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Detection of morphological and eco-physiological traits of ornamental woody species to assess their potential Net O_3 uptake

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ABSTRACT

Urban greening can improve cities' air quality by filtering the main gaseous pollutants such as tropospheric ozone (O_3). However, the pollutant removal capacity offered by woody species strongly depends on eco-physiological and morphological traits. Woody species with higher stomatal conductance (g_s) can remove more gases from the atmosphere, but other species can worsen air quality due to high O_3 forming potential (OFP), based on their emitting rates of biogenic volatile organic compounds (bVOCs) and Leaf Mass per Area (LMA). Presently, there is a lack of data on eco-physiological (g_s, bVOCs emissions) and foliar traits (LMA) for several ornamental species used in urban greening programs, which does not allow assessment of their O_3 removal capacity and OFP. This study aimed to (i) parameterize g_s, assess bVOCs emissions and LMA of 14 ornamental woody species commonly used in Mediterranean urban greening, and (ii) model their Net O_3 uptake. The g_s Jarvis model was parameterized considering various environmental conditions alongside isoprene and monoterpene foliar bVOCs emission rates trapped in the field and quantified by gas chromatography-mass spectrometry. The results are helpful for urban planning and landscaping; suggesting that *Catalpa bignonioides* and *Gleditsia triacanthos* have excellent O_3 removal capacity due to their high maximum g_s (g_{max}) equal to 0.657 and 0.597 mol H_2O m^{-2} s^{-1}. Regarding bVOCs, high isoprene (16.75 μg g_{dw}^{-1} h^{-1}) and monoterpene (13.12 μg g_{dw}^{-1} h^{-1}) emission rates were found for *Rhamnus alaternus* and *Cornus mas*. In contrast, no bVOCs emissions were detected for *Camellia sasanqua* and *Paulownia tomentosa*. In conclusion, 11 species showed a positive Net O_3 uptake, while the use of large numbers of *R. alaternus*, *C. mas*, and *Chamaerops humilis* for urban afforestation planning are not recommended due to their potential to induce a deterioration of outdoor air quality.

1. Introduction

Ornamental trees and shrubs provide important ecosystem services in urban environments (Francini et al., 2022), and their presence in parks, private gardens, or along the roadside is beneficial for human health and well-being (Wolf et al., 2020). The protection of biodiversity (Alvey, 2006), soil erosion control (Berland et al., 2017), noise reduction (Ow and Ghosh, 2017) and climate mitigation (Wong et al., 2021) are

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other positive effects associated with urban greening although air phytoremediation is among the most crucial and under-investigated effects (Lee et al., 2020).

Global urbanization dramatically increased outdoor air pollution in cities (Sicard et al., 2023). Reducing pollutant concentrations is now a pressing priority (World Health Organization, 2021). For this reason, large-scale tree planting initiatives are taking place around the world. In the United States "Million Trees" planting campaigns were carried out in Los Angeles and New York City, while in Beijing the "One Million-Mu Plain Afforestation Project" led more than 50 million urban trees being planted (Sousa-Silva et al., 2023). Under the European Green Deal, the European Union Biodiversity Strategy aims to plant an additional three billion trees by 2030 (European Commission, 2021) to tackle climate change and overcome urban challenges such as air pollution.

Tropospheric ozone (O_3) is a threat to terrestrial ecosystems and biodiversity (Agathokleous et al., 2020), as well as one of the most harmful air pollutants for human health, as protracted exposure to high concentrations of O_3 causes an increase in respiratory diseases (Chen et al., 2007) and cardiovascular mortality (Manisalidis et al., 2020). Ozone is a secondary pollutant produced in the presence of sunlight, nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbons such as Volatile Organic Compounds (VOCs), emitted mainly in urban areas by anthropogenic activities (Reimann and Lewis, 2007) and from natural vegetation (i.e., biogenic Volatile Organic Compounds - bVOCs). Global bVOCs emissions significantly contribute to O_3 formation (Wedow et al., 2021), as their release in the atmosphere is estimated to be approximately ten times higher than anthropogenic VOCs (Zulkifli et al., 2022). The bVOCs are secondary metabolites naturally produced by several plant species, and are involved in plant responses to biotic and abiotic stresses (Brunetti et al., 2023), including O_3 exposure (Moura et al., 2022a). Isoprene and monoterpenes are the constitutive terpenoid compounds identified in the bVOCs profile of several woody species (Niinemets, 2010; Ghirardo et al., 2016). Interestingly, bVOCs emissions are highly species-specific (Bao et al., 2023), and different profiles of bVOCs are released dependent on environmental factors, i.e., light intensity, air temperature (Hakola et al., 2001; Tarvainen et al., 2005; Saunier et al., 2017), or water availability (Fitzky et al., 2023). Also leaf morphological traits, such as Leaf Mass per Area (LMA), seem to be correlated with bVOCs emissions, with greater LMA values being typically linked with higher isoprene and monoterpenes release (Yuan et al., 2020).

While bVOC emissions alter tropospheric chemistry, contributing to surface O_3 formation (Steiner, 2020), O_3 can also be partially removed by plants, especially by absorption through stomata (Nowak et al., 2014). Stomatal conductance (g_s) is a species-specific trait strongly related to environmental parameters such as air temperature (Urban et al., 2017), photosynthetically active radiation (PAR - Xiong et al., 2018), vapor pressure deficit (VPD - Li et al., 2019) and soil water availability (Anav et al., 2018). Several approaches are used to model g_s, e.g., Ball et al. (1987) or Farquhar and Wong (1984) models, with the multiplicative algorithm developed by Jarvis (1976) used to describe its regulation due to climatic drivers being one of the most adopted (Vitale et al., 2007). Model parameterization of g_s is crucial to accurate estimation of stomatal O_3 uptake (Alonso et al., 2008) for urban trees and shrubs.

Considering the species-specific feature of g_s, bVOCs and LMA, exploring the biological potential of ornamental woody species for O_3 removal is essential for future urban planning and optimal tree selection to maximize air quality improvement. The hypothesis underlying this work is that species-specific key parameters, including g_s model parameterization, bVOCs emissions rate, and LMA, play a crucial role in categorizing ornamental species as either being suitable or unsuitable for planting to remove O_3 in urban environments. These key parameters are still missing for important ornamental tree or shrub species recently introduced or commonly used in urban greenery; the present study aimed to address this knowledge gap. An innovative model to estimate the O_3 stomatal flux as well as the O_3 forming potential at leaf level was developed, and the Net O_3 uptake was assessed for 14 species as a case study in southern Europe (Tuscany, Italy), encompassing nine trees, four shrubs, and one palm tree. The following questions were addressed: (i) Which woody species are better suited for O_3 removal? (ii) Which species contribute to O_3 formation, resulting in a negative O_3 balance? and (iii) Positive correlation occur between LMA and bVOCs emissions?

2. Materials & methods

A list of acronyms for terms used in the study and their explanation is provided in Table 1.

2.1. Study area and data collection

The measurements were performed during the summer season 2021 inside the plant nursery "Mati 1909" located in the Pistoia Nursery District, Tuscany region, central Italy (43°54'N, 10°41'E, 30 m asl). Meteorological parameters such as air temperature (°C), relative humidity (%), wind speed (m s^{-1}), and solar radiation (W m^{-2}) were recorded hourly by a wireless meteorological station (Davis Vantage Pro 2, Davis Instrument, Hayward, USA) positioned close to the study area. Conversely, hourly O_3 concentrations (ppb) were obtained from the Tuscany Region Environmental Protection Agency (ARPAT) for the closest monitoring station located in Montale (Pistoia). The daily trend of meteorological parameters and O_3 concentrations for the experimental period is provided in the supplementary materials (Fig. S1).

2.2. Plant species

All 14 species considered in this study are currently marketed by the main nurseries in central Italy as they are commonly used as ornamentals in urban greening in the Mediterranean region. Stomatal conductance measurements were performed for six deciduous trees (*Catalpa bignonioides* Walter, *Parrotia persica* C.A. Mey, *Gleditsia triacanthos* L., *Lagerstroemia indica* L., *Ostrya carpinifolia* Scop., *Cercis siliquastrum* L.) and one evergreen shrub (*Pyracantha coccinea* M. Roem) (see detail in section 2.3). For the other seven species, g_{max} values were already present in the scientific literature (Table S1).

The bVOCs emissions were assessed for four deciduous trees (*Paulownia tomentosa* Steud., *Quercus palustris* Münchh, *Cornus mas* L., *Parrotia persica* C.A. Mey), three evergreen shrubs (*Escallonia rubra* (Ruiz & Pav.) Pers., *Camellia sasanqua* Thunb., *Rhamnus alaternus* L.) and one

Table 1
List of acronyms used in this study and relative explanation.

Acronyms	Explanation
LMA	Leaf Mass per Area
g_s	Stomatal conductance
g_{max}	Maximum stomatal conductance
bVOCs	Biogenic Volatile Organic Compounds
PAR	Photosintetic Active Radiation
VPD	Vapor Pressure Deficit
f_{VPD}	Function of g_s variation with vapor pressure deficit
f_{light}	Function of g_s variation with photosynthetic active radiation
f_{temp}	Function of g_s variation with temperature
f_{min}	Minimum stomatal conductance
F_{st}	Stomatal O_3 flux
R_b	Boundary layer resistance
R_c	Leaf surface resistance
E_{iso}	Emission rates of isoprene
E_{mono}	Emission rates of monoterpene
R_{iso}	Reactivity factor for isoprene
R_{mono}	Reactivity factor for monoterpene
OFP	Ozone Forming Potential
SGS	Start of the Growing Season
EGS	End of the Growing Season

palm tree (*Chamaerops humilis* L.) (see detail in section 2.4). For the remaining six species, bVOCs emission rates had been previously investigated by other authors (Table S2).

All species investigated were cultivated outdoors in plastic pots on universal potting soil and regularly watered using an automated irrigation system to maintain field capacity and avoid water stress.

2.3. Stomatal conductance parameterization

To parameterize the stomatal conductance (g_s) model for *C. bignonioides*, *P. persica*, *G. triacanthos*, *L. indica*, *O. carpinifolia*, *C. siliquastrum,* and *P. coccinea*, about 300-point measurements for each species were carried out according to various meteorological conditions (air temperature, air humidity, solar radiation) by using a flow-through differential porometer (LI-600, Li-Cor, Lincoln, USA). Three individuals per species were randomly selected, and the measurements were made on three representative fully expanded leaves of each plant. The parameterization allowed application of the following modified multiplicative Jarvis model (Moura et al., 2022b) for stomatal conductance estimation:

$$g_s = g_{max} \bullet f_{light} \bullet \max\{f_{min}, (f_{temp} \bullet f_{VPD})\} \tag{1}$$

where g_{max} and f_{min} are the maximum and minimum stomatal conductance assessed as 95th and 5th percentile of all g_s species-specific measurements. f_{light}, f_{temp}, and f_{VPD} are functions (scaled from 0 to 1) estimated by a boundary line analysis (Alonso et al., 2008; Hoshika et al., 2020), dependent on Photosynthetic Active Radiation (PAR), temperature and vapor pressure deficit (VPD). In detail, the three cited functions were expressed as follows:

$$f_{light} = 1 - \exp(-a \bullet \mathrm{PAR}) \tag{2}$$

$$f_{temp} = \left(\frac{\mathrm{T}-\mathrm{T}_{min}}{\mathrm{T}_{opt}-\mathrm{T}_{min}}\right)\left\{\left(\frac{\mathrm{T}_{max}-\mathrm{T}}{\mathrm{T}_{max}-\mathrm{T}_{opt}}\right)^{\left(\frac{\mathrm{T}_{max}-\mathrm{T}_{opt}}{\mathrm{T}_{opt}-\mathrm{T}_{min}}\right)}\right\} \tag{3}$$

$$f_{VPD} = \min\left[1, \max\left\{f_{min}, \left(\frac{(1-f_{min}) \bullet (\mathrm{VPD}_{min}-\mathrm{VPD})}{(\mathrm{VPD}_{min}-\mathrm{VPD}_{max})}\right) + f_{min}\right\}\right] \tag{4}$$

where a is a parameter defining the shape of the g_s-light exponential response, T_{opt}, T_{min}, and T_{max} are the species-specific optimum, minimum and maximum temperature for g_s, and VPD_{min} and VPD_{max} indicate the threshold of VPD for attaining minimum and maximum stomatal opening. If $\mathrm{VPD} > \mathrm{VPD}_{min}$ then f_{VPD} was set to f_{min} while if $\mathrm{VPD} < \mathrm{VPD}_{max}$ then f_{VPD} was 1.

2.4. Detection of biogenic volatile organic compounds emissions

To carry out the sampling of bVOCs emissions for *P. tomentosa*, *Q. palustris*, *C. mas*, *P. persica*, *E. rubra*, *C. sasanqua*, *R. alaternus,* and *C. humilis*, was applied the approach proposed by Loreto et al. (2001). The measurements were carried out from 9:00 to 12:00 (local time), in standard conditions of PAR equal to 1000 μmol m^{-2} s^{-1}, leaf temperature (30 °C), and CO_2 concentration (410 ppm) by using a portable infrared gas analyzer system (LI-6800, Li-Cor, Lincoln, USA). Each leaf ($n = 3$ per species) was inserted into the instrument chamber (6 cm^2). The bVOCs emissions (isoprene and monoterpenes) were assessed at a steady state of g_s, using an adsorbent trap filled with 200 mg of Tenax positioned at the end of the airflow (6 L sampled at a rate of 200 ml min^{-1}) coming from the LI-6800 cuvette using an external pump (AP Buck pump VSS).

The traps were desorbed using a Markes Unity 1 thermal desorber. The released compounds were then detected by gas chromatography-mass spectrometry (GC-MS) (6850 GC, MSD 5975C, Agilent Technologies, Wilmington, USA), equipped with a 30 m long HP-5ms capillary column (J&W Scientific USA, Agilent Technologies, Palo Alto, CA, USA) with an inner diameter of 0.25 mm with the following oven temperature setting: 3 min at 35 °C; +3 °C min^{-1} up to 50 °C; +5 °C min^{-1} up to 250 °C that was kept for 5 min. The GC–MS was calibrated by sampling different concentrations of bVOCs produced after dilution of the same gas standard with pure nitrogen (S.I.A.D. S.p.A., Italy). The chromatograms obtained were analyzed with Agilent MassHunter Workstation Qualitative Analysis 10.0 (Agilent Technologies, Wilmington, USA).

2.5. Leaf mass per area (LMA)

To assess the species-specific LMA for all the 14 species, 5 leaf-discs of 0.50 cm^2 (∅ 0.8 cm) were obtained by a leaf punch (Fujiwara Scientific Company Co., Ltd., Tokyo, Japan) for each sampled leaf ($n = 5$ leaves × 3 plants). The leaf discs were oven-dried at 70 °C for 72 h and subsequently weighed by an analytical balance (Sartorius, Goettingen, Germany). The species-specific LMA, expressed in g m^{-2}, was calculated as the ratio between the average dry leaf-discs biomass and area.

2.6. Net ozone uptake assessment

The Net O_3 uptake (mmol m^{-2}) was obtained using the following formula (5), which considers O_3 stomatal flux (F_{st}) and the O_3 forming potential (OFP). The period considered for the calculation covered the entire growing season between 15th April (Start of the Growing Season, SGS) and 31st October (End of the Growing Season, EGS).

$$\text{Net } O_3\text{uptake} = \sum_{i=\mathrm{SGS}}^{\mathrm{EGS}} F_{st,i} - \mathrm{OFP}_i \tag{5}$$

In detail, F_{st} (mmol m^{-2}) was calculated as:

$$F_{st} = [O_3] \bullet \left\{\frac{1}{\mathrm{R_b} + \mathrm{R_c}}\right\} \bullet \left\{\frac{g_s}{g_s + g_{ext}}\right\} \tag{6}$$

where $[O_3]$ is the hourly O_3 concentration, $\mathrm{R_b}$ is the boundary layer resistance, and $\mathrm{R_c}$ is the leaf surface resistance ($\mathrm{R_c} = 1/g_s + g_{ext}$). g_s is the stomatal conductance modelled using the Jarvis algorithm, and g_{ext} is the cuticular conductance set to 0.0004 m s^{-1}. $\mathrm{R_b}$ is equal to $1.3 \cdot 150 \cdot (L_d/u)^{0.5}$ where u is the wind speed (m s^{-1}), and L_d is the cross-wind leaf dimension (CLRTAP, 2017).

The OFP (mmol m^{-2}) was calculated according to the modified formula proposed by Benjamin and Winer (1998):

$$\mathrm{OFP} = \mathrm{LMA} \cdot [(\mathrm{E_{iso}R_{iso}}) + (\mathrm{E_{mono}R_{mono}})] \tag{7}$$

where LMA is the Leaf Mass per Area for a target species (g m^{-2}), $\mathrm{E_{iso}}$ and $\mathrm{E_{mono}}$ are species-specific light and temperature-dependent emission rates of isoprene and monoterpene, while $\mathrm{R_{iso}}$ and $\mathrm{R_{mono}}$ are reactivity factors $[(g\ O_3)\ (g\ \mathrm{bVOCs})^{-1}]$ equal to 9.1 for isoprene and 3.8 for monoterpenes (Carter, 1994). $\mathrm{E_{iso}}$ and $\mathrm{E_{mono}}$ were calculated thanks to the following formula proposed by Guenther et al. (1995), Owen et al. (2002), and Staudt and Lhoutellier (2011):

$$\mathrm{E_{iso}} = E_s C_{Ti} C_{Li} \tag{8}$$

$$\mathrm{E_{mono}} = M_{Ts} C_{Tm} C_{Lm} \tag{9}$$

$$C_{Ti} = \frac{\exp\left[95,000\ (\mathrm{T} - \mathrm{T_s})\ (\mathrm{RT_sT})^{-1}\right]}{1 + \exp\left[230,000\ (\mathrm{T} - \mathrm{T_m})\ (\mathrm{RT_sT})^{-1}\right]} \tag{10}$$

$$C_{Tm} = \exp\left(\beta\ (\mathrm{T}-\mathrm{T_s})\right) \tag{11}$$

$$C_{Li} = \frac{1.066\ \alpha_i\ \mathrm{L}}{\sqrt{1 + \alpha_i^2 \mathrm{L}^2}} \tag{12}$$

$$C_{Lm} = \frac{1.086\ \alpha_m\ \mathrm{L}}{\sqrt{1 + \alpha_m^2 \mathrm{L}^2}} \tag{13}$$

where E_s and M_{Ts} are species-specific bVOCs mass emission rates (μg leaf dry weight^{-1} h^{-1}) obtained after direct measurements or from the scientific literature. C_{Ti}, C_{Tm}, C_{Li} and C_{Lm} are constants depending on temperature (T) and light (L), while α_i, α_m and β are empirical coefficient, $T_s = 303$ °K, $T_m = 314$ °K and $R = 8.314$ JK^{-1}mol^{-1}.

2.7. Statistical analysis

One-way ANOVA, followed by a post-hoc Tukey's test was used to assess the significant difference of LMA values among species after checking the normality of the distribution (Kolmogorov-Smirnov test). Pearson linear correlation analysis was used to test whether there was an association between LMA and bVOCs emissions (isoprene, monoterpenes, and total bVOCs). The statistical significance was considered at $p \leq 0.05$. All statistical analyses were conducted with OriginLab software®.

3. Results

3.1. Stomatal conductance parameterization

The highest g_{max} was found in *C. bignonioides*, followed by *G. triacanthos* (Table 2). Similar g_{max} values were estimated for *L. indica* and *C. siliquastrum*, while *P. persica* and *O. carpinifolia* showed the lowest values. Conversely, the constant *a* for f_{light} was higher for these last two species than the other species, suggesting a steeper initial slope of the g_s-light response curve. Regarding the optimal temperature for stomatal opening (T_{opt}), only *P. persica* exceeded the threshold of 30 °C, while the other species settled in a range between 25.0 and 28.1 °C. The lowest T_{opt} was reached by *C. siliquastrum* and *P. coccinea*. The function f_{temp} suggested that all the species closed stomata when $T_{max} \geq 40$ °C and $T_{min} \leq 15$ °C. In detail, *L. indica* and *O. carpinifolia* reached the highest T_{max}, while the lowest T_{min} was found in *P. persica*. The parameterization showed that *P. persica* and *G. triacanthos* can keep stomata open until a VPD of 6.4 kPa, while *C. bignonioides* and *C. siliquastrum* showed stomatal closure with lower values of VPD. In particular, in *C. siliquastrum*, g_s rapidly decreased after VPD > 4.1 kPa. For the other species, published data of g_{max} (Table S1) were used, while for the Jarvis model functions describing the g_s response to environmental factors generic parameters were applied as the average of the values reported in Table 2 (Table S3).

3.2. bVOCs emissions and leaf mass per area (LMA)

No bVOCs emissions for *C. sasanqua* and *P. tomentosa* were detected (Fig. 1). In contrast, *C. humilis*, *P. persica,* and *Q. palustris* showed both isoprene and monoterpenes emissions, while the other species investigated in this study released only isoprene (*R. alaternus*) or monoterpenes compounds (*C. mas* and *E. rubra*). Among the emitter species, the highest values of isoprene and monoterpenes were reached by *R. alaternus* and *C. mas*, respectively. On the other hand, *P. persica* showed the lowest values for both the terpenoid classes, and similar low values for monoterpenes were recorded for *Q. palustris*. The emissions rates of monoterpenes divided into classes of terpenes are listed in the supplementary materials (Table S4) and shown in Fig. 1. In detail, *C. humilis* and *Q. palustris* emitted only α-pinene, and this compound was found in all species except *P. persica*. High emission of β-myrcene, 3-carene, and limonene were detected for *C. mas*. Sabinene, β-pinene, cis-β-ocimene, and trans-β-ocimene were emitted by both *E. rubra* and *P. persica*. For *E. rubra,* the following aromatic compounds were identified: β-myrcene, para-cymene, and limonene. Data of isoprene and monoterpenes emission rates for the other species were available in the scientific literature and are reported in the supplementary material (Table S2).

The palm tree *C. humilis* showed the highest LMA values, while the lowest LMA was recorded for *O. carpinifolia* (Table 3). Evergreen shrubs

Table 2
Summary of species-specific Jarvis-type g_s model parameters. In detail, g_{max} is the maximum stomatal conductance; f_{min} is the minimum stomatal conductance (fraction); f_{temp}, f_{light}, and f_{VPD} are the variation of g_s with temperature (T, °C), photosynthetic active radiation (PAR, μmol m^{-2} s^{-1}) and vapor pressure deficit (VPD, kPa). T_{max}, T_{opt}, and T_{min} are the maximum, optimal, and minimum air temperatures for stomatal opening; *α* determines the shape of the exponential relationship in f_{light}. VPD_{max} and VPD_{min} are the vapor pressure deficit for attaining maximum and minimum stomatal opening.

Parameter		Unit	*Catalpa bignonioides*	*Parrotia persica*	*Gleditsia triacanthos*	*Lagerstroemia indica*	*Ostrya carpinifolia*	*Cercis siliquastrum*	*Pyracantha coccinea*
g_{max}		mol H_2O m^{-2} s^{-1}	0.657	0.174	0.597	0.321	0.167	0.318	0.202
f_{min}		Fraction	0.052	0.151	0.079	0.124	0.108	0.063	0.129
f_{temp}	T_{max}	°C	40.3	40.9	40.3	42.7	42.8	40.0	40.0
	T_{opt}	°C	27.1	30.2	28.0	26.1	28.1	25.0	25.0
	T_{min}	°C	15.0	7.6	15.0	15.0	15.0	10.0	10.0
f_{light}	*α*	constant	0.0076	0.0152	0.0067	0.0044	0.0147	0.0057	0.0065
f_{VPD}	VPD_{max}	kPa	2.7	2.7	2.0	2.0	2.7	4.1	2.0
	VPD_{min}	kPa	4.7	6.4	6.4	5.5	6.3	4.6	6.1

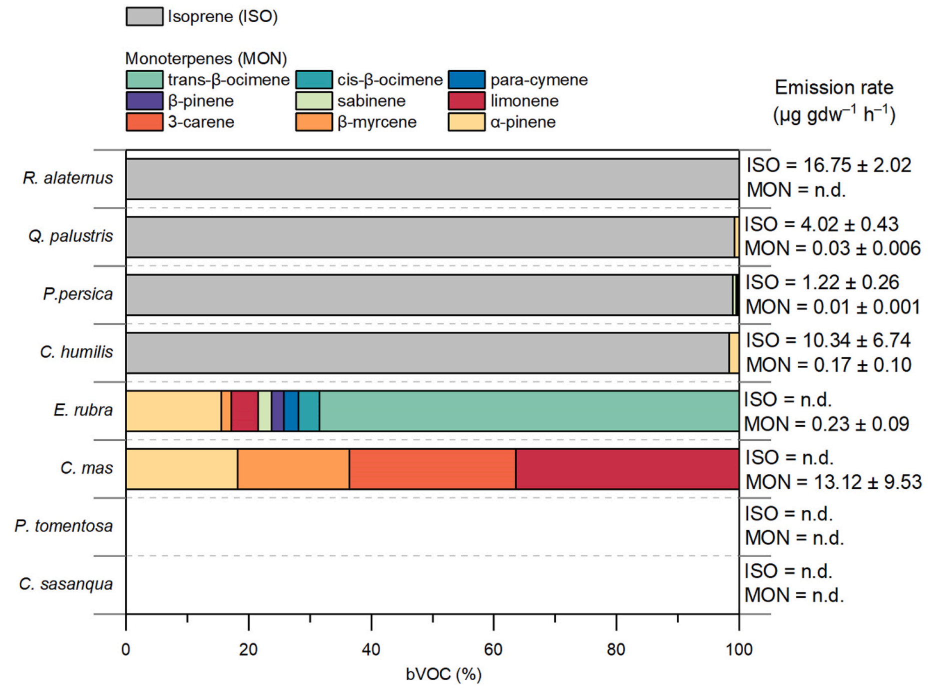

Fig. 1. Percentage of bVOCs compounds and emission rate (average values ± standard error, n = 3) of isoprene and monoterpenes (divided in class of terpenes) for the species investigated. n.d. emissions not detected.

Table 3
Species-specific Leaf Mass per Area (average values ± standard error, n = 3). Different letters indicate statistically different values of LMA according to one-way ANOVA followed by Tukey's test ($p \leq 0.05$).

Species	LMA (g m^{-2})
Parrotia persica	91.56 ± 8.29 bc
Quercus palustris	59.71 ± 6.90 def
Chamaerops humilis	141.99 ± 9.29 a
Cornus mas	82.27 ± 1.33 cd
Escallonia rubra	111.13 ± 9.48 b
Camellia sasanqua	96.87 ± 3.51 bc
Rhamnus alaternus	84.93 ± 3.51 bcd
Paulownia tomentosa	41.14 ± 5.78 fg
Lagerstroemia indica	57.86 ± 2.89 ef
Ostrya carpinifolia	22.77 ± 0.90 g
Catalpa bignonioides	44.90 ± 3.30 f
Cercis siliquastrum	43.19 ± 2.18 fg
Gleditsia triacanthos	66.30 ± 3.23 de
Pyracantha coccinea	90.99 ± 7.10 bc

like *E. rubra*, *C. sasanqua*, *P. coccinea*, and *R. alaternus* had higher values than deciduous species with the exception of *P. persica* and *C. mas*, which showed LMA comparable with *P. coccinea* and *R. alaternus*.

A statistically significant positive correlation (Fig. 2, Table S5) was found both between LMA and isoprene ($p = 0.002$) or total bVOCs emission rates ($p = 0.04$), while monoterpenes were not related with this leaf trait ($p = 0.92$).

3.3. Net O_3 uptake

Eleven species showed a positive O_3 balance (Fig. 3A). The highest values of Net O_3 uptake were reached by *G. triacanthos* (72.90 mmol m^{-2}) and *C. bignonioides* (59.87 mmol m^{-2}) despite an OFP for both species equal to 2.85 and 10.85 mmol m^{-2}. Very similar Net O_3 uptakes were found for *L. indica* (50.04 mmol m^{-2}) and *C. siliquastrum* (49.79 mmol m^{-2}), followed by *P. coccinea* (37.77 mmol m^{-2}). As no bVOCs emissions were detected for *O. carpinifolia*, *C. sasanqua*, *P. tomentosa*, and *L. indica*, their OFP was equal to zero. Conversely, increasing values of OFP were observed for *E. rubra* (2.84 mmol m^{-2}), *P. persica* (24.63 mmol m^{-2}), and *Q. palustris* (52.94 mmol m^{-2}), leading to the lowest, although positive, values of Net O_3 uptake for these species. Curiously, *Q. palustris* showed a high O_3 removal capacity (57.18 mmol m^{-2}), only lower than the values calculated for *G. triacanthos* (75.79 mmol m^{-2}) and *C. bignonioides* (70.72 mmol m^{-2}), but at the same time the highest OFP calculated value (52.94 mmol m^{-2}). In Fig. 3B, species with negative O_3 balance are reported. Among these three species, *C. humilis* had the highest negative OFP (325.75 mmol m^{-2}) and the lowest O_3 removal capacity (22.55 mmol m^{-2}). *Cornus mas* (38.39 mmol m^{-2}) and *R. alaternus* (37.64 mmol m^{-2}) had broadly comparable capabilities to absorb O_3, but contrasting values of OFP: 119.02 and 312.30 mmol m^{-2}.

4. Discussion

At global, regional and national levels, directives (e.g., DM n.183 06/08/2022 of the Italian Ministry of Ecological Transition) suggest the preferential selection of more efficient species in terms of the removal of air pollutants alongside good physiological adaptation to local characteristics. The results obtained in this study expand knowledge of common ornamental species of Mediterranean (*C. humilis*, *R. alaternus* and *C. siliquastrum*), continental (*C. mas*, *O. carpinifolia* and *P. coccinea*), or extra-European origin (*C. bignonioides*, *G. triacanthos*, *L. indica*, *C. sasanqua*, *P. tomentosa*, *P. persica*, *Q. palustris,* and *E. rubra*) that are well adapted and readily available for Mediterranean urban greening. These findings enrich the scientific literature with unexplored species-specific parameters and can provide useful information to support and improve guidelines for urban afforestation to municipalities and policymakers world-wide. Indeed, the measured values allow to apply models specifically developed for tree selection such as FlorTree (Manzini et al., 2023) that identifies suitable species for urban contexts characterized by different climate and pollution conditions (i.e., Florence, Bucharest and Tokyo). Although it is recommended to choose the right tree in term of low bVOCs emission, high emitters should not be fully discarded, but their presence should be reduced to safeguard the fundamental ecophysiological aspect of biodiversity.

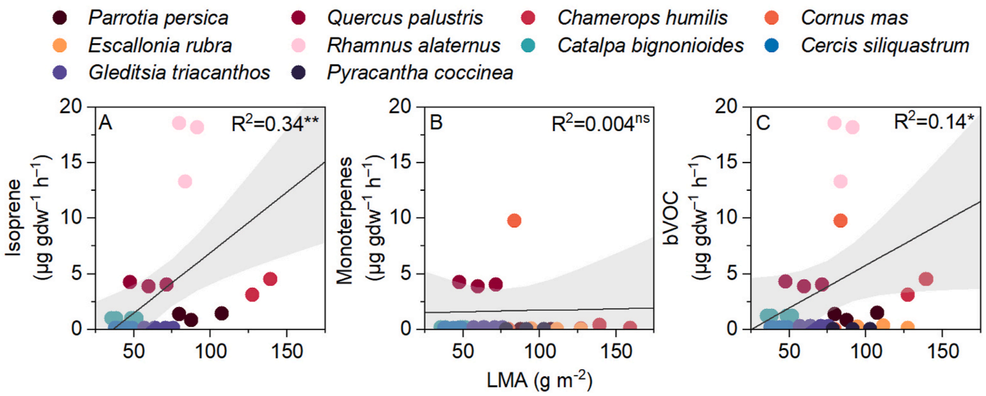

Fig. 2. A) Linear relationship ($p = 0.002$) between species-specific LMA and isoprene (n = 27). B) Linear relationship ($p = 0.92$, ns) between species-specific LMA and monoterpenes (n = 33). C) Linear relationship ($p = 0.04$) between species-specific LMA and total bVOCs emissions (n = 36). The linear regression lines show 95% confidence intervals in grey.

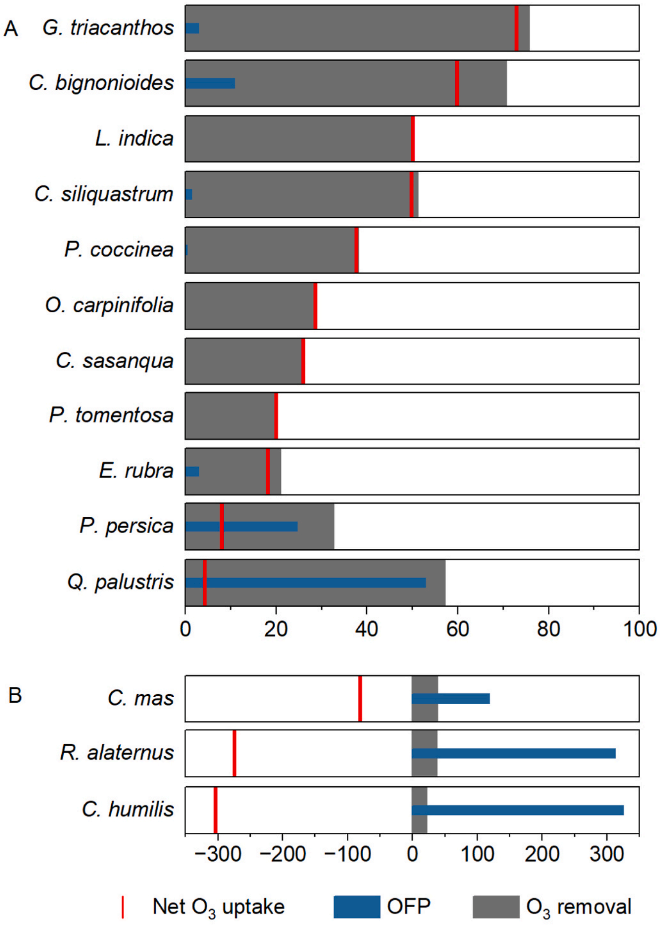

Fig. 3. A) species with a positive Net O_3 uptake. B) species with a negative O_3 balance. Net O_3 uptake was obtained as a subtraction between O_3 removal and O_3 forming potential (OFP).

4.1. Stomatal conductance parametrization and net O_3 uptake

A careful parametrization of g_s is essential to model the stomatal O_3 flux, allowing an understanding of which species have higher performance to absorb this harmful pollutant. In this framework, the key parameter is g_{max} (e.g., Tuovinen et al., 2007), and the species with the highest values (i.e., *C. bignonioides* and *G. triacanthos*) are indicated as excellent candidates for new planting in an urban context where O_3 concentrations exceed the administrative limit. Nevertheless, after prolonged O_3 exposure, both species could develop typical O_3 foliar visible injury and defoliation, impairing their bio-filtering standards. Indeed, Orendovici et al. (2003) reported that *Catalpa speciosa* evolves yellow-brown stipples and necrotic patches, while Cathey and Heggestad (1982) found that *G. triacanthos* responds to O_3 stress, by gradually losing the older leaflets. Despite a lower g_{max}, *C. siliquastrum, L. indica, P. persica,* and *P. coccinea* were effective in terms of O_3 removal. Interestingly, these last three species were also recommended by Ghafari et al. (2020) for urban green spaces through multi-criteria decision-making techniques, including aesthetics, maintenance, and growth features.

In the Jarvis multiplicative algorithm, the response function of g_s to soil water content (f_{swc}) was not considered, as plants were well irrigated till field capacity during the experiment. However, proper irrigation is often missing in urban environments, leading to drought stress and partial or total stomatal closure by plants to avoid water loss and tissue dehydration (Pirasteh-Anosheh et al., 2016). Therefore, the model might overestimate the actual O_3 uptake (De Marco et al., 2016), especially in cities characterized by dry and hot summers where water supply is limited or not provided. It should be also considered that in the future, forecasted extreme summer heat waves can alter the physiological response of woody species in terms of g_s deregulation, such as a paradoxical stomatal opening to prevent leaf overheating (Marchin et al., 2022). For this reason, the g_s variation with temperature (f_{temp}) estimated in this model could be different, changing the expected Net O_3 uptake.

The g_s parametrization highlighted a different inter-specific response to environmental variables, providing indications about the ecology of these species. For instance, parameter a of f_{light} function suggested that *P. persica* and *O. carpinifolia* could be considered shade tolerant species, while *C. bignonioides*, *G. triacanthos*, *L. indica*, *C. siliquastrum,* and *P. coccinea* prefer greater light exposure. Kunert and Hajek (2022) corroborate these findings for *O. carpinifolia*, while Wu et al. (2018) found that *Catalpa bungei* shows the ability to fully utilize relatively high PAR intensity, confirming that the *Catalpa* genus is light-demanding.

To provide a deeper insight about species-specific Net O_3 uptake, further biochemical analyses may be needed to assess whether higher concentrations of foliar antioxidant defenses are able to avoid the formation of Reactive Oxygen Species (ROS). Accumulation of ROS in the apoplast can influence stomatal regulation (Sierla et al., 2016), preventing an efficient O_3 removal which could be different from that modelled in this research.

4.2. Species-specific bVOCs emissions and OFP

The bVOCs mass emission rate and LMA values are generally required to estimate the species-specific OFP as proposed by Benjamin and Winer (1998). Remarkable values of isoprene and monoterpenes observed for *C. humilis*, *C. mas*, and *R. alaternus* implied an OFP far higher than O_3 removal, while *Q. palustris* was able to offset OFP thanks to a high stomatal O_3 uptake. According to Caissard et al. (2004), the Mediterranean dwarf palm *C. humilis* produces volatile compounds at a foliar level to attract its species-specific pollinator, i.e., *Derelomus chamaeropsis*. Results showed that *C. humilis* was a strong isoprene emitter, while few monoterpenes were released. Similar findings were obtained for other palms belonging to Arecaceae family (Baraldi et al., 2005). Bracho-Nuñez et al. (2013) found comparable values for *C. humilis* with an hourly emission rate of 18.93 and 0.14 µg g_{dw}^{-1} of isoprene and monoterpenes, respectively, during a study conducted in the south of France. The high isoprene emission detected for the evergreen shrub *R. alaternus* is inside the range 12–22 µg g_{dw}^{-1} h^{-1} measured by Owen et al. (1998) for *Rhamnus lycoides*. Kesselmeier and Staudt (1999) confirmed that other *Rhamnus* species (i.e., *R. californica* and *R. crocea*) had a strong capacity to release isoprene (29.3 and 54.4 µg g_{dw}^{-1} h^{-1}, respectively) but not monoterpenes. The results of this study did not find isoprene emission from *C. mas* leaves. Similar results were found in another *Cornus* species (i.e., *Cornus florida*), as reported by Mochizuki and Tani (2021) during their measurement campaign in the summer season in Japan. On the other hand, Geron et al. (2000) reported that α-pinene, 3-carene, and limonene composed the majority of monoterpenes compounds emitted in *C. florida*; supporting data collected for *C. mas*, although β-myrcene was not detected as it is probably linked to environmental stressor e.g., high O_3 levels during sampling period (Moura et al., 2022a). Typically, the genus *Quercus* is known to release high amounts of isoprene in the atmosphere (Fitzky et al., 2019), with a significant inter-specific variability (range 0.1–151 µg g_{dw}^{-1} h^{-1}; Kesselmeier and Staudt, 1999). However, some Mediterranean evergreen oaks (i.e, *Q. ilex*, *Q. suber* and *Q. coccifera*) are recognized as monoterpene emitters (Staudt et al., 2004; Karl et al., 2009) or emit neither isoprene nor monoterpenes such as *Q. cerris* (Owen et al., 1997; Calfapietra et al., 2009; Baraldi et al., 2019). The results suggest that *Q. palustris* belongs to the isoprene-emitting oaks, although its detected value was moderate (4.02 µg g_{dw}^{-1} h^{-1}) and close to other North American species, such as *Q. rubra* (4.72 µg g_{dw}^{-1} h^{-1}) (Benjamin and Winer, 1998).

Research carried out by Xiaoshan et al. (2000) found no isoprene emissions for *P. tomentosa*. Likewise, the current study provided more information in terms of respeated analysis of *P. tomentosa* and examination of the potential emission of monoterpene compounds. Baraldi et al. (2019) agreed with our findings of the emission rates of *P. persica*. In contrast, Yuan et al. (2020) and Benjamin et al. (1996) found very low values of bVOCs emissions for two species belonging to the same genera of *C. sasanqua* and *E. rubra,* (i.e., *Camellia japonica* and *Escallonia exoniensis*).

It is interesting to note that bVOCs measurements were performed in standard condition of CO_2 (410 ppm), but rising CO_2 levels in the near future can increase or decrease bVOCs emissions (especially isoprene), as already found for other ornamental species such as *Ginkgo biloba* (Li et al., 2009), *Quercus robur* (Possell et al., 2004) *Eucalyptus globulus*, *Liquidambar styraciflua*, *Populus deltoides* and *Populus tremuloides* (Wilkinson et al., 2009).

Evergreen shrubs (*E. rubra, P. coccinea, C. sasanqua, and R. alaternus*) and the palm tree (*C. humilis*) showed higher LMA than the deciduous woody species due to their coriaceous and thicker leaves. LMA was positively related to isoprene emission, but not with monoterpenes, suggesting that species with high LMA such as *C. humilis* are potential candidates for high OFP. Li et al. (2016) and Feng et al. (2018) proved that this leaf trait is also strongly related to O_3 tolerance, underlining that species with high LMA can dilute O_3 on a larger leaf mass basis. Therefore, evergreen shrubs characterized by great LMA but low bVOCs emissions, such as *E. rubra*, *P. coccinea*, and *C. sasanqua*, could be suitable for planting in areas characterized by high tropospheric O_3 concentrations.

5. Conclusions

The study underscores that Net O_3 uptake is a parameter highly dependent on species-specific characteristics (g_s, LMA and bVOCs emissions), and could be used as a promising "proxy" for tree selection in cities. Among the fourteen species examined, eleven showed a positive Net O_3 uptake, while *C. mas*, *R. alaternus,* and *C. humilis* showed a negative O_3 balance. As an application of these results, woody species with high Net O_3 uptake should have a priority for urban greening, especially in critical areas where O_3 limits are constantly exceeded. In particular, *G. triacanthos* and *C. bignonioides* can be preferred in view of their remarkable capabilities to remove O_3.

A limitation of this study is that Net O_3 uptake can vary in different environments as bVOCs emission rates and stomatal opening depend on meteorological factors (i.e., light, temperature, and relative humidity). The obtained results are therefore only applicable for careful tree selection to enhance air quality and mitigate the impact of O_3 exposure in a Mediterranean climate context. Further research is also needed to better understand whether climatic changes that promote additional plant stress (e.g., heat and drought), can severely affect morphological and eco-physiological leaf traits of ornamental woody species changing their potential Net O_3 uptake.

CRediT authorship contribution statement

Jacopo Manzini: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yasutomo Hoshika:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Pierre Sicard:** Writing – review & editing, Funding acquisition. **Alessandra De Marco:** Writing – review & editing. **Francesco Ferrini:** Writing – review & editing. **Emanuele Pallozzi:** Writing – review & editing, Methodology, Formal analysis. **Luisa Neri:** Writing – review & editing, Formal analysis. **Rita Baraldi:** Writing – review & editing, Formal analysis. **Elena Paoletti:** Writing – review & editing, Supervision, Funding acquisition. **Barbara Baesso Moura:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation, 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.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2024.118844.

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