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Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review

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ABSTRACT

Biogenic Volatile Organic Compounds (BVOC) play a critical role in biosphere–atmosphere interactions and are key factors of the physical and chemical properties of the atmosphere and climate. However, few studies have been carried out at urban level to investigate the interactions between BVOC emissions and ozone (O_3) concentration. The contribution of urban vegetation to the load of BVOCs in the air and the interactions between biogenic emissions and urban pollution, including the likely formation of O_3, needs to be investigated, but also the effects of O_3 on the biochemical reactions and physiological conditions leading to BVOC emissions are largely unknown. The effect of BVOC emission on the O_3 uptake by the trees is further complicating the interactions BVOC–O_3, thus making challenging the estimation of the calculation of BVOC effect on O_3 concentration at urban level.

1. Introduction

Urban forests are living systems integrated in highly anthropic areas, where they establish close interactions with all the other systems around. Among the most important interactions, we focus here on the gas exchange with the atmosphere occurring through stomata, whose action is mainly regulated by water pressure, carbon dioxide concentration and the biochemical activity within the leaves.

The climatic conditions and the specific composition of urban forests, in particular, influence the absorption and emissions of gases by vegetation, both under qualitative and quantitative aspects, ultimately influencing the composition of the atmosphere, and air quality in urban environments. Quality of pollutants absorbed or BVOCs emitted vary depending on species (Steinbrecher et al., 2009) and climatic conditions, such as for instance temperature and pollutants concentration in the atmosphere. Also quantity of pollutants absorbed or BVOCs emitted depends on species and environmental condition. In the case of particulate matter for instance, coniferous species, or in general species with a complex foliar system, have a higher capacity of pollutant uptake as demonstrated in various studies (Beckett et al., 2000; Freer-Smith et al., 2005).

This review illustrates some of the recent findings about how plants can interact with biogenic emissions in urban environments discussing available literature on the topic (Table 1).

In addition to the well-known gases exchanged with the atmosphere (oxygen, carbon dioxide and water vapor), plants, in particular trees, emit a considerable amount of different compounds known as Biogenic Volatile Organic Compounds (BVOCs). Guenther et al. (1995) reported a BVOC emission at planetary level of 1150 Tg C year^{-1}, an estimate roughly confirmed by recent models (Guenther et al., 2012). The importance of BVOC emission into the urban atmosphere is related to their reactivity with some of the compounds released from anthropogenic sources, especially nitrogen oxides (NO_x). Ozone, peroxyacil nitrates, aldehydes and ketones, hydrogen peroxide, secondary organic aerosol and particulate matter can be formed by the photochemically-driven reaction between NO_x and BVOCs (Fehsenfeld et al., 1992; Fuentes et al., 2000, this work, see next heading). Especially in Mediterranean areas, where summer is usually characterized by high temperature and scarce precipitations, BVOC and ozone formation is maximized, and their interactions need more attention.

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Table 1
List of papers dealing with BVOCs and urban/periurban environment (mod: article based on modeling activity; exp: article based on experimental activity).

Reference	Environment	Study area	Type	Remarks
Baumgardner et al., 2012	Periurban	Mexico City	Mod/exp	Comparison UFORE – WRF Chem.
Chang et al., 2012	Urban/periurban/rural	Hangzhou Great Area	Mod	Large areas
Seguel et al., 2012	Urban/periurban	Santiago del Chile	Mod/exp	VOC/NO$_x$ ratio – long term period
Im et al., 2011	Urban	Istanbul	Mod	Models comparison: MM5 – CMAQ
Nichol and Wong 2011	Urban/periurban	Hong Kong	Mod/exp	Remote sensing and field data – Large areas
Simpson and McPherson 2011	Urban/periurban/rural	Sacramento Region	Mod	Predictive model. Regional scale
Zemankova and Brechler 2010	Urban/periurban/rural	Czech Republic	Mod/exp	Remote sensing. Comparison BVOCs/AVOCs
Leung et al., 2010	Urban/periurban	Hong Kong	Mod/exp	Long term period
Davison et al., 2009	Periurban	Rome	Exp	Disjunct Eddy Covariance (DEC)
Fares et al., 2009	Periurban	Rome	Exp	Urban–periurban interactions
Curci et al., 2009	Urban/periurban/rural	Southern Europe	Mod	Focus on large areas
Chang et al., 2009	Urban/periurban	Taiwan	Mod	Large areas
Paoletti, 2009	Urban/periurban/rural	Milan/Florence/Bari	Mod	Ozone pollution – urban to rural gradients
Papiez et al., 2009	Urban/periurban	Las Vegas	Mod/exp	Evidence of low emissions and high impacts
Tsui et al., 2009	Urban/periurban/rural	Hong Kong	Mod/exp	Measurements on 13 local tree species
Wang et al., 2008	Urban/periurban	Eastern China	Mod	Effects on ozone formation
Niinemets and Peñuelas 2008	Urban	/	Review	Urban trees in global change scenarios
Michelozzi et al., 2008	Periurban	Florence	Exp	Terpene measurements on *P. halepensis*
Noe et al., 2008	Urban	Barcelona	Exp	Focus on 11 ornamental tree species
Filella and Peñuelas 2006	Periurban	Barcelona	Exp	Relationship between VOCs/NO$_x$/O3
Gulden and Yang 2006	Urban/periurban/rural	Texas	Mod/exp	Regional scale
Geron et al., 2006	Periurban	Yunnan Province	Exp	Measurements on 95 local species
Donovan et al., 2005	Urban/periurban	Birmingham	Mod	30 trees species considered
Yang et al., 2005	Urban	Beijing	Mod	UFORE model application
Owen et al., 2003	Metropolitan area	West Midlands	Mod	BVOCs/AVOCs comparison
Wang et al., 2003	Urban	Beijing	Mod/exp	BVOCs inventory
Zhihui, 2003	Urban	Beijing	Mod/exp	Inventory from 39 vegetation types
Nowak et al., 2000	Urban/periurban/rural	Washington DC	Mod	Effects on ozone concentration
Steinbrecher et al., 2000	Periurban	Frankfurt	Exp	Flux – gradient relationship
Diem 2000	Urban/periurban	Tucson	Mod	Weekend ozone peaks
Yassaa et al., 2000	Urban	Algiers	Exp	E. globulus, C. atlantica, P. halepensis
Benjamin and Winer 1998	Urban/periurban/rural	Southern California	Mod/exp	Focus on OFP of urban trees and shrubs
Benjamin et al., 1996	Urban/periurban/rural	Southern California	Mod	BVOCs emissions rates based on taxonomy
Corchnoy et al., 1992	Urban	Los Angeles	Exp	Emission rates on 11 potential shade trees
Chameides et al., 1988	Urban	Atlanta	Mod	Urban photochemical smog formation

Anthropogenic volatile organic compounds known as AVOC can also be produced in urban areas. The AVOC emission sources can be grouped in four categories: transport, solvent use, production and storage processes and combustion processes. Chemically, AVOC are mostly aliphatic and aromatic hydrocarbons, and in lower quantity alcohols, especially isopropanol, alkenes, esters, glycol derivates, aldehydes and ketones, with alkynes and halogenated hydrocarbons also contributing occasionally to the emission (Theloke and Friedrich, 2007).

Since BVOC emission is species-specific, the contribution to the photochemical reactivity in urban environment is very much related to plant biodiversity in urban forests. Most of BVOCs emitted by plants belong to the chemical class of isoprenoids or terpenes. The main volatile isoprenoids are *isoprene*, (2-methyl-1,3-butadiene, (C_5H_8)), the simplest and most volatile isoprenoid, and the backbone molecule of all isoprenoids; *monoterpenes*, *sesquiterpenes*, and *homoterpenes*, widespread constituent of flowers fragrances and for this reason quite relevant in urban parks and gardens (Boland and Gabler, 1989). Isoprene is the most abundant compound emitted by plants; its annual emission is about half of the total BVOC emissions, and is comparable to the total emission of methane from all sources (Guenther et al., 2006; Sharkey et al., 2008).

Steinbrecher et al. (2009) listed 115 trees species highly diffused in Europe with its volatile compound basal emission. From this and other general inventories (e.g. http://www.es.lancs.ac.uk/cnhgroup/download.html; http://bai.acd.ucar.edu/Data/BVOC/index.shtml) a few general observations can be made. For example, widespread broadleaved species used in urban environment such as *Populus* and *Salix* genera emit mostly isoprene, while conifers such as *Pinus* spp. generally emit a range of monoterpenes. However, this broad generalization has several exceptions. For example, *Abies* spp. emit both isoprene and monoterpenes despite being a conifer. Among the broadleaved oaks, there are species such as *Q. pubescens* or *Q. robur* which are strong isoprene emitters, others such as *Q. ilex* or *Q. suber* which are strong monoterpene emitters, and others such as *Q. cerris* which is considered a non emitter of BVOCs (Loreto et al., 1998, with *Q. suber* emission revised by Loreto et al., 2009). As showed later on this paper, the choice of an emitting or non-emitting species could be important in determining the air quality in an urban area. Adding BVOCs to the urban atmosphere can change the ratio between VOC and NO$_x$ triggering photochemical reactions, thus ozone formation.

The environment also has an important role in eliciting emission of constitutive or induced BVOCs. High temperature, oxidative stress conditions and herbivory or pathogens attacks are some of the factors which are known to stimulate BVOC emissions, especially isoprenoids (Loreto and Schnitzler, 2010). Trees of urban environments can be particularly subjected to stresses as those listed above, alone, or in combination. Emission of volatile isoprenoids is a metabolic cost for plants, but benefits may outweigh the cost, especially under high temperatures and oxidative stresses (Fineschi and Loreto, 2012). Benefits include improved thermotolerance and higher antioxidant capacity (Loreto and Schnitzler, 2010).

Isoprenoid protection against heat stress may be important in urban environments for several reasons. Large urbanized areas are usually subjected to the "Urban Heat Island" (UHI) effect (Giridharan et al., 2004; Kleerekoper et al., 2012). Moreover, heat flecks are frequently recorded during the central hours of the day in urban environments, mainly because of the heat capacity of man-made infrastructures. Under solar radiation, asphalt, concrete and buildings can reach temperatures between 50° and 60 °C (Takebayashi and Moriyama, 2009). Thus urban trees must withstand higher temperature stress than trees of rural areas, and isoprenoid emission may be a key feature for improved resistance and adaptation to the urban environments. Moreover, as isoprenoid emission strongly depends on temperature (Guenther et al., 1995), a significant increase of the emission due to the UHI effect is expected.

Episodes of high ozone also characterize the urban environments. As for the thermal stress, isoprenoids can again help plants successfully cope with high oxidative properties of the atmosphere, and isoprenoid emission may be stimulated by high ozone levels (Loreto et al., 2004; Calfapietra et al., 2009). Indeed observations that isoprenoid emission reduces ozone damage have been often made over the last decade (Loreto et al., 2001; Loreto and Velikova, 2001; Loreto et al., 2004; Fares et al., 2006; Vickers et al., 2009a,b), although the mechanisms by which such a protection is achieved are still under discussion (Vickers et al., 2009b).

It should also be observed that UHI and oxidative stresses may combine and may also be associated to other stresses exacerbated by the urban environment. Most notably, plants of the urban environment undergo episodes of summer droughts that are also known to transiently stimulate isoprenoid emission in plants recovering from stress (Sharkey and Loreto, 1990). Isoprenoid emission is maintained even when the stress severity totally inhibits photosynthesis, which makes the carbon budget of plants negative (Fortunati et al., 2008).

As Holopainen and Gershenzon (2010) showed, it is important to focus on tree responses in field conditions, where multiple stress factors occur simultaneously. In this view the urban environment can represent an “open-lab” to study possible effects of global change on BVOC emission under the assumption that urban environments may reproduce future atmospheric composition and microclimate conditions. If we accept a future global scenario of climate change, a likely perspective in environmental changes will include an increase in temperature, higher concentration of carbon dioxides and longer drought periods. Urban areas, due to atmospheric pollution derived from human activity and the heat island effect, can simulate future natural scenarios under climate change.

Whereas isoprenoid emissions help plants coping with stresses exacerbated in urban environments, the same compounds may catalyze photochemical cycles that make worse air pollution in urban areas, as shown in the next section.

2. BVOCs and ozone formation in urban environment

Ozone (O_3) is transported by eddy fluxes from the stratosphere to the troposphere, but it is also formed by photochemical reactions in the troposphere due to interactions between both anthropogenic and Biogenic Volatile Organic Compounds (collectively called hereafter VOCs) and NO_x, in the presence of sunlight (Roelofs and Lelieveld, 1997; Fuentes and Wang, 1999). Isoprenoids, in particular, play an important role in the photochemistry of the troposphere, also contributing to the formation of other secondary pollutants (Fehsenfeld et al., 1992; Fuentes and Wang, 1999). If no VOCs are present in the air, the levels of O_3 are determined by the so called photostationary state of NO_x ($NO + NO_2$). Ozone photolysis generates small amounts of OH radicals. The first effect of adding VOCs to the system is their rapid oxidation to peroxy radicals, and NO is converted to NO_2. Other products of this reaction are hydroperoxy radicals and carbonyl compounds, such as aldehydes and ketones.

The amount of O_3 produced strongly depends on the ratio between VOCs and NO_x, and also on the VOCs composition. Isoprene and monoterpenes have a different O_3 forming potential (OFP), which can be defined as the grams of O_3 produced per gram of VOC molecule. The ratio between VOCs and NO_x may determine: a VOC-limited zone ($VOC/NO_x < 4$); an optimum O_3 production zone ($15 > VOC/NO_x > 4$); and a NO_x-limited zone ($VOC/NO_x > 15$). The VOC-limited conditions, in which O_3 production is limited by a high concentration of NO_x, are often observed in urban areas (Fig. 1). On the other hand, NO_x-limited conditions, in which O_3 production is limited by low concentration of NO_x, commonly occur in rural areas. The optimum conditions for ozone production are found in transition zones, such as peri-urban areas. The VOC/NO_x ratio explains why the highest O_3 concentrations are often found outside the urban areas (Derwent, 1996; Finlayson and Pitts, 1999). However, if high BVOC emitters are common in urban areas, VOC/NO_x ratios optimal for O_3 production may be also reached in the city centers (Fig. 1). Such a condition may be typical in Mediterranean environments. Fig. 2 shows BVOC emissions by some of the most common tree species of the urban forest of Rome showing how different could be the BVOC load depending on the tree species chosen. *Quercus ilex* and *Pinus pinea* are heavy monoterpenes emitters while *Platanus hybrida* is a medium isoprene emitter. As evidenced by Fig. 2 BVOC emission is highly dominating during summer also for evergreen species such as *Q. ilex* and *P. pinea*, thus potentially creating optimal conditions for episodes of O_3 production during summer heat waves and in absence of transport of air masses by ventilation.

Landscape planning of urban areas should take into account the potential for BVOC emissions when considering how to reduce emission of O_3 precursors, and to mitigate urban air pollution, especially when planning large scale tree planting programs.

Benjamin and Winer (1998) estimated the ozone forming potential (OFP) of urban trees and shrubs as: $OFP_{species} = B[(E_{iso}R_{iso}) + (E_{mono}R_{mono})]$, where B is the biomass factor [(g leaf dry weight m^{-2} ground area)], E_{iso} and E_{mono} are species-specific mass emission rates [(μg VOC) g^{-1} leaf dry weight day^{-1}] for isoprene and monoterpenes respectively, R_{iso} and R_{mono} are reactivity factors [g O_3 g^{-1} VOC].

Isoprene, when compared with other BVOCs, forms a higher quantity of reactive oxygen compounds, so potentially rising O_3 levels. A reactivity factor of 9.1 g O_3 g^{-1} VOC to isoprene-emitting species has been assigned, while for α-pinene, the most commonly emitted monoterpene, the assigned reactivity factor was 3.3 g O_3 g^{-1} VOC (Carter, 1994). Note, however, that for monoterpene emitters this estimation was characterized by greater uncertainties, principally because isoprene is emitted only during days while monoterpenes are emitted also during nights (Laffineur et al., 2011). Even in the case of isoprene, however, one isoprene emission factor is not sufficient to characterize all isoprene emitters. Emission factor may change among and within plant species, and also due to weather, plant physiology and ontogeny (Geron et al., 2000; Wiberley et al., 2005; Guenther et al., 2012). As a case study, Fig. 3 shows the OFP values for different species among the ones chosen for the MillionTreesNYC planting campaign. *Koelreuteria paniculata* has been planted in great number even though it is characterized by a high OFP, while *Zelkova serrata* does not emit BVOCs. This figure shows the large differences in OFP among tree species normally used in urban environment and evidences also the poor attention to this topic often reserved in large planting campaigns.

Chang et al. (2012) calculated the contribution of several tree species to the total BVOC emissions within the Greater Hangzhou Area, China, suggesting to control BVOCs emission by planting low emitting species and restoring broad-leaved forest in peri-urban and rural areas. The Tree BVOC index (TBI), developed by Simpson and McPherson (2011), is a dimensionless ratio that provides an estimation of projected and actual emission reduction from a proposed planting to that of a target, thus yielding the emission reduction. This approach helps users to select the best

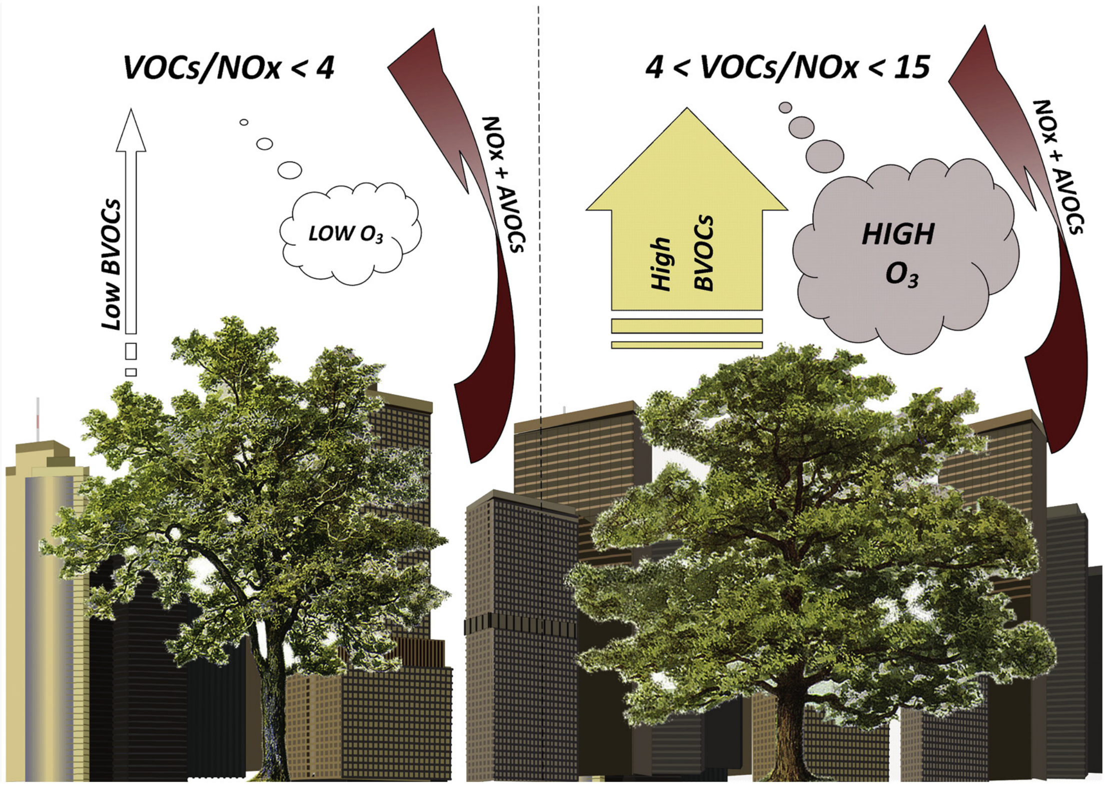

Fig. 1. Effect of BVOC emission by urban trees on O_3 formation. As in several cities and conditions VOC/NO_x ratio is <4, thus O_3 formation is VOC-limited, the use of low BVOC emitter could help to keep this ratio low and thus also O_3 at low levels (left panel). On the other hand the use of high BVOC emitters could move the VOC/NO_x ratio toward optimal values for O_3 formation, thus favoring high O_3 levels. This is an exemplification provided that NO_x and AVOC emissions remain constant.

species to match local site condition as long as a TBI of 1 or less is reached. Another tool to estimate emission from urban trees and shrubs is UFORE-B (Urban Forest Effects model, module B). UFORE-B estimates hourly isoprene, monoterpenes and other BVOC emissions by an existing urban forest, based on species leaf biomass calculations, hourly weather data, basal BVOC emission factors, and emission temperature and light correction factors (Guenther et al., 1994; Nowak et al., 2008).

Chaparro and Terradas (2009) applied UFORE model to Barcelona Urban Ecosystem. The study shows the effects of urban forest on atmosphere investigating both the aspect of pollutants removal and the potential ozone production linked to BVOCs emission on an annual scale. It is reported that the total amount of BVOCs emitted in one year corresponds to about 184 tons. They calculated that BVOCs emission per square meter of plant cover for each land use is higher in the class Institutional (land use class defined by authors as “Hospital, cemetery, education center or port area”) followed by Natural forest and Residential (8.3 and 8.1 g m^{-2}, respectively), Intensively used area without buildings (7.1 g m^{-2}), Urban forest (6.9 g m^{-2}), Transport (6.7 g m^{-2}) and, finally, Industrial (6 g m^{-2}) and Multifamily residential (5 g m^{-2}).

Further on the same study the potential O_3 formation is calculated by land use, for a total amount of about 305 tons of ozone produced. The Net O_3 produced is calculated from the difference between potential O_3 formed and the O_3 absorbed by plants. If we relate the Net O_3 produced with the BVOCs emitted it emerges that there is not a direct correlation among the land use classes.

As evidenced in the Table 2 the classes with a higher ratio between Net O_3 produced and BVOCs (O_3/BVOC) emitted are the Commercial, Urbanized areas and Transport. On the same table the relative abundances of tree species for each land use, expressed in terms of number of trees, are reported (Table 2). The ratio O_3/BVOCs is a good indicator of major potential risk of O_3 pollution. In the case of Commercial/Industrial class high levels of O_3 can be explained by the lower O_3 absorption, caused by lower percentage of tree cover, but in the case of Intensive Used Areas and Transport class, high O_3 levels are probably caused by high levels of NO_x. This hypothesis can be confirmed by pollution level concentration reported by the local agency of pollution control (Generalitat de Catalunya Departamento de Medio Ambiente – www.gencat.net).

Urban Forest structure reported by Chaparro and Terradas (2009) explains the high BVOCs levels in Barcelona: among the six most important species for leaf area extension three are medium and strong BVOCs emitters. The Table 3 shows the results from Barcelona linked with the BVOCs emission by species as reported by Steinbrecher et al. (2009).

Simulations of O_3 formation at regional scale were performed considering NO_x, AVOCs, and BVOCs emissions in California (Steiner et al., 2006). NO_x and AVOC emissions characterized mostly the urban areas, while BVOC emissions characterized the green areas around the cities. Highest O_3 concentrations were recorded downwind the city areas, confirming the indications given above in this report. In Santiago, Chile, higher ratios of VOC/NO_x were observed during weekends due to lower emission of NO_x from traffic, again resulting in higher O_3 concentration during weekends (Seguel et al., 2012). Kleinman et al. (2002), related O_3 production rates to hydrocarbon reactivity in five US cities. Among the five cities, in Houston it was estimated an O_3 production two to five times higher than in the other cities due to high anthropogenic emissions, with comparable NO_x levels. The high VOCs concentration in Houston influenced the VOC/NO_x ratio determining the optimum condition for O_3 formation.

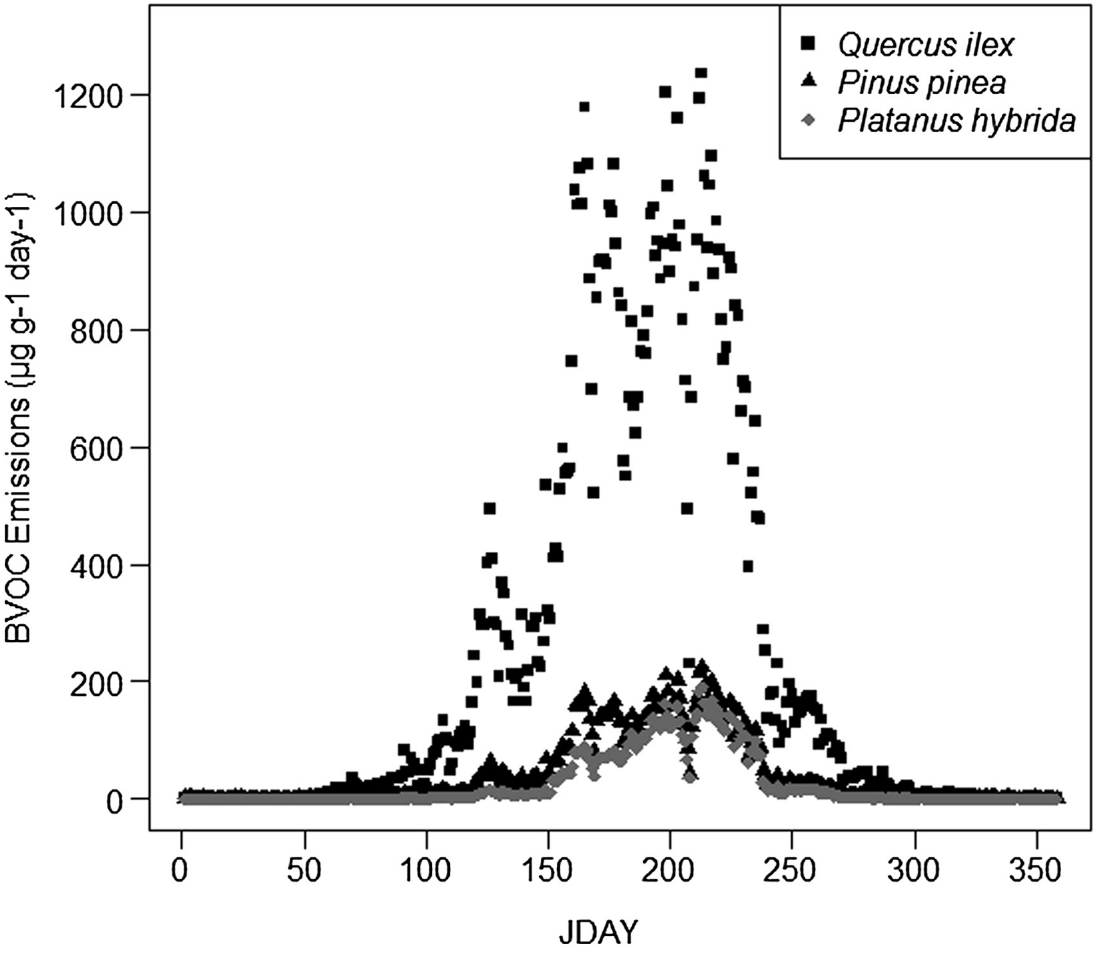

Fig. 2. BVOC emission rates from three plant typologies (evergreen broadleaves, evergreen conifers, deciduous broadleaves) in the urban forestry of Rome throughout one year. *Quercus ilex* (squares, monoterpene emitter), *Pinus pinea* (triangles, monoterpene emitter), *Platanus hybrida* (diamonds, isoprene emitter). The estimations were carried out for the year 2003 within the FP7 Hereplus project (http://www.hereplusproject.eu/).

Even though the examples showed above evidenced negative effects of BVOCs emitter species, caution should be used in selecting low BVOC-emitting species. BVOC emission is used by plants as a protection against stressful agents, so the selection of low – emitters for an urban environment could be disadvantageous. Low BVOCs emission can decrease tolerance of urban trees to oxidative stresses generated in urban environment such as high temperatures, drought and presence of oxidative compounds. The consequences of a stressful situation for urban trees is evidenced in lower growth rates, thus in reduced ecological services, as for instance the mitigation of the urban heat island effect and the absorption of air, soil and water pollutants.

3. Role of BVOCs in ozone removal: from inside the leaves to within-canopy spaces

We have described that BVOCs can increase O_3 formation in the atmosphere and at the meantime increase plant resistance against this pollutant. A third role of these compounds may be related to O_3 removal within canopies, through stomatal and non stomatal processes.

3.1. Ozone removal via stomata

The scientific community focused its attention on stomatal flux of ozone that has been demonstrated more relevant to leaf physiology than ozone exposure (Matyssek et al., 2007; UNECE, 2011). Recent experiments and reviews evidenced that the uptake of O_3 inside mesophyll causes wall cells oxidation, damage to photosynthetic apparatus with detrimental effects on growth rate, biomass production and accelerates leaf senescence (Fares et al., 2006; Ashmore, 2005; Wittig et al., 2009). Stomatal conductance to O_3 regulates the O_3 flux through stomata, and represents the inverse of the sum of an array of resistances that O_3 meets along the path from outside the leaf to the reaction sites inside the apoplast (Fares et al., 2008). Ozone moves inside leaves according to the Fick's law, following the condition that a concentration gradient exists between the air spaces outside the leaves and the intercellular spaces inside the leaves. This gradient is kept high because O_3 is thought to disappear after entering leaves due to reactions with cell walls but also to reaction with antioxidants (Laisk et al., 1989). More recent findings highlighted that during episodes of high tropospheric O_3 (>60 ppb) a non-linear relationship between stomatal conductance and stomatal O_3 flux exists, suggesting that O_3 can accumulate inside the intercellular spaces (Loreto and Fares, 2007; Fares et al., 2010a; Moldau and Bikele, 2002). When gaseous O_3 enters stomata, it rapidly generates reactive oxygen species (ROS: O_2^-, H_2O_2, OH) which plant tries to detoxify through catabolic processes driven by plants as a response to the abiotic stress (Dizengremel et al., 2012). There is a growing evidence that O_3 stomatal uptake may also take place at night (Mereu et al., 2009; Grulke et al., 2004) and that the night-time uptake may be more

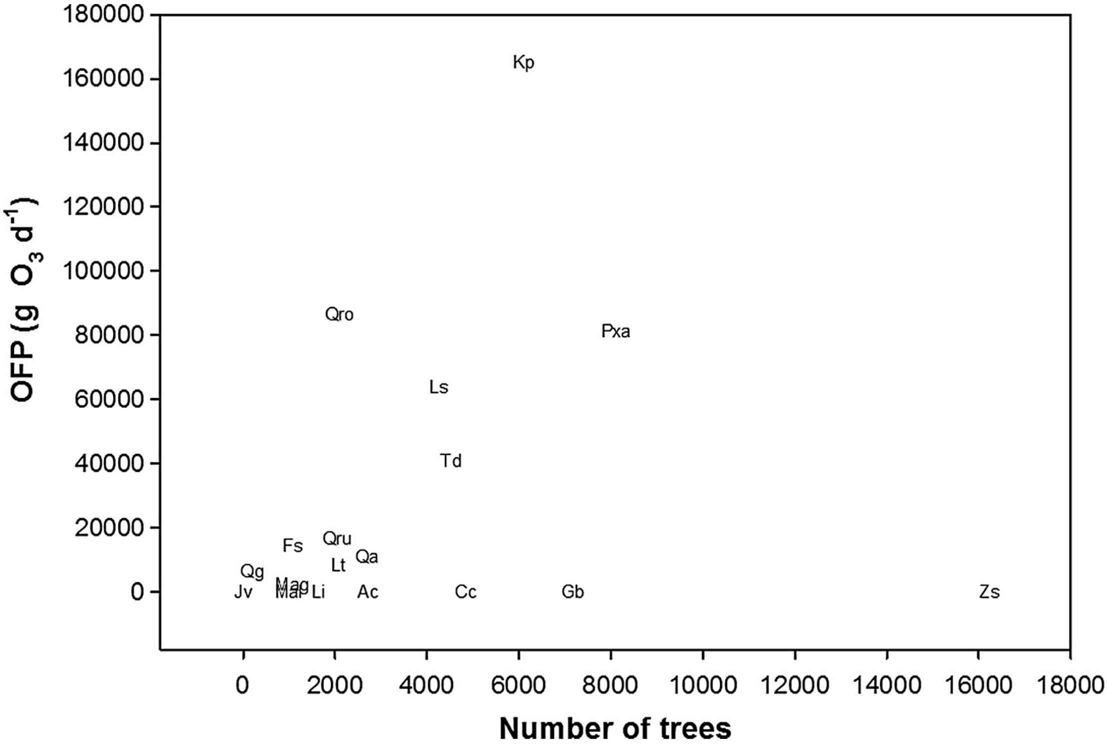

Fig. 3. Relationship between number of trees planted by the NYRP (New York Restoration Project) in the public parks and the Ozone Forming Potential (OFP) for those trees within the OneMillionTrees initiative in New York City. The OFP calculation is based on Benjamin and Winer (1998). *Ac, Amelanchier canadensis*; *Cc, Cercis canadensis*; *Fs, Fagus sylvatica*; *Gb, Ginkgo biloba*; *Jv, Juniperus virginiana*; *Kp, Koelreuteria paniculat;, Li, Lagerstroemia indica*; *Ls, Liquidambar styraciflua*; *Lt, Liriodendron tulipifera*; *Mag, Magnolia spp*; *Mal, Malus spp*; *Pxa, Platanus x acerifolia*; *Pc, Pyrus calleryana*; *Qa, Quercus alba*; *Qg, Quercus garryana*; *Qro, Quercus robur*; *Qru, Quercus rubra*; *Td, Taxodium distichum*; *Zs, Zelkova serrata.*

damaging than diurnal uptake. This is because the antioxidant function of enzymatic and non-enzymatic compounds, including BVOCs, is not active. The antioxidant role of isoprenoids was clearly demonstrated as explained above, and elegantly summarized by Vickers et al. (2009b).

Recently, the reaction products between isoprene and reactive oxygen species (ROS) were detected through pyruvate-2-13C leaf and branch feeding (Jardine et al., 2012). The authors observed a temperature-dependent emission of the labeled products of isoprene oxidation (methyl-vynil chetone and metachrolein), which increased at increasing abiotic oxidative stresses in leaves, thus convincingly suggesting that isoprene oxidation occurs within leaves.

These results also pointed out that carbon investment in isoprene production may be larger than inferred from emissions alone, and suggested that models of biogenic emissions and tropospheric chemistry should incorporate isoprene oxidation for better understanding of the oxidizing sources and sinks in the troposphere. As isoprene is not the only isoprenoid produced in leaves, the capacity to quench oxidizing species by other volatile isoprenoids (e.g. monoterpenes and sesquiterpenes), which are several orders of magnitude more reactive than isoprene with O_3 (Atkinson, 1997; Shu and Atkinson, 1994) deserves to be studied more in detail.

3.2. *Within canopy O_3 removal: chemical reactions between O_3 and BVOC*

Ozone stomatal uptake has been identified as the major contributor to total O_3 flux both at leaf and whole plant level (Fredericksen et al., 1996; Fares et al., 2008, 2010a). Moreover urban trees are exposed to drought stresses caused by soil impermeabilization and constraints to root apparatus. This has a direct effect on plant physiology, mainly through a compromised stomata activity.

Within tree canopy additional non-stomatal O_3 deposition processes take place, and under drought conditions may represent the majority of O_3 sink. These non-stomatal sink include deposition

Table 2
O_3/BVOC ratio in different areas of Barcelona urban area and contribution to this ratio related to the number of trees for the most relevant tree species in terms of leaf area (readapted from Chaparro and Terradas, 2009).

Land use	BVOCs (t)	Net O_3 (t)	Net O_3/BVOCs	Trees number	*P.x acerifolia*	*P. halepensis*	*Q. ilex*	*P. pinea*	*C. australis*	*R. pseudoacacia*
Urban forest	31.4	54.3	1.73	212,437	14,020	43,549	46,948	10,409	4673	3823
Natural forest	87.3	126.1	1.44	799,452	52,763	163,887	176,678	39,173	17,587	14,390
Residential	14.8	28.4	1.92	86,809	5729	17,795	19,184	4253	1909	1562
Multifamily residential	28.2	50.7	1.80	223,404	14,744	44,680	49,372	10,946	4914	4021
Transport	6.0	12.9	2.14	28,214	1862	5783	6235	1382	620	507
Institutional	4.8	4.7	0.99	14,381	949	2948	3178	704	316	258
Commercial/industrial	1.3	3.4	2.62	5856	386	1200	1294	286	128	105
Intensive used areas without building	10.2	23.0	2.34	49,370	3258	10,120	10,910	4838	1086	888
Whole city	183.9	304.5	1.87	1,419,923	93,711	289,962	313,799	71,991	31,233	25,554

Table 3
Most relevant tree species (in terms of leaf area) in Barcelona urban area and their BVOC standard emission rate (in µg g^{-1} h^{-1}); (readapted from Chaparro and Terradas, 2009 and from Steinbrecher et al., 2009).

	Number of trees (%)	Leaf area (Km^2)	Isoprene	Monoterpenes	Other VOCs
Platanus x acerifolia	6.6	20.3	18.5	/	2.2
Pinus halepensis	20.5	15.6	/	/	4.8
Quercus ilex	22.1	10	0.1	43	4.9
Pinus pinea	4.9	5.8	/	3	4.9
Celtis australis	2.2	5	0.1	/	
Robinia pseudoacacia	1.8	2.3	12	/	2.2

to soils, stems, cuticles, and, in general, any external surface. On wet surfaces, considerable amounts of O_3 can react with a multitude of waxes, salts, ions, and many other dissolved compounds (Altimir et al., 2006). Surface adsorption is therefore important, although focus of this section will be a key non-stomatal O_3 sink represented by gas-phase chemical losses involving reactions between O_3 and BVOCs. As explained above, monoterpenes and in particular sesquiterpenes, are the isoprenoids most reactive with O_3, being the reaction time even close to few seconds, e.g. in the case of β-caryophyllene, a sesquiterpene typically emitted by stressed plants (Shu and Atkinson, 1994).

Gas-phase reaction with O_3 were shown to be the major non-stomatal sink in heavy isoprenoid-emitting plant species, namely: in a *Pinus ponderosa* ecosystem (Kurpius and Goldstein, 2003; Fares et al., 2010b), in a sitka spruce ecosystem (Coe et al., 1995), in a Mediterranean oak forest (Gerosa et al., 2005), in a northern mixed hardwood forest (Hogg et al., 2007), in a sub-alpine ecosystem (Zeller and Nikolov, 2000), and in a Citrus plantation (Fares et al., 2012a). Some of these ecosystems can be associated to periurban ecosystems due to the vicinity to urban areas as in the case of the *Pinus ponderosa* forest, the Mediterranean Oak forest, and the Citrus crop. On these plant ecosystems, non-stomatal O_3 deposition ranged between 30 and 70% of the total O_3 deposition. In most of these studies, the non-stomatal sink was calculated as a residual component obtained after subtracting to total O_3 flux measured with micrometeorological techniques the other sinks represented by stomatal flux (calculated from stomatal conductance derived from inversion of Monteith equation or using traditional models based on Jarvis or Ball-Berry type approaches), cuticles, in-canopy aerodynamic resistances, and ground resistances modeled using atmospheric deposition models.

A better understanding of emission dynamics of BVOCs from urban plants may help to promote direct calculation of gas-phase reactions after taking into account for emission rates and reaction constants with O_3. Long-term emission studies are needed to fully characterize the seasonality of BVOC emission, which cannot be explained using conventional emission algorithms, and was shown to change during the year (Fares et al., 2012b; Keenan et al., 2009; Holzinger et al., 2006). The development of new technologies like PTR-TOF-MS (Proton Transfer Reaction Time-Of-Flight Mass Spectrometer), that allows fast and simultaneous measurement of a multitude of reaction products between O_3 and BVOC (e.g. methylvynil ketone, metachrolein, nopinone) thus providing indication on reaction kinetics between BVOC and O_3, will surely assist with accurate computation of O_3 removal by reactive BVOCs.

4. O_3–BVOC interactions in a changing environment: is it higher the O_3 removal by urban trees or the O_3 induced by BVOC emission of those trees?

Despite the well-established role of isoprenoids emitted by plants in atmospheric chemistry and photochemical O_3 production, few studies have been carried out to assess BVOCs role and effects on air quality in city parks, urban and sub-urban forests, and green belts around industrial conurbations (Niinemets and Peñuelas, 2008). The effects of pollutants on the biochemical reactions and physiological conditions leading to BVOC emissions are still quite uncertain (Calfapietra et al., in press).

As urban environments often simulate conditions which the planet will experience in the future decades according to the IPCC scenarios (2007), integrated monitoring of BVOC emissions and air quality could also provide precious insights and help with forecasts.

The question that urgently arises, especially when dealing with urban environments, is whether the benefits of BVOC emission, namely as antioxidants that allow maintenance of plant performances under stressful conditions, and help scavenging O_3 from the atmosphere, outweigh their impact as O_3 precursors.

Nowak et al. (2000) developed models to estimate the O_3 uptake by urban trees, as well as the O_3 formation due to BVOC emission under changing microclimatic conditions. These tools provide some useful elements in order to better evaluate the role of urban trees in the balance of O_3 in an urban area. They showed in different urban areas of Eastern US, that the day-time O_3 decrease due to O_3 uptake by trees was generally higher than the O_3 formed by the same trees, and that night-time O_3 concentrations generally increased due to reduced wind speed and decreased NO_x which are able to scavenge large amounts of O_3. In the same study they also showed that changing tree species composition did not have an overall significant effects on O_3 concentrations (Nowak et al., 2000), even though we argue that depending on the species being exchanged and the environmental conditions the effects on O_3 concentration might be considerably different. Donovan et al. (2005) developed an atmospheric chemistry model to assess the effects of trees on urban air quality, considering both pollution removal and BVOCs emission. Different scenarios were used to elaborate a score that could rank tree species on their potential to improve air quality.

Another study regarding the effect of urban trees on O_3 budget was carried out on three Italian cities applying the UFORE model based on species-specific O_3 removal and BVOC emission, although an estimation of O_3 formed due to these emission was not shown (Paoletti, 2009). Manes et al. (2012) highlighted the role of urban tree diversity to maintain an inter-annual stability in O_3 removal rate, and estimated that urban trees of Rome removed up to 311 Mg of O_3 per year. Another study estimated the maximum O_3 increase due to BVOC emission in the same Mediterranean area in the order of 10 µg m^{-3} (Thunis and Cuvelier, 2000).

These interesting findings call for more field measurements to validate and improve models, especially when more models are used simultaneously, thus increasing the uncertainty of the estimations.

Recent campaigns have investigated the relationships between BVOC emission and O_3 uptake using the disjunct eddy covariance (DEC) method (Rinne et al., 2001) in which short separate samples are taken from the continuous time series, and analyzed by a proton transfer reaction mass spectrometer (PTR-MS) for isoprene or monoterpene concentration. Results showed that emission of oxidation products between isoprenoids and O_3 occurred in coincidence with high non-stomatal O_3 fluxes, suggesting that reactive isoprenoids (e.g. sesquiterpenes and some monoterpenes) contribute to O_3 removal at the canopy level (Fares et al., 2010b).

Normally in urban environment the VOCs/NO_x ratio is low for the high NO_x concentration levels. If high BVOCs emitter species are chosen in the urban forest, it is likely that we move toward optimum conditions, in terms of VOCs/NO_x ratio, for O_3 formation (Fig. 1). This is also confirmed by a modeling study where the photochemical reactivity due to BVOC is of primary importance in different cities of the USA, especially in those cities where AVOC contribution is low (Kleinman et al., 2002).

Moreover, in an O_3-rich world that plants might contribute to create, it may be envisioned that isoprenoid-emitting species will have evolutionary advantage over non-emitting species, leading to a positive loop between BVOC emission and O_3 formation which could have detrimental effects (Lerdau, 2007).

In conclusion, realistic estimations of "losses" and "gains" of O_3 due to urban vegetation are challenging. It is however quite likely that in climatic conditions that do not limit plant physiology and productivity, O_3 uptake dominates over O_3 potentially formed from BVOCs. However, in dry conditions, such as those often occurring in the Mediterranean area, stomatal conductance and consequently O_3 uptake are expected to dramatically decrease and possibly become negligible. On the other hand, BVOC emission are expected to be highly stimulated by the simultaneous occurrence of high temperatures and drought.

Besides to the physiological conditions of the trees the atmospheric conditions in a typical Mediterranean summer are generally characterized by high irradiance and thus particularly favorable for O_3 formation. In urban environment the role of BVOC can be even more important because we are often in VOC limited conditions due to the high NO_x generally emitted from anthropogenic sources. Thus, in those conditions, the load of BVOC emission into the atmosphere can be highly relevant and the choice of a low BVOC emitter becomes crucial to reduce the O_3 forming potential.

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