PM2.5) while only a minor part can be included in the "coarser particles" category. Furthermore, more than half of fine particles captured has a diameter of 1  $\mu$ m or less. The results are shown in Table 1.

#### 3.3. Chemical composition of PM

Chemical composition of PM is reported in Fig. 7. Carbon (C) and oxygen (O) are always present in high quantities. Silicium (Si) is averagely the third most represented element in terms of quantity and frequency.

A series of eight elements is always present, even if in proportions variable from species to species and between the different seasons: iron (Fe), calcium (Ca), potassium (K), phosphorus (P), aluminium (Al), magnesium (Mg) and sodium (Na). Titanium (Ti) and sulphur (S) occur in the 10 % and 20 % of samples, respectively. Finally, there is a series of trace elements (i.e. element present in less than 10 % of samples): zirconium (Zr), chromium (Cr), copper (Cu), chlorine (Cl), manganese (Mn), indium (In), rhenium (Re), zinc (Zn), cobalt (Co), fluorine (F), nitrogen (N), barium (Ba), nickel (Ni), yin (Sn) and caesium (Ce).

Table 2 shows the values of percentual atomic mass of control areas, taken on leaves of each species in both seasons. As expected, the most frequent elements are C and O, that are basic elements of biological molecules. Na, P and K are always present, instead of Mg and Al that were detected only on leaves of *Celtis australis* in spring and on leaves of *Fraxinus ornus* in autumn. Si and Ca are more frequent but not always detected in the control areas.

Results of PCA are shown in Fig. 8, which reports the analysis of the principal components for each year. In 2019 four components have been identified: the first (A) comprises Al, Si, K, N and F; the second (B) includes C, Zr, Re and Cl; the third (C) includes Cu, Zn, S, Co, Ni, Cr, Fe, Na, In, P, and Mn, Mg, Ti and the last (D) include Mn, Mg, Ti, O. In 2020 (Fig. 7b) Al, Si, O, K, Mg, Zr and Ti segregate together to form a first component (A); the second component (B) is composed of C, N, S, Na, Cl, Ca, Ce, Zn, Ba; the third component (C), is composed of Fe, Cr, Ni, Mn, Ti. Fluoride, unlike 2019, segregates by itself (D). Lastly, in 2021 (Fig. 7c) four components have been identified: the first consists of Al,



Fig. 2. Rainfall data (provided by ARPAE Emilia-Romagna) on the urban area of Reggio Emilia from 1st of April to 30th of September in 2019-2020-2021.



Fig. 3. Boxplot representing data of PM trapped by the four species in both seasons during the three-years period. Each sample is identified by the genus name, year of sampling and season of sampling (S= spring; A = autumn).

Si, Cl and K; the second composed of C and Cu, the third formed by Na, Zr, F, P, Ca, S and Ba; the latter is made up of Mn, Fe, Ti, Cr, O and Mg.

#### 3.4. Leaf micromorphology

Micro-morphological features of each plant species have an important role in the PM capture. The analysis conducted at SEM/FEG enabled the examination of micro-morphological details (Fig. 9). C. australis leaves exhibit cubic to rectangular shaped epidermal cells with rough surface, also due to the presence of single and quite long hairs, distributed over the entire surface, both adaxial and abaxial (Fig. 9a-b). The epidermal cells in leaves of Fraxinus ornus appear with a characteristic shape, separated by deep reliefs on the edges of the cells, cuticular folds of cuticle, which increase the roughness of the surface. Equally deep margins are also present between venation system. This species has not trichomes in both the leaf epidermis (Fig. 9c-d). Leaves of M. alba (Fig. 9e-f) show epidermis glossy and without hairs. Epidermal cells are roughly cubic in shape with smoother surfaces than C. australis and F. ornus: this is due to shallow margins and the absence of hairs; in this species characteristic glandular hairs appear on abaxial surface. T. cordata leaves show tufts of rusty brown hairs at the junctions of veins on the abaxial page. Leaf epidermis has rectangular shaped cells with pronounced cuticular ridges - also occurring between vascular elements - and with deep intercellular margins (Fig. 9g-h).

#### 4. Discussion

The amount of PM trapped by plants depends on plants characteristics, leaves micro-morphological details and also on PM concentration in the air. According to Air Quality reports by ARPAE Emilia-Romagna (ARPAE, 2019; ARPAE 2020; ARPAE 2021), during the three years of monitoring, mean annual values of PM fall within the maximum thresholds established by the law (40  $\mu$ g/m<sup>3</sup>). However, the absolute amount of PM has overcome the daily threshold (50  $\mu$ g/m<sup>3</sup>) more than 35 times, especially in 2020, when it has been overcome by the highest number of monitoring stations, *i.e.* 25 out of 43 total ones (ARPAE, 2020). Frequently exceedances occur when pollutants couldn't be spread due to wind unfavourable conditions (Janhäll, 2015; Litschike and Kuttler, 2008). Therefore, 2020 has been reported by Air Quality Report by ARPAE Emilia-Romagna 2020 (ARPAE, 2020) as one of three worst years for pollutants accumulation since 2003. Beyond air quality data, rainfall data provided by ARPAE have been considered, in order to evaluate how it could influence the amount of PM collected on leaves. Cumulative daily precipitation data have been reported in Fig. 2. Comparing rainfall data, the wettest year was 2019, while the least rainfall, 2021. Considering the possible effect of rain on PM accumulation by leaves surface, as already been described by Xu et al. (2017), rainfall data seem to agree with the PM concentration found in 2019 and 2020. However, this correlation doesn't occur in 2021, when air PM values remain very low (ARPAE, 2021). The result of this research confirms the trend reported by ARPAE agency, since the number of particles retained in 2020 is higher than other years, especially in *F. ornus* and *C. australis*.

If we consider the average over three years (Fig. 4), there is a significant difference among the quantity of PM trapped by Fraxinus ornus and Celtis australis compared with those captured by Morus alba and Tilia cordata. Dissimilar leaf macro- and micromorphological features could explain these quantitative differences. As several studies have highlighted, leaf shape and size influence the ability of plant to capture PM. Leonard et al. (2016) noted that lanceolate leaves capture a larger concentration of airborne particles than obovate and elliptical ones. Regarding to the effect of leaf size, different results were found: smaller leaves seem to capture less PM with respect to the bigger ones (Weerakkody et al., 2018; Freer-Smith et al., 2005; Leonard et al., 2016), while Sæbø et al. (2012) found no significant evidence of leaf size influence. Moreover, many fine and coarse particles accumulate on the adaxial surface, while mostly coarse particles accumulate on the lower surface, in particular near the stomata, as the positive correlation between PM deposition and stomata (Sgrigna et al., 2020; Redondo-Bermúdez et al., 2021). Previous works underlined also the role of leaves margins and veins in PM adsorption phenomenon. Leaf blade margin is a further macromorphological characteristic together with the leaf shape, leaf growth expansion and foliage feature, which have been identified as driving parameters for PM capture (Sgrigna et al., 2020). Depending on the margin features and complexity, leaves could show a higher or lower PM capture capability. Specifically, leaves exhibiting serrated or lobate margins and palmate shapes seem more efficient in PM trapping, while those with smooth margins and ellipsoid shapes were described as less efficient, indicating a simpler leaf structure (Chelli et al., 2019; Sgrigna et al., 2020). These observations could be confirmed also by results found in this work, where composted leaves and serrated margins of F. ornus proved to be more efficient in particulate retention than those of



**Fig. 4.** Number of particles captured per area every year of sampling (2019, 2020, 2021). Average data and SD are shown. Different letters indicate significant differences (p-value <0.05).

the other species.

Furthermore, deep and narrow grooves, (i.e., intercellular margins) scales, glands, leaf hairs, veins and ridges increase leaf surface roughness, that can contribute to the capture of airborne particles, as already observed by previous authors (Chen et al., 2017; Redondo-Bermúdez et al., 2021). SEM/FEG observations highlight that on F. ornus leaves the particles are concentrated precisely into these grooves (Fig. 9c-d) and based on the analysis shown in Table 1, this species traps mostly fine particles. Several studies underlined the importance of hairs in the capture of PM, together their density and distribution (Chiam et al., 2019). In this regard, C. australis leaves are characterised by a low density of hairs (Fig. 9a-b) and this treat could be related to their relatively limited ability to trap airborne PM. The main feature of Celtis australis leaves is the presence of single and quite long hairs, distributed over the entire upper and lower surfaces, including venation system. They can be involved in temperature and water loss regulation and moisture retainment, also influencing the growth of bacteria and fungi.

Leaf surface temperature mitigation depends on transpiration process, which in turn is regulated by boundary layer thickness. Specifically, the hairs, trichomes and sub-stomata cavities increase the resistance of boundary layer. In details, broad hairs cover the surface and maintain aqueous vapor close to epidermal surface, retaining atmospheric moisture (Ripley et al., 1999). At the same time, the retention of water vapour by hairs is influenced by their shape, heigh and density. Furthermore, a high density of hairs, grooves, thick veins makes the leaf surface a temporary and advantageous environment for spore germination. Consequently, these leaf traits are often related to a high colonization by fungi and epiphylles (Allen et al., 1991). In this regard, also the presence of a mycelium forming a wide web on leaves blade seems to contribute to the particles retention (Przybysz A., et al., 2023; Sánchez-López et al., 2015). However, our findings did not evidence the presence of mycelia on leaves samples.

The micromorphology analysis highlights the details on species specific cuticle shape, formation and abundancy. Cuticle, secreted by epidermic cells, has an important role in plant survival: it is involved in limiting plant transpiration increasing leaf impermeability, reflection of solar radiation and defence against bacteria and fungi; at the same time, cuticle layer contributes to wettability, that varies with adaptation to the environment.

As shown in Fig. 9, C. australis and F. ornus do not show any particular difference in the structure of the cuticle, having similar shape folds and thickness. C. australis has intercellular margins between cubic to rectangular cells and they are narrow but less deep than F. ornus ones, so the intercepted particles could be more easily re-suspended (Redondo-Bermúdez et al., 2021). Therefore, the intercell depressions on epidermis could be an important trait involved in PM concentration and retention. The surface of Morus alba appears the smoothest one: the edges between cells are wide and shallow, probably more suitable to capture coarser particulate than the fine one (Redondo-Bermúdez et al., 2021). The surface is interested by the presence of glands around which some cuticular ridges rise in radial arrangement. These contribute to slightly increase leaf surface roughness, providing specific areas where airborne particles mainly cluster. Tilia cordata produces the most pronounced cuticular folds among the four species, while the intercellular edges form wide and superficial grooves, more suitable for capture of coarser particles (Redondo-Bermúdez et al., 2021). The results of the micromorphological analysis allow to stress that more than one leaf trait may influence the capture and retention of PM, and that the best ability seems to be related to a number of micromorphological traits, in agreement with the statements of other authors (Zhang et al., 2018). This study gives the possibility to evaluate the efficiency of different combinations of micromorphological traits species by species. Indeed, Tilia cordata is the species with the most pronounced cuticular ridges but nevertheless it is the species that trapped the least amount of PM; Celtis australis and Morus alba have quite similar grooves, but thanks to contribution of hairs, the first species captures more PM than the second one. Furthermore, the analyses show that all four species capture more PM<sub>2.5</sub> than PM<sub>10</sub> or coarser fraction. In fact, more than 70 % of trapped PM belongs to fine particles having a diameter lower than 2.5 µm; this represents the most harmful fraction of PM, since it could enter into the respiratory tract, laying into alveoli, and it is able to reach bloodstream, leading to respiratory and cardiovascular disease. In this regard, as Tilia cordata overcomes the other three species, it could be usefully used in an urban context to improve air quality, providing advantages in terms of health of citizens (Diener and Mudu, 2021).

Analysing the chemical composition of particulate matter and their frequency allows to determine the presence of hazardous substances to both human and environment. Among the most abundant and most frequent elements, C, O, Na, Mg, K, Ca and P are natural component of living cells; Si and Al are compounds of soil and dust-derived. Titanium and sulphur have been identified in 10 % and 20 % of samples respectively: titanium is one of nine most frequent elements in soil and it is not a toxic compound (Zierden and Valentine, 2016)<sup>-</sup> while sulphur can



Fig. 5. Number of airborne particles intercepted by the four species. The two seasons are marked as "S" = spring and "A" = autumn. Different letters identified statistically different samples (p-value <0.05). The average data and SD of three years are shown.



Fig. 6. Number of airborne particles per area collected by each species. Average data and SD of three years are shown. Different letters indicate significant differences (p-value <0.05).

# Table 1 Percentage (%) of different fractions of PM trapped by leaves samples during the three-year monitoring period.

		Tilia cordata	Fraxinus ornus	Celtis australis	Morus alba
%PM <sub>2.5</sub>	$%PM_{>1}$	10.20	9.25	6.89	8.24
	$\text{%PM}_{<1}$	64.67	63.32	62.74	61.02
% PM <sub>10</sub>		20.39	22.14	23.31	24.05
Coarser particles (>10 µm)		4.74	5.29	7.06	6.69

cause irritation of mucous membranes and asthma (Komarnisky et al., 2003) when the exposure is excessive. Fe was found with a high frequency, even if in small amounts, while some heavy metals (Cu, Zn, Ni, Mn, Cr, Co) have been rarely recorded and always in low quantities.

Additional trace elements found in very few samples (<5 %) are zirconium, rhenium, cerium, tin, barium, indium, chlorine, fluorine. These could represent health problems if the exposure is excessive. Considering that the studied area is a residential one, located in the suburbs,



Fig. 7. Chemical composition of PM: atomic mass percentage and relative frequency of each element detected. The columns show the percentage of atomic mass of each element referred to the total, while the lines show the relative frequencies of the elements, during spring and autumn. The average data and SD of three years are shown.

Chemical composition of control areas on leaves: percentage of atomic mass (%) of elements found on leaves of each species in both seasons.	Table 2
	Chemical composition of control areas on leaves: percentage of atomic mass (%) of elements found on leaves of each species in both seasons.

Species	Season	С	0	Na	Mg	Al	Si	Р	К	Ca
C. australis	Spring	64.68	32.75	1.43	0.02	0.01	0,02	0.19	0.62	0.23
	Autumn	60.83	34.33	1.27	0.00	0.00	2.81	0.18	0.35	0.24
F. ornus	Spring	74.94	23.76	0.83	0.00	0.00	0.00	0.11	0.23	0.14
	Autumn	66.22	30.76	1.60	0.00	0.03	0.11	0.48	0.42	0.40
M. alba	Spring	55.54	37.52	1.45	0.00	0.00	4.67	0.25	0.31	0.25
	Autumn	66.89	30.49	1.91	0.00	0.00	0.00	0.19	0.37	0.15
T. cordata	Spring	68.28	30.23	0.98	0.00	0.00	0.00	0.20	0.30	0.00
	Autumn	70.16	27.48	1.46	0.00	0.00	0.44	0.18	0.29	0.00

close to the countryside and far from industrial activities, the rare presence of some potentially toxic element on plants leaves could be easily explained. A recent work describes as different areas have differences in PM sources, and consequently, differences in PM composition and quantity (Moura et al., 2024). These Authors have identified disparities across urban and rural zones: the urban area indeed was distinguished by elevated concentrations of Ba, Fe, and Zn, in contrast to the rural zone, which exhibited the lowest levels of these elements.

PCA analysis results suggest some hypotheses about the possible sources of particulate. In 2019 natural source identified is soil erosion, which provides Al, Si, K and N; a second component represented by C, Zr, Re, Cl and F could be referred to emissions from new building works in particular Zr is used for glass and ceramic. The remaining two components are attributable to vehicular traffic. In details, the presence of Mn, Ti, Mg and O is linked to vehicle exhaust gases, while PM made up of Ni, Cr, Cu, Zn, S, P, Ca, Fe, Ba, S and In can represent dust road, possibly due to two roads near the study area. In 2020, the principal components are attributable to soil erosion (Al, Si, Mg, O, K, Zr, Ti), vehicle exhaust gases (Fe, Mn, Ni, Cr) and road dust (C, Na, Cl, Zn, P, Ba, Ce). Fluorine doesn't relate to any other compounds. The "traffic" component is present in both the seasons, despite the restrictions due to Covid-19 pandemic, because, as said before, there are not suitable conditions for the dispersion of pollutants in that period (Litschike and Kuttler, 2008). Also, the model studied by Li et al. (2023) reported that some trace elements such as Ca, Na, Al, Mg and K represent mainly the contents of the crust elemental species, while the presence of Cu, Mn, Ni, Cr, Pb, Li, and Cd is correlated with the anthropogenic activities.

In 2021, the sources of pollutants seem to be mainly linked to vehicular traffic: one component is represented by exhaust gases (Fe, O, Mg, Cr, Ti, Mn), the second one to brake wear (C, Cu) and the third one to road dust (Ba, S, Ca, P, Na, Zn). Comprehensively, the principal source of pollution in this study seems to be erosion soil, followed by vehicle traffic. Other authors have corroborated these findings. Yang et al. (2023) similarly pinpointed soil dust and combustion as primary sources to total PM, detecting the prevalence of ions containing S, N, Cl, Na, K, and Ca, along with several trace elements such as Si, Al, Fe, Ba, Mn, Cr, Ni, Cu, Zn, and Cd.

During the first two years, these two sources were also joined by the one represented by the building construction activity, which was no longer recorded with the end of the works. As already revealed by Fang et al. (2024) the building construction sites are an alarming source of PM getting worse the air quality of the area, as found during the first two years in the present work.

A

0

D

1

0,75

Si



Fig. 8. Results of PCA analysis on PM data collected in a) 2019, b) 2020 and c) 2021.

2020

С

Variables (axes F1 and F2: 21,13 %)

In CICI

-0.25

0

F1 (12,03 %)

0,25

0,5

b.

1

0,75

0,5

0,25

-0,5

-0,75

-1

-1

В

-0,75 -05

#### 5. Conclusion

The findings from this research may give a significant contribution for comprehending the mechanism with which plants capture PM. The activities of PM monitoring in the experimental urban forest set in the city of Reggio Emilia highlight how Fraxinus ornus and Celtis australis are the most effective species in capturing and retaining PM particles, outstanding Morus alba and Tilia cordata in their PM-trapping capabilities.

The micromorphology of the leaves plays an essential role in determining the ability of each species to capture particulate matter.

Some specific morphological traits may have a role in the ability to retain airborne particulate on leaf surfaces. Therefore, the intercell depression occurring on F. ornus leaf epidermis could be one of the main structural micro-morphological traits involved in PM retention. The presence of hairs confirms to be a morpho-functional trait, able to differently regulate the plants-environment interactions. However, the efficiency in PM trapping seems depend on several features combined with each other. Despite the differences, all four species play an important role in improving urban air quality, largely collecting particulate matter with a diameter equal to or less than 2.5  $\mu$ m, which is most dangerous for people's health. The main sources of PM have been identified as erosion soil and vehicle traffic: among them, some elements could represent human and environmental risk (as Fe, Ni, Cr, Ba, Ce, Mn). However, in this study the concentration and the frequency recorded for these elements were never as high as to rise concern. Plants have demonstrated their effectiveness as a valuable role to face air pollution issues; further studies implementing the experimental design with more plant species could give useful information to develop a strategy to manage public green areas to environmental and human health protection.

#### CRediT authorship contribution statement

Giulia Santunione: Writing – original draft, Investigation, Formal analysis, Data curation. Alice Barbieri: Writing - original draft, Investigation, Formal analysis. Elisabetta Sgarbi: Writing - review & editing, Validation, Supervision, Methodology, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



**Fig. 9.** Scanning Electron Microscopy Images of leaf samples collected in autumn; a) *Celtis australis* (mag = 500x), b) *Celtis australis* (mag = 2000x), c) *Fraxinus ornus* (mag = 500x), d) *Fraxinus ornus* (mag = 2000x), e) *Morus alba* (mag = 500x), f) *Morus alba* (mag = 2000x), g) *Tilia cordata* (mag = 500x) and h) *Tilia cordata* (mag = 2000x). All of images were taken on High Vacuum mode. Only upper epidermis is shown.

#### Data availability

Data will be made available on request.

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