Published January 11, 2016

Journal of Environmental Quality

SPECIAL SECTION

THE URBAN FOREST AND ECOSYSTEM SERVICES

Removal of Ozone by Urban and Peri-Urban Forests: Evidence from Laboratory, Field, and Modeling Approaches

Carlo Calfapietra,* Arianna Morani, Gregorio Sgrigna, Sara Di Giovanni, Valerio Muzzini, Emanuele Pallozzi, Gabriele Guidolotti, David Nowak, and Silvano Fares

Abstract

A crucial issue in urban environments is the interaction between urban trees and atmospheric pollution, particularly ozone (O_3). Ozone represents one of the most harmful pollutants in urban and peri-urban environments, especially in warm climates. Besides the large interest in reducing anthropogenic and biogenic precursors of O_3 emissions, there is growing scientific activity aimed at understanding O_3 removal by vegetation, particularly trees. The intent of this paper is to provide the state of the art and suggestions to improve future studies of O_3 fluxes and to discuss implications of O_3 flux studies to maximize environmental services through the planning and management of urban forests. To evaluate and quantify the potential of O_3 removal in urban and peri-urban forests, we describe experimental approaches to measure O_3 fluxes, distinguishing laboratory experiments, field measurements, and model estimates, including recent case studies. We discuss the strengths and weaknesses of the different approaches and conclude that the combination of the three levels of investigation is essential for estimating O_3 removal by urban trees. We also comment on the implications of these findings for planning and management of urban forests, suggesting some key issues that should be considered to maximize O_3 removal by urban and peri-urban forests.

Core Ideas

- Urban and peri-urban forests can contribute to O_3 removal in cities.
- Combining different experimental approaches allows us to improve estimates of O_3 fluxes.
- Choice of the right species and its physiological status can maximize O_3 removal by vegetation.

In the last decades, tropospheric ozone (O_3) has become one of the most harmful air pollutants on Earth, particularly in warm climates of the midlatitudes where anthropogenic precursors and high solar radiation promote formation of this pollutant (Chameides et al., 1994). However, critical O_3 levels have also been reached at higher and tropical latitudes due to global warming, increased UV levels, and stabilized or even increased levels of precursor emissions due to industrial development (IPCC, 2014).

Exposure to high levels of tropospheric O_3 is linked to numerous diseases, including lung inflammatory reactions, respiratory symptoms, cardiovascular diseases, asthma, and premature mortality (Bell et al., 2004; Levy et al., 2005; Zscheppang et al., 2008). In plants, exposure to elevated O_3 concentrations might produce damages such as a reduction of light-saturated photosynthesis, tree biomass, and gross primary production (Wittig et al., 2007; Wittig et al., 2009; Fares et al., 2013b). It is evident that O_3 is an issue both in rural and urban environments, affecting ecosystems and human health (Bell et al., 2006).

In addition to the efforts to reduce various anthropogenic and biogenic precursors emissions in cities (Calfapietra et al., 2013), there is growing interest in understanding O_3 flux and consequently the O_3 removal by vegetation, particularly trees (Nowak et al., 2006; Paoletti, 2009; Manes et al., 2012). Ozone can be removed from the air by chemical reactions with reactive compounds emitted by vegetation: oxidation of biogenic volatile organic compounds (BVOCs) by OH in the presence of nitric oxide (NO) produces molecules of O_3 (Di Carlo et al., 2004). Furthermore, O_3 can be removed primarily by leaves through stomatal and nonstomatal mechanisms (Fares et al., 2010a). Ozone can penetrate stomata, and once inside the leaves it reacts with several biogenic compounds (Calfapietra et al., 2009), whereas a negligible role is played by anthropogenic compounds at the

C. Calfapietra, A. Morani, G. Sgrigna, S. Di Giovanni, V. Muzzini, E. Pallozzi, and G. Guidolotti, Institute of Agro-Environmental & Forest Biology (IBAF), National Research Council (CNR), Via Marconi 2, 05010 Porano (TR), Italy; D. Nowak, USDA-Forest Service, Northern Research Station, 5 Moon Library, SUNY-ESF, Syracuse, NY13210; S. Fares, Council for Agricultural Research and Economics, Research Center for the Soil-Plant System, Via della Navicella 2-4, 00184 Rome, Italy; C. Calfapietra, Czechglobe, Global Change Research Centre, Academy of Sciences of the Czech Republic, Bělidla 986/4a, 603 00 Brno, Czech Republic; G. Sgrigna, UniMol, DiBT. Molise Univ., Dep. of Biosciences and Territory, Pesche (IS), Contrada Fonte Lappone, 86170, Italy. Assigned to Associate Editor Stephen Livesley.

Abbreviations: BVOC, biogenic volatile organic compound; EC, eddy covariance.

J. Environ. Qual. 45:224–233 (2016)
doi:10.2134/jeq2015.01.0061
Supplemental material is available online for this article.
Received 31 Jan. 2015.
Accepted 7 July 2015.
*Corresponding author (carlo.calfapietra@ibaf.cnr.it).

cellular level. Stomatal conductance is the main parameter regulating O_3 removal within the leaves (Emberson et al., 2000) and can be influenced by several environmental factors, including O_3 concentration (Wittig et al., 2007). Nonstomatal flux is mainly represented by deposition on plant surfaces. Whereas nonstomatal flux is usually lower than stomatal flux and is often minimal, especially in dry conditions (Cape et al., 2009), nonstomatal flux can be quite important on wet canopies (Altimir et al., 2006).

When O_3 reaches the intercellular spaces in leaves, it may oxidize cells and damage or injure plant tissues. When plants produce BVOCs, they can reduce the intercellular O_3 concentration before this pollutant oxidizes leaf tissues. Consequently, plants maintain a high O_3 flux from the air into the leaves (Loreto and Fares, 2007). Evidence that oxidized BVOCs are emitted by leaves as reaction products between BVOCs and reactive oxygen species supports this thesis (Jardine et al., 2012).

The idea that O_3 removal maintains a gradient into a leaf is in line with the idea of O_3 accumulation in the mesophyll (Moldau and Bichele, 2002) but is against the hypothesis that all O_3 reacts after entering stomata, bringing its concentration close to zero (Laisk et al., 1989).

Recently, much effort has been put into estimating O_3 penetration inside leaves with the intent to assess O_3 risks for plants. There is a general consensus that a metric based on a dose–response relationship is a better predictor of risk than a metric solely based on accumulated concentrations because the latter does not take into account the effective amount of phytotoxic O_3 entering stomata (Matyssek et al., 2007). A number of models have been developed for this purpose that have been tested for mainly rural tree species (Büker et al., 2012).

More recently, the focus has been expanded to estimating the mitigation potential of plants, with a particular interest in urban trees (Nowak et al., 2006; Escobedo et al., 2011). Different experimental approaches have been performed to estimate the O_3 removal by urban plants and trees. At the leaf, branch, or small plant level, mainly cuvettes of different sizes have been used, either in the laboratory or in the field, and coupled with a gas exchange measuring system to parameterize O_3 removal under controlled microclimatic and environmental conditions (Fares et al., 2010a,b). At the ecosystem level, the eddy covariance (EC) technique, which was originally established to estimate CO_2 and H_2O fluxes, has been extended to O_3 fluxes (Fares et al., 2013b).

Different models have been developed to estimate the O_3 fluxes by urban forests with the purpose to evaluate ecosystem services provided by urban vegetation, such as the i-Tree (formerly UFORE) model developed in the United States (Nowak et al., 2014), or with the purpose of O_3 risk assessment based on the penetration of phytotoxic O_3 within stomata (DOSE) (Emberson et al., 2000).

This paper reviews the main techniques used to estimate O_3 removal by urban woody vegetation, discusses their weaknesses and strengths, and presents case study examples. The main goals of this paper are to provide insights and suggestions to improve the experimental layout of future studies of O_3 fluxes and to discuss implications of O_3 flux studies on the planning and management of urban forests to maximize environmental services.

Measuring and Modeling O_3 Removal by Urban Trees

Laboratory Experiments

Experimental designs to measure O_3 removal in a laboratory require that O_3 fumigation is conducted in a closed and controlled system to isolate specific plant elements and to control environmental parameters that influence the physiological behavior of the plants. In controlled experiments, different plants can be fumigated with different O_3 concentrations, used as target values to evidence the effect of O_3 concentration in the leaf O_3 flux (Fig. 1; Supplemental Appendix S1). Ozone fluxes in cuvettes are generally measured using open dynamic systems in which gas exchange is measured by calculating the difference in O_3 concentration at the inlet and at the outlet of the enclosure. Ozone is a reactive molecule; therefore, closed dynamic systems are less appropriate because the long retention time of O_3 in the cuvette may lead to consistent and unrealistic reaction of O_3 with plant and cuvette surfaces. To minimize O_3 reactivity, O_3 generated with a UV light source must be diverted to the cuvette using tubes and connectors made of inert material like polytetrafluoroethylene (Teflon), which minimizes the reaction of O_3 with the surfaces. To avoid O_3 depletion inside the cuvettes, the

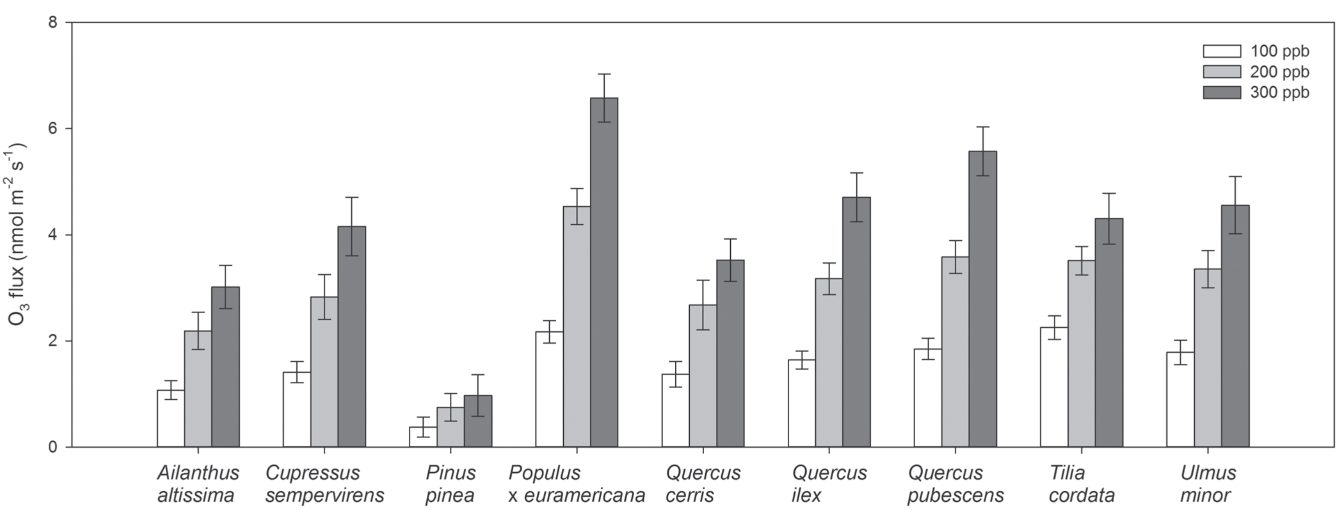

Fig. 1. Ozone uptake measured on common tree species used in Rome, Italy, performed in large cuvette experiments fumigated with 100, 200, and 300 ppb of O_3.

cuvettes have a thin internal Teflon coating (Tholl et al., 2006). Every device inside the cuvette, in particular fans, might react with O_3 and thus decrease its concentration. Therefore, different approaches have been implemented to minimize this issue, such as extremely small plastic fans (Morani, 2013), Teflon fans (Fares et al., 2008), and rigid diffusion tubes in the Teflon (Fares et al., 2010c). There are cuvettes of different sizes with distinct pros and cons: the use of small cuvettes (Loreto and Velikova, 2001) allows overcoming problems with water condensation due to plant transpiration, but the use of larger branch cuvettes (Fares et al., 2006; Fares et al., 2010a; Morani, 2013) reduces the signal to noise ratio, which is particularly useful when the O_3 signal is low, such as when it is measured simultaneously with other reactive trace gases. Finally, stirred tank reactors (Neubert et al., 1993), made with either glass or Teflon, can accommodate different plants and can be located in phytotrons for the adjustment of some environmental conditions (e.g., temperature and light), although the limitations of large cuvettes are mainly due to water condensation due to plant transpiration and slow air turnover.

High relative humidity can alter the O_3 concentration and can affect the detector's reliability. A list of strengths and weaknesses in the use of cuvettes coupled with gas exchange systems is presented in Table 1.

Laboratory experiments of O_3 fumigation have improved our knowledge about the interaction of O_3 with BVOCs (Fares et al., 2006; Fares et al., 2010a; Loreto and Velikova, 2001; Loreto and Fares, 2007). Having standard conditions during experiments makes this approach ideal for comparative studies among different species and environmental conditions (Fig. 1 and 2; Supplemental Appendixes S1 and S2). This standardized approach could be very useful in selecting the best species for urban environments to remove O_3, accounting also for long-term adaptation of the plants, as suggested by Calfapietra et al. (2015).

Eddy Covariance Technique

Ozone fluxes at the ecosystem level are typically measured by the EC method, a micro-meteorological technique that measures the fluxes above the surface layers (Aubinet et al., 2012). It is based on the turbulent upward and downward movements of the air (eddies) that transport mass and energy (Baldocchi et al., 1988).

Since the early 1990s, EC has been used by the ecological community to measure atmosphere–biosphere trace gas exchanges without altering the surrounding environment (Baldocchi et al., 1988; Foken et al., 2012). More recently, O_3 fluxes have been investigated with the implementation of fast-response O_3 sensors based on coumarin-induced chemiluminescence (Bauer et al., 2000; Fares et al., 2014; Hogg et al., 2007). These sensors allow the use of EC for directly measuring O_3 fluxes at the ecosystem level in a multitude of crop and forest ecosystems, including peri-urban forests (Bauer et al., 2000; Hogg et al., 2007; Fares et al., 2010a; 2014).

In the absence of advection, the fluxes are calculated from Eq. [1]:

$$F_c = \overline{w'C'} \qquad [1]$$

where F_c is the O_3 flux, w is the vertical wind speed, and C is the O_3 concentration. The prime indicates the instantaneous deviation from the mean, and the overbar indicates the time average. Basically, EC needs sonic anemometers to measure the vertical wind speed variations, sonic thermometry for temperature variations, and a sensor for scalar density variations (O_3 in our case). All the variables need to be measured above plant canopies in a well-mixed surface layer (Munger et al., 2012) at high frequencies (>10 Hz) to ensure accurate measurement of the smaller and faster eddies (Foken et al., 2012). Moreover, the height of the measurement, together with the surface roughness and thermal stability, determines the area or "footprint" that contributes to the flux (Burba and Anderson, 2010).

For in situ measurement of O3 concentrations, there are several types of analyzers: electro- chemical, spectroscopic, and chemiluminescence (Zahn et al., 2012). The chemiluminescence technique detects the chemiluminescence produced by an organic dye in the presence of O3 (Gosten and Heinrich, 1996). It has a fast response time that is suitable to the EC set up (Rummel et al., 2007); however, it requires frequent calibration with a slow device. Therefore, experimental field sites equipped for O3 flux measurements often require a slow O3 analyzer (the same used in laboratory experiments) sampling from the same height to produce correction factors to

Table 1. Advantages and disadvantages of the different techniques presented to study the O_3 uptake in an urban environment.

Methodology	Advantages	Disadvantages
Gas exchange cuvette experiments	possibility to disentangle the effects of single environmental factors and of plant species	unnatural conditions imposed on the sample
	possibility to measure the potential O_3 absorption of urban plants	limited size of samples and a large signal-to-noise ratio
	possibility to manipulate environmental conditions	the whole gas exchange system made up of inert materials
Eddy covariance technique	long time series of O_3 uptake measurements	many requirements: homogeneous and flat terrain, atmospheric turbulence, and fast sensors
	reports O_3 removal at ecosystem level	frequent calibration of the chemiluminescence O_3 analyzer
	no alteration of the surrounding environment	Complex databases to be analyzed
	provides information about the interactions between anthropogenic and biogenic compounds	
Modeling approaches	integrate O_3 flux estimates across space and time	need to be parameterized by laboratory and/or eddy covariance measurements
	provide information how the different factors and scenarios (vegetation type, O_3 level, etc.) can affect O_3 uptake	Inverse relationship between the spatial scale applicability and the accuracy
		scarce attention to plant's physiological status

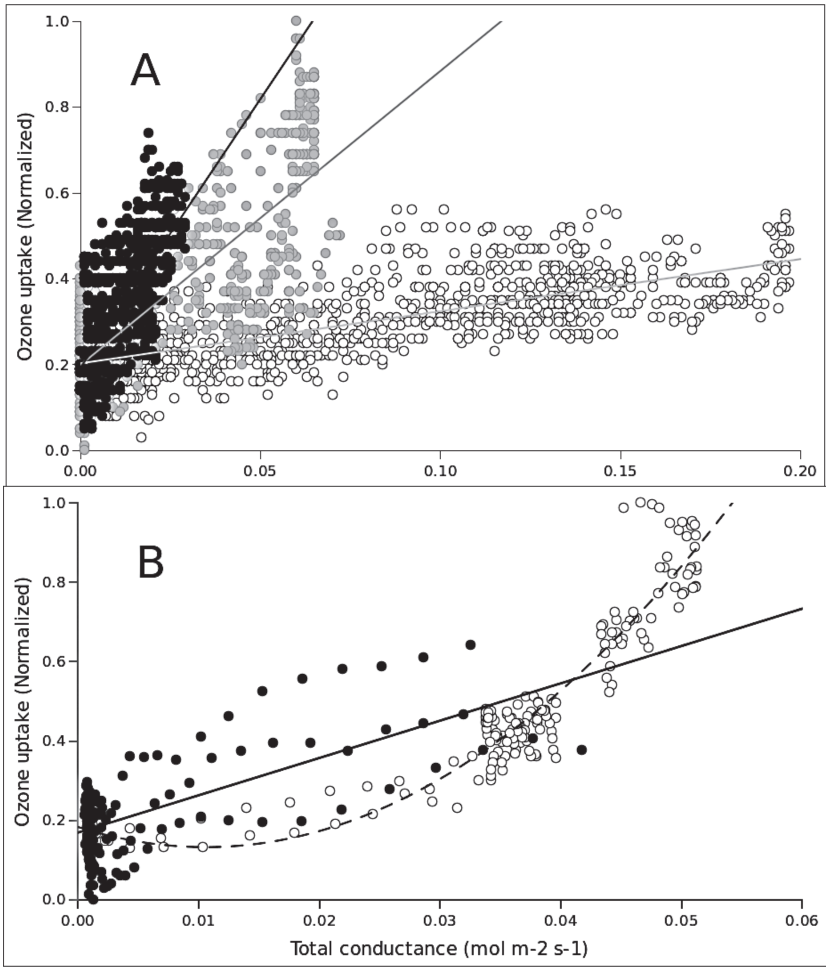

Fig. 2. Relationship between total conductance (expressed as the sum of stomatal, cuticular, and mesophyll conductance) and O_3 uptake (normalized to maximum rates) in laboratory cuvette experiments in (A) *Pinus pinea* L. (black dots), *Quercus ilex* L. (gray dots), and *Populus nigra* L. (white dots) and (B) *Q. ilex* exposed to light (white dots) and dark (black dots) cycles in the same laboratory cuvette experiments presented in (A).

transform high-frequency voltage outputs to ppbv (Muller et al., 2010). This technique has recently been applied to urban and peri-urban forests (Fig. 3; Supplemental Appendix S3) (Fares et al., 2010a, 2014).

As shown in Fig. 3, seasonal changes in air temperature regulate the response of O_3 concentration and O_3 removal in the Mediterranean peri-urban forest used here as a case study (Supplemental Appendix S3).

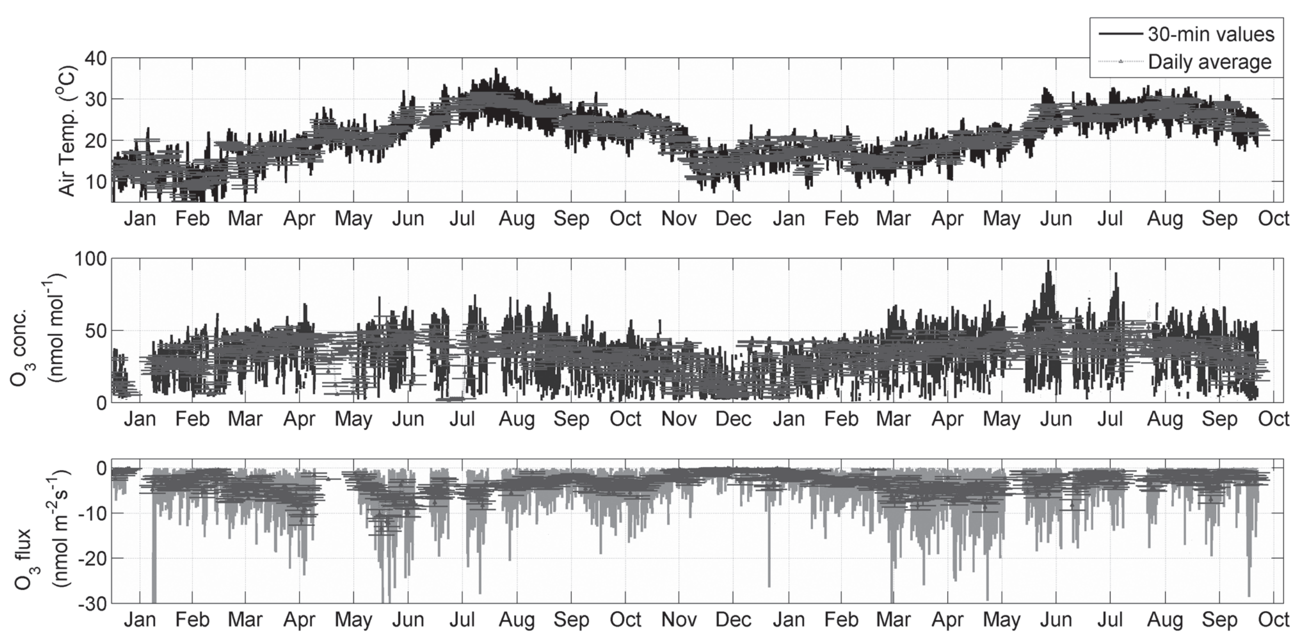

Fig. 3. Air temperature, O_3 concentration, and O_3 fluxes measured from January 2013 to October 2014 with eddy covariance in a Mediterranean peri-urban *Quercus ilex* forest located inside the Presidential Estate of Castelporziano, 25 km southwest from the center of Rome.

Modeling Approaches

The O_3 exchange between the vegetation and the atmosphere is controlled by complex biophysical interactions (Grünhage et al., 1997). This complexity requires a modeling approach to integrate O_3 flux estimates across space and time. This flux includes O_3 formation and transformations due to atmospheric chemistry and O_3 deposition to earth surfaces. There are various models that estimate all O_3 processes at the regional level (e.g., CMAQ [Appel et al., 2007], ECMWF [Vautard et al., 2001], and CHIMERE [Alonso et al., 2011]), but the focus of this paper is on O_3 deposition processes. The goal of modeling O_3 deposition is to identify and integrate the major sinks in the soil–plant–atmosphere continuum. Several models have been developed to estimate O_3 deposition, with most models focusing on area-based estimates using a big-leaf or multilayer modeling approach (Baldocchi et al., 1987; Baldocchi, 1988; Grünhage et al., 1997; Vitale et al., 2005; Nowak et al., 2006; Manes et al., 2012). Some models have been applied at a larger spatial scale and are specifically parameterized to predict the contribution of stomata to O_3 sequestration using semiempirical algorithms to model stomatal conductance based on the ecophysiological responses of plants to environmental conditions (Emberson et al., 2000; Nowak et al., 2014). The general concept of these models is that the downward pollutant flux (F, in μg m $^{-2}$ s^{-1}) is calculated as the product of the deposition velocity (Vd, in m s^{-1}) and the pollutant concentration (C, in μg m^{-3}) (F = Vd C). Deposition velocity is often calculated as the inverse of the sum of the aerodynamic, quasilaminar boundary layer and canopy resistances. The canopy resistance values for O_3 are often calculated based on a big-leaf or multilayer canopy deposition models.

Results from modeling numerous US cities and US national assessments using i-Tree reveal that the average O_3 flux in the United States is 5.5 g m^{-2} of tree cover yr^{-1} (Nowak et al., 2014) but can vary in cities from 2.1 to 7.6 g m^{-2} of tree cover yr^{-1} (Nowak et al., 2006). Individual city annual flux rates to trees (per m^2 of tree cover) vary across the world (Fig. 4; Supplemental Appendix S4) based on differences in pollution concentrations and plant features such as leaf area indices, stomatal conductance, and assimilation rates. These variations are strictly dependent on weather conditions (e.g., temperature, humidity, wind speed, solar radiation, and precipitation) and length of growing season (Nowak et al., 2006). Total removal rates within a city also vary based on the amount of tree cover. Average leaf-on daytime dry deposition velocities for O_3 varied among the US cities from 0.40 to 0.71 cm s^{-1} and varied throughout the day, similar to transpiration patterns (Nowak et al., 2006). Such modeling efforts ultimately allow us to consider O_3 removal as an ecosystem service provided to the citizens to ameliorate quality of life. This important ecosystem service, together with a range of other services (e.g., carbon sequestration, recreation, and amelioration of urban microclimate), contributes to an overall benefit provided by green infrastructures, which challenges the scientific community to evaluate the best method to quantify the financial value and a potential market.

Discussion

Enclosures versus Eddy Covariance Measurements

Understanding which approach provides more precise values of O_3 removal in urban and peri-urban forests is challenging. Measurements over ecosystems with EC are preferable if the intent is to quantify the actual absorption of O_3 over time (Bauer et al., 2000; Fowler et al., 2001; Löw et al., 2006; Fares et al., 2010a; 2012) and/or to correlate the environmental changes with the macroscopic effects related to absorption of O_3 (Goldstein et al., 2004; Altimir et al., 2006). The EC method is widely considered as the best micrometeorological technique to measure ecosystem-level fluxes. However, several conditions need to be met to properly apply this technique in urban areas. Although the variable footprints of EC often include different land covers and thus can provide important information about the urban forest effect on air quality and on the interactions between anthropogenic and biogenic compounds, it is not easy to disentangle the effect of the single factors because several factors (e.g., patchy vegetation, roads, building, and anthropogenic sinks and sources) occur at the same time at the ecosystem level (Wang et al., 1995; Tuovinen et al., 2004; Morani et al., 2014). It is also not possible to provide tree-specific information in a mixed forest ecosystem. The EC method easily applies to flat and homogeneous terrains and applies under turbulent conditions. Patchy vegetated areas, typical of urban forests, are a challenge for the application of the EC technique.

Therefore, coupling leaf cuvettes and the gas exchange technique (Wang et al., 1995; Field et al., 2000) to measure the O_3 removal at the leaf level is the best tool to develop environmental

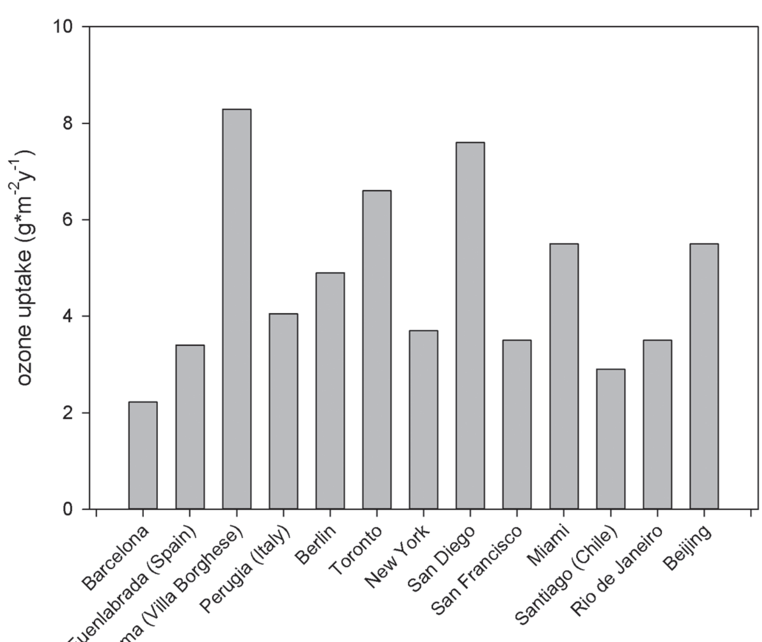

Fig. 4. Ozone uptake estimated using the i-Tree model in different case studies. Data for Barcelona are from Chaparro and Terradas (2009); for Fuenlabrada from USDA Forest Service (unpublished data); for Rome and Perugia from Morani (2013) and Sgrigna (2011); for Berlin from Aevermann et al. (unpublished data, 2015); for Toronto from Nowak et al. (2013); for New York, San Diego, San Francisco, and Miami from Nowak et al. (2006); for Santiago del Chile from Escobedo and Nowak (2009); for Rio de Janeiro from USDA Forest Service (unpublished data, 2015); for Beijing from Yang et al. (2005). Removal rate is standardized to grams of O_3 removed per square meter of tree cover per year.

response functions and to parameterize O_3 removal (Fares et al., 2010a). This approach can disentangle the effects of single factors, such as humidity levels, temperature, and the boundary layer, which can influence O_3 removal (Loreto and Velikova, 2001; Loreto and Fares, 2007). However, the use of enclosures has some limitations, including the unnatural conditions imposed on the leaf within the cuvette and the limited sample size that can be measured. These limitations can be minimized by the use of small chambers with an efficient control of the environmental parameters (generally CO_2, temperature, light, and vapor pressure deficit) developed since the beginning of the 1990s (Collatz et al., 1991) and larger cuvettes or reactors (Neubert et al., 1993; Fares et al., 2008). Despite the disadvantages, the application of this technique could be particularly useful in the urban environment. A qualitative study, aimed at comparing a number of tree species under the same environmental conditions to quantify differences in O_3 removal, will be important to determine which of numerous urban tree species would be the best for enhancing O_3 removal in cities. In addition, cuvette and gas exchange techniques might be used in situ (Grulke et al., 2002) to measure the O_3 removal of large trees under the natural urban environmental conditions also for comparison with the seedlings often used in the laboratory experiments (Nunn et al., 2005). Finally, gas exchange techniques might have a key role for proper parametrization of process-based models due to the measurements of physiological status and biochemical parameters estimation (e.g., Velocity of Carboxilation by Rubisco enzyme), especially in different biodiverse vegetation types such as those found in the various cities of the world.

Species-Specific and Environmental Factors Influencing O_3 Removal

In canopies, structural characteristics affect O_3 deposition: plant density and the overall amount of biomass and leaf area are directly linked to O_3 removal. Among the environmental factors influencing O_3 removal, a key role is played by tropospheric O_3 concentration, temperature, and air humidity. Although the effect of air humidity on O_3 removal has not been studied adequately, laboratory tests indicate that an increase in moisture can destroy O_3 (Cox and Penkett, 1972; McClurkin et al., 2013). Moreover, Chen et al. (2011) observed that O_3 reacts with water to form hydroxyl radicals, which might have an effect on O_3 concentration and phytotoxicity. In any case, specific and environmental factors are strictly connected to O_3 removal: temperature, light, and water availability in the soil–plant system may change the absorption of O_3 by trees and ecosystems by influencing stomatal opening (Fredericksen et al., 1996; Bauer et al., 2000; Löw et al., 2006). Paoletti and Grulke (2010) observed that a prolonged exposure to O_3 induces a stomatal sluggishness, which makes stomata less responsive to rapid changes of light, thus directly affecting the stomatal removal of O_3.

Measuring total O_3 flux offers the ability to develop atmospheric models that partition fluxes between stomatal and nonstomatal sinks. Some studies covering a wide range of ecosystems (Gerosa et al., 2005; Hogg et al., 2007; Fares et al., 2012, 2014) have partitioned total O_3 fluxes between various sinks and have estimated that between 30 and 70% of fluxes can be attributed to stomata, illustrating the importance of this sink. Species-specific differences are largely responsible for a broad range of variation of stomatal contribution to total O_3 sink. Broadleaves with high rates of stomatal conductance will have stomata as the main sinks, as in the case of poplar plantations (Zona et al., 2014). As highlighted in Fig. 2, different species tested in laboratory cuvette experiments showed considerably different O_3 fluxes (normalized for the maximum flux) not explained by leaf conductance (sum of stomatal, cuticular, and mesophyll conductance). However, such controlled conditions produced considerable differences in O_3 removal among various species even after normalizing for stomatal conductance (Fig. 2a). Moreover, testing the transition between light and dark (Fig. 2b) also supports the hypothesis that other parameters besides stomatal openings might affect O_3 removal.

Certain species emit reactive BVOCs, such as monoterpenes and sesquiterpenes, which were found to react within a few seconds with O_3, thereby removing the pollutants through gas-phase reactions (Kurpius and Goldstein, 2003). This is the case of pine forests, which are high emitters of reactive hydrocarbons with low stomatal conductance in comparison with broadleaf trees (Fares et al., 2010a). More recently, evidence has shown that BVOCs can react with O_3 in the intercellular spaces as described by Jardine et al. (2012), who showed direct emissions of oxidized products of isoprene from leaves. Although a direct O_3–BVOCs reaction inside leaves has yet to be demonstrated, it is plausible that reactive oxygen species formed in leaves by O_3 oxidation are reacting with BVOCs. Ozone removal in leaves thus contributes to maintaining a high gradient and thus a high flux between the leaf and the air (Loreto and Fares, 2007; Fares et al., 2008). Moreover, O_3 can stimulate or inhibit BVOC emission, and this can influence interactions and feedback events that are difficult to forecast and model (Calfapietra et al., 2009). Thus, BVOC-emitting tree species can explain nonstomatal sinks in the canopy (Goldstein et al., 2004; Kurpius and Goldstein, 2003; Fares et al., 2010b) that atmospheric models based solely on atmospheric resistance to O_3 removal cannot resolve. Urban environments are also characterized by a high presence of anthropogenic volatile organic compounds, which, together with BVOCs, can considerably influence the reactivity of O_3 at the biosphere–atmosphere interface.

Cuticle deposition also represents an important O_3 sink. However, the physicochemical processes driving O_3 deposition to plant surfaces are not fully understood. Despite the low water solubility of O_3, wet plant surfaces were found to represent an active O_3 sink (Altimir et al., 2006), perhaps due to the presence of a thin layer of reactive BVOCs, which forms at the wet surface. Soils are responsible for some O_3 deposition. Direct EC measurements of O_3 fluxes at the soil level in a Holm Oak forest revealed that up to 30% of O_3 is deposited to a forest soil (Fares et al., 2014). However, the main sinks of O_3 in soils remain unknown, and differences between soils with different biological and structural composition may exist.

Opportunities and Challenges to Integrate Leaf and Field Observations to Parameterize Models

Although EC field measurement campaigns are important to provide empirical evidence of O_3 flux to urban trees and to compare with model outputs, they are expensive and limited in their practical application to aid managers in developing specific strategies to improve air quality. Modeling of O_3 fluxes allows for the integration of complex processes that are not easily measured and provides a means to assess the potential impact of complex landscape designs on O_3 concentrations. Modeling also provides a relatively low-cost and straightforward means to aid managers in understanding the role of vegetation and other surfaces on removing O_3 and in improving air quality management in cities (Nowak et al., 2014). The online tool provided by UFORE is a clear example. For example, the tree species selection tool (i-Tree, 2013) developed for US cities helps in identifying the best species according a number of requested benefits, including O_3 removal derived from experimental activities.

The various big-leaf/multilayer hybrid–based deposition models (Baldocchi, 1988; Grünhage et al., 1997; Vitale et al., 2005; Nowak et al., 2006; Manes et al., 2012) have several advantages and disadvantages. The main advantage is that they are available and that they can provide reasonable estimates for gaseous pollution removal at an hourly time frame based on locally measured tree parameters, pollution data, and meteorological data. Another advantage is that the model can be used globally if the input data are available. Some models have been developed and applied to several urban contexts, demonstrating the key role played by the urban and peri-urban forest on O_3 removal (Alonso et al., 2011; Baumgardner et al., 2012; Manes et al., 2012; Kroeger et al., 2014; Morani et al., 2014). In addition to the large spatial scale, an important goal of modeling is simulating how different scenarios (e.g., vegetation type, O_3 level, etc.) affect urban air quality.

However, this modeling approach also has some limitations, which are often related to the plant's physiological status. Although the soil water status and air quality have been recently coupled in large spatial-scale models (Simpson et al., 2012; de Andrés et al., 2012), the standard versions of the two models (CHIMERE [Alonso et al., 2011] and i-Tree [Morani et al., 2014]) that are commonly used in the estimation of O_3 removal in urban environment do not account for the drought effect and the consequent reduced stomata opening. This omission of a drought effect is a primary reason for overestimating O_3 removal in Mediterranean environments when drought conditions are limiting the O_3 removal and sink capacity (Fig. 5; Supplemental Appendixes S3 and S4). However, drought effects are often not realized in urban environments due to supplemental water from city residents or from the municipality. A first attempt to overcome this drought omission was introduced in the update (Büker et al., 2012) of the original model developed by Emberson et al. (2000). This model estimates O_3 flux through stomata and includes the effect of plant phenology and climatic conditions on stomatal conductance, allowing a separation of stomatal and nonstomatal O_3 fluxes. Process-based hydrological models to predict water retention in soils coupled with O_3 deposition models are highly desired, especially for drought-prone urban forests.

Another limitation associated with the modeling approach is the level of observation, which often has to do with the limitations of the input data. Although high-resolution, spatially distributed tree parameters can be obtained from LiDAR-based approaches (e.g., Koetz et al., 2007), high-resolution spatially and temporally distributed weather and pollution data are often limited. Thus, data from various pollution monitors or weather stations are often used to represent the pollution and weather conditions across an area or are produced from other model estimates. Improvements in O_3 concentration estimates can be reached through a spherical cokriging interpolation model (Isaaks and Srivastava, 1989). This methodology has been applied successfully in urban areas as a base to model O_3 removal at the ecosystem level (Manes et al., 2012).

Chemical transport models are often used to model the concentration of pollutants at a regional level (down to 1 km^2 of spatial resolution) (e.g., the WRF-CHEM model [Tie et al., 2009]). There is a high potential for transport models to improve local pollution removal estimates with more accurate and spatially resolved estimates.

Another challenge is understanding the role of isoprenoids in removing O_3 at different levels and their influence on O_3 removal. This effect has been demonstrated in the laboratory (Loreto and

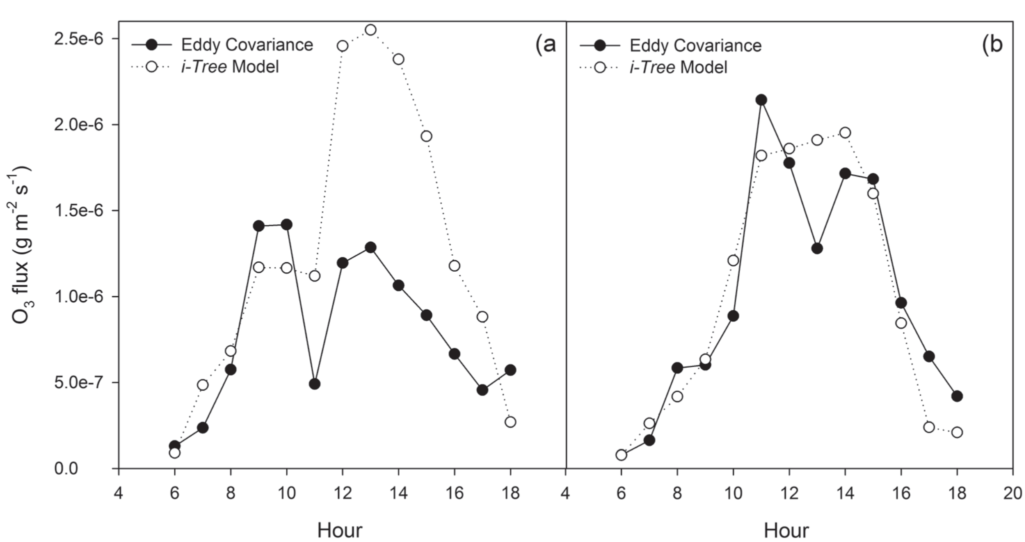

Fig. 5. Daily course of O_3 uptake estimated by the i-Tree model and measured using eddy covariance techniques in a peri-urban forest near Rome, Italy. (a) A typical summer day with high temperature and low soil water availability. (b) A typical late summer day after rain events characterized by lower temperature and good soil water availability. For details see Supplemental Appendixes S3 and S4 and Morani et al. (2014).

Fares, 2007) and in field studies (Goldstein et al., 2004; Fares et al., 2010b) and is accounted for in some models, although there are very few applications in the urban environment (Simpson et al., 2012; Alonso et al., 2011; Kim et al., 2014). Investigating this phenomenon along a gradient of physiological conditions throughout different seasons and taking advantage of the environmental gradient present along an urbanrural transect is essential (Calfapietra et al., 2015). Moreover, a multilayer model may reconcile observations collected at the single-leaf and at the ecosystem level because different retention times and reactivity rates with O_3 in various experiments produced large divergences in the magnitude of chemical O_3 removal. Thus, the integration of different levels of investigation appears crucial to increase our understanding of O_3 removal in urban ecosystems and to provide guidelines for urban planners and managers, as shown in Fig. 6.

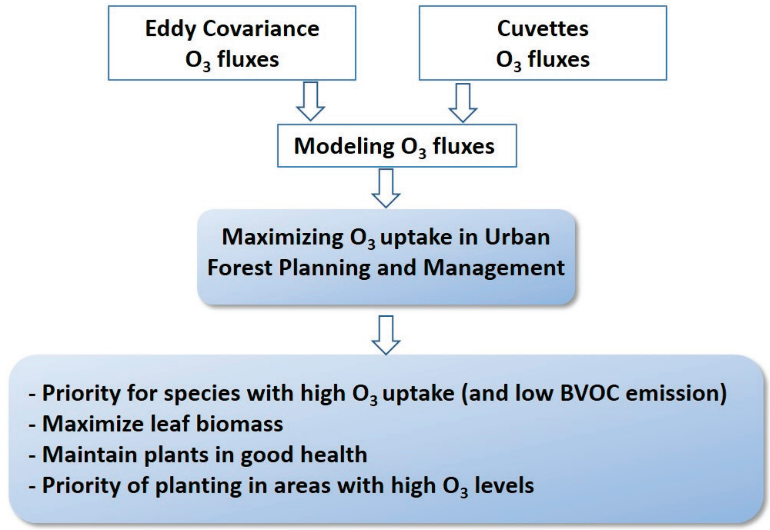

Fig. 6. The importance of estimating O_3 fluxes for the planning and the management of urban forests and best practices to maximize the O_3 uptake.

Conclusions

Reconciling leaf-level and ecosystem-level measurements is important given the limitations and opportunities. It is evident that synergy among leaf cuvette, eddy covariance, and modeling techniques is needed to better evaluate the capacity of O_3 removal by vegetation in the urban environment. Models can help us move from the EC footprint to a larger spatial level (city level), which is essential to developing plans to improve air quality and to developing urban forest management plans. The use of leaf cuvettes can help to parameterize process-based models. This parameterization could provide more realistic simulation of stomatal conductance, help integrate the contribution from different layers to ecosystem fluxes, and help parameterize multilayer models (Sprintsin et al., 2012). Moreover, field observations with EC may be used to parameterize deposition models, as in the case of the Castelporziano Estate (Morani et al., 2014).

Providing scientific evidence on how to maximize the O_3 removal in an urban environment is of paramount interest to urban forest planners and managers. Model application may be used to predict the ideal vegetation for a given area and certain meteorological conditions that could maintain appropriate, healthy vegetation to considerably increase the O_3 sink capacity in our cities. Such provision may provide socioeconomic awareness to invest in proper urban tree structure.

We believe that future modeling efforts should address the issue of single tree effects on pollution concentration (i.e., how do tree configurations alter local pollutant concentrations?) (Emberson et al., 2000; Nowak et al., 2006). Spatial variability of urban forest and vegetation designs within the urban landscape might also have a key role in air pollution removal, as shown by Escobedo and Nowak (2009). Local pollution concentrations can be increased or decreased depending on designs and source of pollutant (Nowak et al., 2014). More research is needed that accounts for vegetation configuration and source–sink relationships to maximize beneficial tree effects on pollutant concentrations and to minimize human exposure to air pollution.

We conclude that pollution removal by trees is not the only way that trees affect local O_3 concentrations. Trees reduce air temperatures, which can lead to reduced emissions from various anthropogenic sources (Cardelino and Chameides, 1990). Trees around buildings alter building energy use (Heisler, 1986) and consequent emissions from power plants. Trees reduce wind speeds, lowering mixing heights, and can therefore increase O_3 concentrations (Nowak et al., 2006). Trees also emit varying levels of BVOCs that are precursor chemicals to O_3 formation (Chameides et al., 1988). Certain BVOC species, such as isoprenoids, have been described as high O_3–forming hydrocarbons in the presence of anthropogenic emissions of NOx (Gentner et al., 2014). More research and modeling is needed on how these factors combine to affect air pollution concentrations.

Acknowledgments

This work was supported by European Projects COST Action FP1204 GREENINURBS, EXPLO3RVOC (FP7-PEOPLE-2012-CIG, proposal n. 321711) and the funded MIUR projects RITMARE and PRIN 2012/2013 NEUFOR. The research in Castelporziano was also supported by the Scientific Commission of Castelporziano and the Multi-disciplinary Center for the Study of Coastal Mediterranean Ecosystems and the MIUR-PRIN 2010/2011 TREECITY project.

References

Alonso, R., M.G. Vivanco, I. González-Fernández, V. Bermejo, I. Palomino, J.L. Garrido, S. Elvira, P. Salvador, and B. Artíñano. 2011. Modelling the influence of peri-urban trees in the air quality of Madrid region (Spain). Environ. Pollut. 159:2138–2147. doi:10.1016/j.envpol.2010.12.005

Altimir, N., P. Kolari, J.-P. Tuovinen, T. Vesala, J. Bäck, T. Suni, M. Kulmala, and P. Hari. 2006. Foliage surface ozone deposition: A role for surface moisture? Biogeosciences Discuss. 2:1739–1793. doi:10.5194/bgd-2-1739-2005

Appel, K., A. Gilliland, G. Sarwar, and R. Gilliam. 2007. Evaluation of the Community Multiscale Air Quality (CMAQ) model version 4.5: Sensitivities impacting model performance part I: Ozone. Atmos. Environ. 41:9603–9615. doi:10.1016/j.atmosenv.2007.08.044

Aubinet, M., T. Vesala, and D. Papale. 2012. Eddy covariance: A practical guide to measurement and data analysis. Springer, Dordrecht, The Netherlands.

Baldocchi, D. 1988. A multi-layer model for estimating sulfur dioxide deposition to a deciduous oak forest canopy. Atmos. Environ. 22:869–884. doi:10.1016/0004-6981(88)90264-8

Baldocchi, D.D., B.B. Hicks, and P. Camara. 1987. A canopy stomatal resistance model for gaseous deposition to vegetated surfaces. Atmos. Environ. 21:91–101. doi:10.1016/0004-6981(87)90274-5

Baldocchi, D.D., B.B. Hincks, and T.P. Meyers. 1988. Measuring biosphere-atmosphere exchanges of biologically related gases with micrometeorological methods. Ecology 69:1331. doi:10.2307/1941631

Bauer, M.R., N.E. Hultman, J.A. Panek, and A.H. Goldstein. 2000. Ozone deposition to a ponderosa pine plantation in the Sierra Nevada Mountains (CA): A comparison of two different climatic years. J. Geophys. Res. 105(D17):22123. doi:10.1029/2000JD900168

Baumgardner, D., S. Varela, F.J. Escobedo, A. Chacalo, and C. Ochoa. 2012. The role of a peri-urban forest on air quality improvement in the Mexico City megalopolis. Environ. Pollut. 163:174–183. doi:10.1016/j.envpol.2011.12.016

Bell, M.L., A. McDermott, S. Zeger, J. Samet, and F. Domimici. 2004. Ozone and short-term mortality in 95 US urban communities, 1987-2000. JAMA 292:2372–2378. doi:10.1001/jama.292.19.2372

Bell, M.L., R.D. Peng, and F. Dominici. 2006. The exposure–response curve for ozone and risk of mortality and the adequacy of current ozone regulations. Environ. Health Perspect. 114:532–536. doi:10.1289/ehp.8816

Büker, P., T. Morrissey, A. Briolat, R. Falk, D. Simpson, J.-P. Tuovinen, R. Alonso, S. Barth, M. Baumgarten, N. Grulke, P.E. Karlsson, J. King, F. Lagergren, R. Matyssek, A. Nunn, R. Ogaya, J. Peñuelas, L. Rhea, M. Schaub, J. Uddling, W. Werner, and L.D. Emberson. 2012. DO_3SE modelling of soil moisture to determine ozone flux to forest trees. Atmos. Chem. Phys. 12:5537–5562. doi:10.5194/acp-12-5537-2012

Burba, G., and D. Anderson. 2010. A brief practical guide to eddy covariance flux measurements: Principles and workflow examples for scientific and industrial applications. LI-COR, Inc., Lincoln, NE.

Calfapietra, C., S. Fares, and F. Loreto. 2009. Volatile organic compounds from Italian vegetation and their interaction with ozone. Environ. Pollut. 157:1478–1486. doi:10.1016/j.envpol.2008.09.048

Calfapietra, C., S. Fares, F. Manes, A. Morani, G. Sgrigna, and F. Loreto. 2013. Role of biogenic volatile organic compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review. Environ. Pollut. 183:71–80. doi:10.1016/j.envpol.2013.03.012

Calfapietra, C., J. Peñuelas, and Ü. Niinemets. 2015. Urban plant physiology: Adaptation-mitigation strategies under permanent stress. Trends Plant Sci. 20:72–75.

Cape, J.N., R. Hamilton, and M.R. Heal. 2009. Reactive uptake of ozone at simulated leaf surfaces: Implications for "non-stomatal" ozone flux. Atmos. Environ. 43:1116–1123. doi:10.1016/j.atmosenv.2008.11.007

Cardelino, C., and W. Chameides. 1990. Natural hydrocarbons, urbanization, and urban ozone. J. Geophys. Res. Atmos. 95:13971–13979. doi:10.1029/JD095iD09p13971

Chameides, W., R. Lindsay, J. Richardson, and C. Kiang. 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241:1473–1475. doi:10.1126/science.3420404

Chameides, W.L., P.S. Kasibhatla, J. Yienger, and H. Levy. 1994. Growth of continental-scale metro-agro-plexes, regional ozone pollution, and world food production. Science 264:74–77. doi:10.1126/science.264.5155.74

Chaparro, L., and J. Terradas. 2009. Ecological services of urban forest in Barcelona. Centre de Recerca Ecològica i Aplicacions Forestals, Universitat Autònoma de Barcelona, Bellaterra, Spain.

Chen, H., C.O. Stainer, M.A. Young, and V.H. Grassian. 2011. A kinetic study of ozone decomposition on illuminated oxide surfaces. J. Phys. Chem. 115:11979–11987. doi:10.1021/jp208164v

Collatz, G.J., J.T. Ball, C. Grivet, and J.A. Berry. 1991. Physiological and environmental regulation of stomatal conductance, photosynthesis and transpiration: A model that includes a laminar boundary layer. Agric. For. Meteorol. 54:107–136. doi:10.1016/0168-1923(91)90002-8

Cox, R.A., and S.A. Penkett. 1972. Effect of relative humidity on the disappearance of ozone and sulphur dioxide in contained systems. Atmos. Environ. 6:365–368. doi:10.1016/0004-6981(72)90203-X

de Andrés, J., R. Borge, D. de la Paz, J. Lumbreras, and E. Rodríguez. 2012. Implementation of a module for risk of ozone impacts assessment to vegetation in the Integrated Assessment Modelling system for the Iberian Peninsula: Evaluation for wheat and Holm oak. Environ. Pollut. 165:25–37. doi:10.1016/j.envpol.2012.01.048

Di Carlo, P., W.H. Brune, M. Martinez, H. Harder, R. Lesher, X.R. Ren, T. Thornberry, M.A. Carroll, V. Young, P.B. Shepson, D. Riemer, E. Apel, and C. Campbell. 2004. Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs. Science 304:722–725. doi:10.1126/science.1094392

Emberson, L.D., M.R. Ashmore, H.M. Cambridge, D. Simpson, and J.-P. Tuovinen. 2000. Modelling stomatal ozone flux across Europe. Environ. Pollut. 109:403–413. doi:10.1016/S0269-7491(00)00043-9

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

Escobedo, F.J., and D.J. Nowak. 2009. Spatial heterogeneity and air pollution removal by an urban forest. Landsc. Urban Plan. 90:102–110. doi:10.1016/j.landurbplan.2008.10.021

Fares, S., C. Barta, F. Brilli, M. Centritto, L. Ederli, F. Ferranti, S. Pasqualini, L. Reale, D. Tricoli, and F. Loreto. 2006. Impact of high ozone on isoprene emission, photosynthesis and histology of developing *Populus alba* leaves directly or indirectly exposed to the pollutant. Physiol. Plant. 128:456–465. doi:10.1111/j.1399-3054.2006.00750.x

Fares, S., F. Loreto, E. Kleist, and J. Wildt. 2008. Stomatal uptake and stomatal deposition of ozone in isoprene and monoterpene emitting plants. Plant Biol. 10:44–54. doi:10.1055/s-2007-965257

Fares, S., R. Vargas, M. Detto, A.H. Goldstein, J. Karlik, E. Paoletti, and M. Vitale. 2013b. Tropospheric ozone reduces carbon assimilation in trees: Estimates from analysis of continuous flux measurements. Glob. Change Biol. 19:2427–2443. doi:10.1111/gcb.12222

Fares, S., M. McKay, R. Holzinger, and A.H. Goldstein. 2010a. Ozone fluxes in a *Pinus ponderosa* ecosystem are dominated by non-stomatal processes: Evidence from long-term continuous measurements. Agric. For. Meteorol. 150:420–431. doi:10.1016/j.agrformet.2010.01.007

Fares, S., E. Oksanen, M. Lännenpää, R. Julkunen-Tiitto, and F. Loreto. 2010b. Volatile emissions and phenolic compound concentrations along a vertical profile of *Populus nigra* leaves exposed to realistic ozone concentrations. Photosynth. Res. 104:61–74. doi:10.1007/s11120-010-9549-5

Fares, S., J.-H. Park, E. Ormeno, D.R. Gentner, M. McKay, F. Loreto, J. Karlik, and A.H. Goldstein. 2010c. Ozone uptake by citrus trees exposed to a range of ozone concentrations. Atmos. Environ. 44:3404–3412. doi:10.1016/j.atmosenv.2010.06.010

Fares, S., F. Savi, J. Muller, G. Matteucci, and E. Paoletti. 2014. Simultaneous measurements of above and below canopy ozone fluxes help partitioning ozone deposition between its various sinks in a Mediterranean oak forest. Agric. For. Meteorol. 198-199:181–191. doi:10.1016/j.agrformet.2014.08.014

Fares, S., R. Weber, J.-H. Park, D. Gentner, J. Karlik, and A.H. Goldstein. 2012. Ozone deposition to an orange orchard: Partitioning between stomatal and non-stomatal sinks. Environ. Pollut. 169:258–266. doi:10.1016/j.envpol.2012.01.030

Field, C.B., J.T. Ball, and J.A. Berry. 2000. Photosynthesis: Principles and field technique. In: R.W. Pearcy, J.R. Ehleringer, H.A. Mooney, and P.W. Rundel, editors, Plant physiological ecology. Springer Netherlands, Dordrecht, the Netherlands. p. 209–253.

Foken, T., M. Aubinet, and R. Leuning. 2012. Eddy covariance. In: M. Aubinet, T. Vesala, and D. Papale, editors, Eddy covariance: A practical guide to measurement and data. Springer Netherlands, Dordrecht, The Netherlands. p. 438.

Fowler, D., C. Flechard, J.N. Cape, R.L. Storeton-West, and M. Coyle. 2001. Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and non-stomatal components. Water Air Soil Pollut. 130:63–74. doi:10.1023/A:1012243317471

Fredericksen, T.S., T.E. Kolb, J.M. Skelly, K.C. Steiner, B.J. Joyce, and J.E. Savage. 1996. Light environment alters ozone uptake per net photosynthetic rate in black cherry trees. Tree Physiol. 16:485–490. doi:10.1093/treephys/16.5.485

Gentner, D., E. Ormeño, S. Fares, T. Ford, R. Weber, J. Park, J. Brioude, W. Angevine, J. Karlik, and A. Goldstein. 2014. Emissions of terpenoids, benzenoids, and other biogenic gas-phase organic compounds from agricultural crops and their potential implications for air quality. Atmos. Chem. Phys. 14:5393–5413. doi:10.5194/acp-14-5393-2014

Gerosa, G., M. Vitale, A. Finco, F. Manes, A. Denti, and S. Cieslik. 2005. Ozone uptake by an evergreen Mediterranean Forest (Quercus ilex) in Italy: Part I. Micrometeorological flux measurements and flux partitioning. Atmos. Environ. 39:3255–3266. doi:10.1016/j.atmosenv.2005.01.056

Goldstein, A.H., M. McKay, M. Kurpius, G. Shade, A. Lee, R. Holzinger, and R. Rasmussen. 2004. Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs. Geophys. Res. Lett. 31:L22106. doi:10.1029/2004GL021259

Grulke, N., H. Preisler, C. Rose, J. Kirsch, and L. Balduman. 2002. O_3 uptake and drought stress effects on carbon acquisition of ponderosa pine in natural stands. New Phytol. 154:621–631. doi:10.1046/j.1469-8137.2002.00403.x

Grünhage, L., H.-J. Jäger, H.-D. Haenel, K. Hanewald, and S. Krupa. 1997. PLATIN (Plant-ATmosphere INteraction) II: Co-occurrence of high ambient ozone concentrations and factors limiting plant absorbed dose. Environ. Pollut. 98:51–60. doi:10.1016/S0269-7491(97)00106-1

Gosten, H., and G. Heinrich. 1996. On-line measurements of ozone surface fluxes: Part I. Methodology and instrumentation. Atmos. Environ. 30:897–909. doi:10.1016/1352-2310(95)00269-3

Heisler, G. 1986. Effects of individual trees on the solar radiation climate of small buildings. Urban Ecol. 9:337–359. doi:10.1016/0304-4009(86)90008-2

Hogg, A., J. Uddling, D.S. Ellsworth, M.A. Carrol, S. Pressley, B. Lamb, and C. Vogel. 2007. Stomatal and non-stomatal fluxes of ozone to a northern mixed hardwood forest. Tellus B Chem. Phys. Meterol. 59:514–525. doi:10.1111/j.1600-0889.2007.00269.x

IPCC. 2014. Climate change 2014: Impacts, adaptation, and vulnerability. Part A: Global and sectoral aspects. In: C.B. Field, V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White, editors, Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge Univ. Press, Cambridge, UK and New York.

Isaaks, E.H., and R.M. Srivastava. 1989. An introduction to applied geostatistics. Oxford Univ. Press, New York.

i-Tree. 2013. i-Tree species selector user's manual 4.0. itreetools.org/resources/manuals/i-tree%20Species%20Users%20Manual.pdf (accessed 10 June 2013).

Jardine, K.J., R.K. Monson, L. Abrell, S.R. Saleska, A. Arneth, A. Jardine, F.Y. Ishida, A.M.Y. Serrano, P. Artaxo, T. Karl, S. Fares, A. Goldstein, F. Loreto, and T. Huxman. 2012. Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein. Glob. Change Biol. 18:973–984. doi:10.1111/j.1365-2486.2011.02610.x

Kim, H., J. Woo, R. Park, C. Song, J. Kim, S. Ban, and J. Park. 2014. Impacts of different plant functional types on ambient ozone predictions in the Seoul Metropolitan Areas (SMAs), Korea. Atmos. Chem. Phys. 14:7461–7484. doi:10.5194/acp-14-7461-2014

Koetz, B., G. Sun, F. Morsdorf, K. Ranson, M. Kneubühler, K. Itten, and B. Allgöwer. 2007. Fusion of imaging spectrometer and LIDAR data over combined radiative transfer models for forest canopy characterization. Remote Sens. Environ. 106:449–459. doi:10.1016/j.rse.2006.09.013

Kroeger, T., F.J. Escobedo, J.L. Hernandez, S. Varela, S. Delphin, J.R.B. Fisher, and J. Waldron. 2014. Reforestation as a novel abatement and compliance measure for ground-level ozone. Proc. Natl. Acad. Sci. USA 111:E4204–E4213. doi:10.1073/pnas.1409785111

Kurpius, M.R., and A.H. Goldstein. 2003. Gas-phase chemistry dominates O3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere. Geophys. Res. Lett. 30:1371. doi:10.1029/2002GL016785

Laisk, A., O. Kull, and H. Moldau. 1989. Ozone concentration in leaf intercellular air spaces is close to zero. Plant Physiol. 90:1163–1167. doi:10.1104/pp.90.3.1163

Levy, J.I., S.M. Chemerynski, and J.A. Sarnat. 2005. Ozone exposure and mortality: An empiric bayes metaregression analysis. Epidemiology 16:458–468. doi:10.1097/01.ede.0000165820.08301.b3

Loreto, F., and S. Fares. 2007. Is ozone flux inside leaves only a damage indicator? Clues from volatile isoprenoid studies. Plant Physiol. 143:1096–1100. doi:10.1104/pp.106.091892

Loreto, F., and V. Velikova. 2001. Isoprene produced by leaves protects the photosynthetic apparatus against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular membranes. Plant Physiol. 127:1781–1787. doi:10.1104/pp.010497

Löw, M., K. Herbinger, A.J. Nunn, K.-H. Häberle, M. Leuchner, C. Heerdt, H. Werner, P. Wipfler, H. Pretzsch, M. Tausz, and R. Matyssek. 2006. Extraordinary drought of 2003 overrules ozone impact on adult beech trees (*Fagus sylvatica*). Trees (Berl.) 20:539–548. doi:10.1007/s00468-006-0069-z

Manes, F., G. Incerti, E. Salvatori, M. Vitale, C. Ricotta, and R. Costanza. 2012. Urban ecosystem services: Tree diversity and stability of tropospheric ozone removal. Ecol. Appl. 22:349–360. doi:10.1890/11-0561.1

Matyssek, R., A. Bytnerowicz, P.-E. Karlsson, E. Paoletti, M. Sanz, M. Schaub, and G. Wieser. 2007. Promoting the O_3 flux concept for European forest trees. Environ. Pollut. 146:587–607. doi:10.1016/j.envpol.2006.11.011

McClurkin, J.D., D.E. Maier, and K.E. Ileleji. 2013. Half-life time of ozone as a function of air movement and conditions in a sealed container. J. Stored Prod. Res. 55:41–47. doi:10.1016/j.jspr.2013.07.006

Moldau, H., and I. Bichele. 2002. Plasmalemma protection by the apoplast as assessed from above-zero ozone concentrations in leaf intercellular air spaces. Planta 214:484–487. doi:10.1007/s00425-001-0678-0

Morani, A. 2013. Selvicoltura urbana e pianificazione urbanistica: Principi e proposte per un'applicazione integrate. Ph.D. thesis, Università la Sapienza di Roma.

Morani, A., D. Nowak, S. Hirabayashi, G. Guidolotti, M. Medori, V. Muzzini, S. Fares, G.S. Mugnozza, and C. Calfapietra. 2014. Comparing i-Tree modeled ozone deposition with field measurements in a periurban Mediterranean forest. Environ. Pollut. 195:202–209. doi:10.1016/j.envpol.2014.08.031

Muller, J., C. Perciva, M. Gallagher, D. Fowler, M. Coyle, and E. Nemitz. 2010. Sources of uncertainty in eddy covariance ozone flux measurements made by dry chemiluminescence fast response analysers. Atmos. Meas. Tech. 3:163–176. doi:10.5194/amt-3-163-2010

Munger, W., H. Loescher, and H. Luo. 2012. Measurement, tower, and site design considerations. In: M. Aubinet, T. Vesala, and D. Papale, editors, Eddy covariance: A practical guide to measurement and data. Springer Netherlands, Dordrecht, the Netherlands. p. 21–58.

Neubert, A., D. Kley, J. Wildt, H.J. Segschneider, and H. Förstel. 1993. Uptake of NO, NO2 and O3 by sunflower (*Helianthus annuus* L.) and tobacco plants (*Nicotiana tabacum* L.): Dependence on stomatal conductivity. Atmos. Environ., A Gen. Topics 27:2137–2145. doi:10.1016/0960-1686(93)90043-X

Nowak, D.J., D.E. Crane, and J.C. Stevens. 2006. Air pollution removal by urban trees and shrubs in the United States. Urban For. Urban Green. 4:115–123. doi:10.1016/j.ufug.2006.01.007

Nowak, D.J., S. Hirabayashi, and E. Greenfield. 2014. Tree and forest effects on air quality and human health in the United States. Environ. Pollut. 193:119–129. doi:10.1016/j.envpol.2014.05.028

Nowak, D.J., R.E. Hoehn III, A.R. Bodine, E.J. Greenfield, T.A. Endreny, and R. Henry. 2013. Assessing urban forest effects and values: Toronto's urban forest. US Forest Service, Newton Square, PA.

Nunn, A., A. Kozovits, I. Reiter, C. Heerdt, M. Leuchner, C. Lutz, X. Liu, M. Low, J. Winkler, T. Grams, K. Haberle, H. Werner, P. Fabian, H. Rennenberg, and R. Matyssek. 2005. Comparison of ozone uptake and sensitivity between a phytotron study with young beech and a field experiment with adult beech (*Fagus sylvatica*). Environ. Pollut. 137:494–506. doi:10.1016/j.envpol.2005.01.036

Paoletti, E. 2009. Ozone and urban forests in Italy. Environ. Pollut. 157:1506–1512. doi:10.1016/j.envpol.2008.09.019

Paoletti, E., and N. Grulke. 2010. Ozone exposure and stomatal sluggishness in different plant physiognomic classes. Environ. Pollut. 158:2664–2671. doi:10.1016/j.envpol.2010.04.024

Rummel, U., C. Ammann, G.A. Kirkman, M.A.L. Moura, T. Foken, M.O. Andreae, and F.X. Meixner. 2007. Seasonal variation of ozone deposition to a tropical rain forest in southwest Amazonia. Atmos. Chem. Phys. 7:5415–5435. doi:10.5194/acp-7-5415-2007

Sgrigna, G. 2011. Atmospheric pollutants absorption by urban forest: Perugia, a case study. MS thesis, Università di Bologna.

Simpson, D., A. Benedictow, H. Berge, R. Bergstrom, L.D. Emberson, H. Fagerli, C.R. Flechard, G.D. Hayman, M. Gauss, J.E. Jonson, M.E. Jenkin, A. Nyıri, C. Richter, V.S. Semeena, S. Tsyro, J. Tuovinen, A. Valdebenito, and P. Wind. 2012. The EMEP MSC-W chemical transport model: Technical description. Atmos. Chem. Phys. 12:7825–7865. doi:10.5194/acp-12-7825-2012

Sprintsin, M., J.M. Chen, A. Desai, and C.M. Gough. 2012. Evaluation of leaf-to-canopy upscaling methodologies against carbon flux data in North America. J. Geophys. Res. Biogeosciences 117:G01023.

Tholl, D., W. Boland, A. Hansel, F. Loreto, U.S.R. Röse, and J.-P. Schnitzler. 2006. Practical approaches to plant volatile analysis. Plant J. 45:540–560. doi:10.1111/j.1365-313X.2005.02612.x

Tie, X., S. Madronich, G. Li, Z. Ying, A. Weinheimer, E. Apel, and T. Campos. 2009. City plumes during the MIRAGE-Mex field campaign using the WRF-Chem Model. Atmos. Chem. Phys. 9:4621–4638. doi:10.5194/acp-9-4621-2009

Tuovinen, J.-P., M. Ashmore, L. Emberson, and D. Simpson. 2004. Testing and improving the EMEP ozone deposition module. Atmos. Environ. 38:2373–2385. doi:10.1016/j.atmosenv.2004.01.026

Vautard, R., M. Beekmann, J. Roux, and D. Gombert. 2001. Validation of a hybrid forecasting system for the ozone concentrations over the Paris area. Atmos. Environ. 35:2449–2461. doi:10.1016/S1352-2310(00)00466-0

Vitale, M., G. Gerosa, A. Ballarin-denti, and F. Manes. 2005. Ozone uptake by an evergreen Mediterranean forest (*Quercus ilex* L.) in Italy: Part II. Flux modelling: Upscaling leaf to canopy ozone uptake by a process-based model. Atmos. Environ. 39:3267–3278. doi:10.1016/j.atmosenv.2005.01.057

Wang, D., T. Hinckley, A. Cumming, and J. Braatneb. 1995. A comparison of measured and modeled ozone uptake into plant leaves. Environ. Pollut. 89:247–254. doi:10.1016/0269-7491(94)00078-R

Wittig, V.E., E.A. Ainsworth, and S.P. Long. 2007. To what extent do current and projected increases in surface ozone affect photosynthesis and stomatal conductance of trees? A meta-analytic review of the last 3 decades of experiments. Plant Cell Environ. 30:1150–1162. doi:10.1111/j.1365-3040.2007.01717.x

Wittig, V.E., E.A. Ainsworth, S. Naidu, D. Karnosky, and S. Long. 2009. Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: A quantitative meta-analysis. Glob. Change Biol. 15:396–424. doi:10.1111/j.1365-2486.2008.01774.x

Yang, J., J. McBride, J. Zhou, and Z. Sun. 2005. The urban forest in Beijing and its role in air pollution reduction. Urban For. Urban Green. 3:65–78. doi:10.1016/j.ufug.2004.09.001

Zahn, A., J. Weppner, H. Widmann, K. Schlote-Holubek, B. Burger, T. Kühner, and H. Franke. 2012. A fast and precise chemiluminescence ozone detector for eddy flux and airborne application. Atmos. Meas. Tech. 5:363–375. doi:10.5194/amt-5-363-2012

Zona, D., B. Gioli, S. Fares, T. De Groote, K. Pilegaard, A. Ibrom, and R. Ceulemans. 2014. Environmental controls on ozone fluxes in a poplar plantation in Western Europe. Environ. Pollut. 184:201–210. doi:10.1016/j.envpol.2013.08.032

Zscheppang, A., F. Manes, G. La Torre, A. Boccia, S. Trueman, D. Sarigiannis, K. Pavlos, B. Artíñano, C. Perrino, R. Fernández Patier, M. Rigby, S. Jankovic, and W. Kirch. 2008. Methodology for measuring environmental health within Europe: Health Risk from Environmental Pollution Levels in Urban Systems (HEREPLUS). Ital. J. Public Health 5:284–287.