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Comparing *i-Tree* modeled ozone deposition with field measurements in a periurban Mediterranean forest

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ABSTRACT

Ozone flux estimates from the *i-Tree* model were compared with ozone flux measurements using the Eddy Covariance technique in a periurban Mediterranean forest near Rome (Castelporziano). For the first time *i-Tree* model outputs were compared with field measurements in relation to dry deposition estimates. Results showed generally a good agreement between predicted and measured ozone fluxes (least sum square = 5.6 e^{-4}) especially when cumulative values over the whole measurement campaign are considered. However at daily and hourly time-step some overestimations were observed in estimated values especially in hot dry periods. The use of different *m* values in the Ball–Berry formula in the different periods, produced the best fit between predicted and measured ozone fluxes. This suggests that a variable value for the coefficient *m* accounting for water availability may be appropriate to improve model estimates for Mediterranean and drought prone regions.

1. Introduction

High levels of ozone (O_3), a principal component of photochemical smog, are often observed in Italy due to its Mediterranean climate with high summer air temperatures and solar radiation triggering photochemical activity (Cieslik, 2009). Photochemical pollution is a form of atmospheric pollution originating from the exposure of volatile organic compounds and nitrogen oxides to the UV component of sunlight. Plants are natural sinks for O_3 (Fares et al., 2012, 2010; Kurpius and Goldstein, 2003) and their role in reducing O_3 levels can be particularly important in urban and periurban areas (Cardelino and Chameides, 1990; Nowak et al., 2000a; Taha, 1996). Ozone removal by trees occurs through stomatal uptake and non-stomatal deposition (Fares et al., 2012) moreover chemical reaction with biogenic volatile organic compounds (BVOCs) emitted by plants, and NO_x can contribute to ozone scavenging (Fares et al., 2012, 2010; Kurpius and Goldstein, 2003). Several models have been developed to simulate ozone fluxes at leaf, ecosystem and or regional level (Beltman et al., 2013; Emberson et al., 2000; Grulke et al., 2007; Grünhage et al., 2000), the *i-Tree* model (formerly Urban Forest Effects, UFORE, model) was developed in the United States to estimate urban forest structure and ecosystem services including carbon storage and sequestration, air pollution removal, BVOCs emission and savings in building energy use. The pollution removal module of *i-Tree* is used to quantify dry deposition (i.e. pollution removal during non-precipitation periods) of pollutants to tree and forest canopies in urban areas (Hirabayashi et al., 2011; Nowak et al., 2006, 2000b, 1998). A basic assumption and potential limitation of *i-Tree*'s pollution deposition module is that urban trees are assumed to have adequate soil moisture for tree transpiration and gas exchange (e.g. due to human watering of trees in cities during drought conditions). This assumption can lead to an overestimation of pollutant removal by leaves when trees are under drought conditions because: the water deficit induces the stomata closure therefore the pollutant removal reduction (Manes et al., 1998). This limitation is of particular concern in Mediterranean climates, usually characterized by long dry summers coupled with high temperature often inducing drought conditions. The Mediterranean regions of Italy are also characterized by tree and shrub species such as *Quercus ilex*, *Quercus suber*, *Pinus pinea* and *Laurus nobilis* which are also the

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main species in the study area of the present study (Castelporziano) (Kesselmeier et al., 1996).

In this work, O_3 fluxes measured with the Eddy Covariance technique were compared to *i-Tree* model estimates. There are few studies (Tuovinen et al., 2004) in which model validation with flux measures have been conducted, especially for O_3 fluxes in a peri-urban area (Fares et al., 2013a). In fact, most flux-model validation has focused on carbon dioxide (CO_2) and energy fluxes (Medlyn et al., 2005). In particular this is the first study comparing estimates from the *i-Tree* model with field data and moreover in an environment characterized by different plant species and different climate from the North American area where the model has been generated.

The objectives of this paper are: 1) to compare *i-Tree* model estimates of O_3 flux with Eddy Covariance measurements from a forest stand proximal to Rome, Italy, and 2) to analyze the sensitivity of the model to specific physiological parameters used in the model in order to suggest a parameterization of the model to better estimate O_3 fluxes in the Mediterranean environment.

2. Materials and methods

2.1. Site description and field measurements

The experimental site was inside the Presidential Estate of Castelporziano, an area of about 6000 ha located along the Latium coast 25 km SW from the center of Rome, Italy. The flux tower was located in "Castello" (41.745009N, 12.409249E), 80 m a.s.l. and 7 km from the seashore of the Thyrrenian Sea. Castelporziano belongs to a Thermo-Mediterranean region (Blasi, 1994) with prolonged warm and dry summer periods and mild to cool winter. The soil of the experimental site had a sandy texture (sand content >60%) with low water-holding capacity (Fares et al., 2013b).

The site is characterized by a mixed Mediterranean forest dominated by *Laurus nobilis* in the understory and *Quercus ilex* in the overstory (Table 1). There were also a few, but large individual trees of *Quercus suber* and *Pinus pinea*. The mean height of the overstory was 25 m, while the leaf Area Index (LAI) was 4.76 m^2_{leaf}/m^2_{ground}, including both understory and overstory (Fares et al., 2013a). More detailed information on the experimental site can be found in Tirone et al. (2003).

Flux measurements were carried out for 74 days in 2011 (days 268–342). The flux tower was 35 m tall. For atmospheric O_3 measurements, air was sampled continuously at one inlet at a 35 m height through Teflon tubes and a Teflon filter (PFA holder, PTFE membrane, pore size 2 μm) located 30 cm from the inlet. Ozone was measured with a UV absorption monitor (2B Technology). The filters were replaced every two weeks to avoid contamination or flow problems. Fast response measurements of O_3 were carried out through a Teflon tube (35 m) and filter inlet by chemiluminescence with an instrument custom developed by the National Oceanic and Atmospheric Administration (NOAA, Silver Spring, MD, Bauer et al., 2000). The chemiluminescence detector was calibrated against 30 min average O_3 concentrations from the second monitor which measured air sampled from the same inlet height. Water and CO_2 concentrations were measured with a closed path infrared gas analyzer (LI-6262, Lincoln, NE, USA). Ozone and water concentrations were correlated with the vertical wind velocity according to the eddy covariance technique. Details on the technique and instrumentations can be found in Fares et al. (2013b).

2.2. i-Tree model inputs

To run the *i-Tree* model for the flux tower forest site, specific tree data were collected within the flux tower footprint. Total height, height to crown base, crown width and other tree variables (Nowak et al., 2008) were measured for all trees within five randomly located 20 m diameter field plots. In addition to tree and forest parameters, local hourly O_3 concentration and meteorological data were used as input as requested by the model (Nowak et al., 2006). Hourly meteorological data as air temperature, relative humidity, precipitation, PAR (Photosynthetically Active Radiation), atmospheric pressure, wind speed and wind direction for 2011 were obtained for the weather station located at the experimental site. Data of soil water content, used to indicate the water shortage of vegetation was continuously collected at Campo di Rota (a station with similar soil characteristics and vegetation cover very close to the flux tower). Hourly O_3 concentrations were collected from measures taken on the flux tower.

Table 1
Species composition of the sampling site in the Castelporziano estate.

Species	%
Laurus nobilis	48.9
Quercus ilex	20.5
Pinus pinea	6.8
Quercus suber	6.8
Rhamnus spp	5.7
Arbutus unedo	4.5
Phillyrea spp	4.5
Crataegus monogyna	1.1
Tamarix spp	1.1

2.3. Model calculations

In *i-Tree*, pollutant flux is calculated by multiplying deposition velocity and pollutant air concentration:

$$F = V_d \cdot C \cdot 3600 \tag{1}$$

where

F = Pollutant flux ($g\ m^{-2}\ h^{-1}$)
V_d = Deposition velocity ($m\ s^{-1}$)
C = Air pollutant concentration ($g\ m^{-3}$)

O_3 deposition velocity (V_d) is calculated as the inverse of the sum of the following resistances expressed in $s\ m^{-1}$: aerodynamic (R_a), quasi-laminar boundary layer (R_b) and canopy resistance (R_c) (Baldocchi et al., 1987). Hourly meteorological and canopy structural parameters data are used to calculate R_a and R_b while R_c is calculated as:

$$\frac{1}{R_{c,In\ Leaf}} = \frac{1}{r_s + r_m} + \frac{1}{r_{soil}} + \frac{1}{r_t} \tag{2}$$

Where

r_s = stomatal resistance ($s\ m^{-1}$)
r_m = mesophyll resistance ($s\ m^{-1}$)
r_{soil} = soil resistance (=2941 $s\ m^{-1}$)
r_t = cuticular resistance ($s\ m^{-1}$)

For more details on variables and equations see Hirabayashi et al. (2010).

The *i-Tree* model estimates stomatal conductance for each canopy layer using the Ball–Berry formula based on a multi-layer/big leaf model. Stomatal conductance (g_s) is computed as a function of the leaf photosynthetic rate (A), relative humidity (rh) and surface CO_2 concentration (C_s).

$$g_s = \frac{mArh}{C_s} + b' \tag{3}$$

where

m = Dimensionless slope (=10)
A = Net CO_2 uptake rate of a leaf ($\mu mol\ m^{-2}\ s^{-1}$)
rh = Relative humidity (calculated from local weather data)
b' = Zero intercept when A is equal to or less than zero
C_s = Leaf surface CO_2 concentration (ppm)

Ball (1988) and Ball et al. (1987) proposed the above equation to describe the response of g_s to the rate of net CO_2 uptake (A), relative humidity (rh) and CO_2 mole fraction (Cs) of the air at the leaf surface. The terms m and b′ are, respectively, the slope and intercept obtained by linear regression analysis of data from gas exchange studies with single leaves in a ventilated, temperature-controlled cuvette. C_s can be calculated as Baldocchi (1994)

$$C_s = C_a - \frac{A}{g_b} \tag{4}$$

where

C_a = Atmosphere's CO_2 concentration (=380 ppm)
g_b = Conductance across the laminar boundary layer of a leaf ($mol\ m^{-2}\ s^{-1}$) for CO_2 exchange

$$g_b = \frac{1}{R_a + R_{b,CO_2}} \tag{5}$$

These parameters are routinely evaluated in gas exchange studies, as described by Ball (1987) and Collatz et al. (1991).

Leaf photosynthesis is a function of the carboxylation (V_c), oxygenation (V_o) and dark respiration (R_d) rates of CO_2 exchange between the leaf and the atmosphere (Baldocchi, 1994; Farquhar et al., 1980). A is expressed as:

$$A = V_c - 0.5V_o - R_d \tag{6}$$

where

V_c = Carboxylation rate of CO_2 exchange between leaf and atmosphere (μmol m^{-2} s^{-1})

V_o = Oxygenation rate of CO_2 exchange between leaf and atmosphere (μmol m^{-2} s^{-1})

R_d = Dark respiration rate of CO_2 exchange between leaf and atmosphere (μmol m^{-2} s^{-1})

The term $V_c - 0.5V_o$ is expressed by Farquhar et al. (1980) and Baldocchi (1994) as

$$V_c - 0.5V_o = min(W_c, W_j)\left(1 - \frac{\Gamma}{C_i}\right) \tag{7}$$

where

W_c = Carboxylation rate when ribulose bisphosphate (RuBP) carboxylase/oxygenase is saturated (μmol m^{-2} s^{-1})

W_j = Carboxylation rate when RuBP regeneration is limited by electron transport (μmol m^{-2} s^{-1})

min (W_c, W_j) = Minimum value between these two rate variables

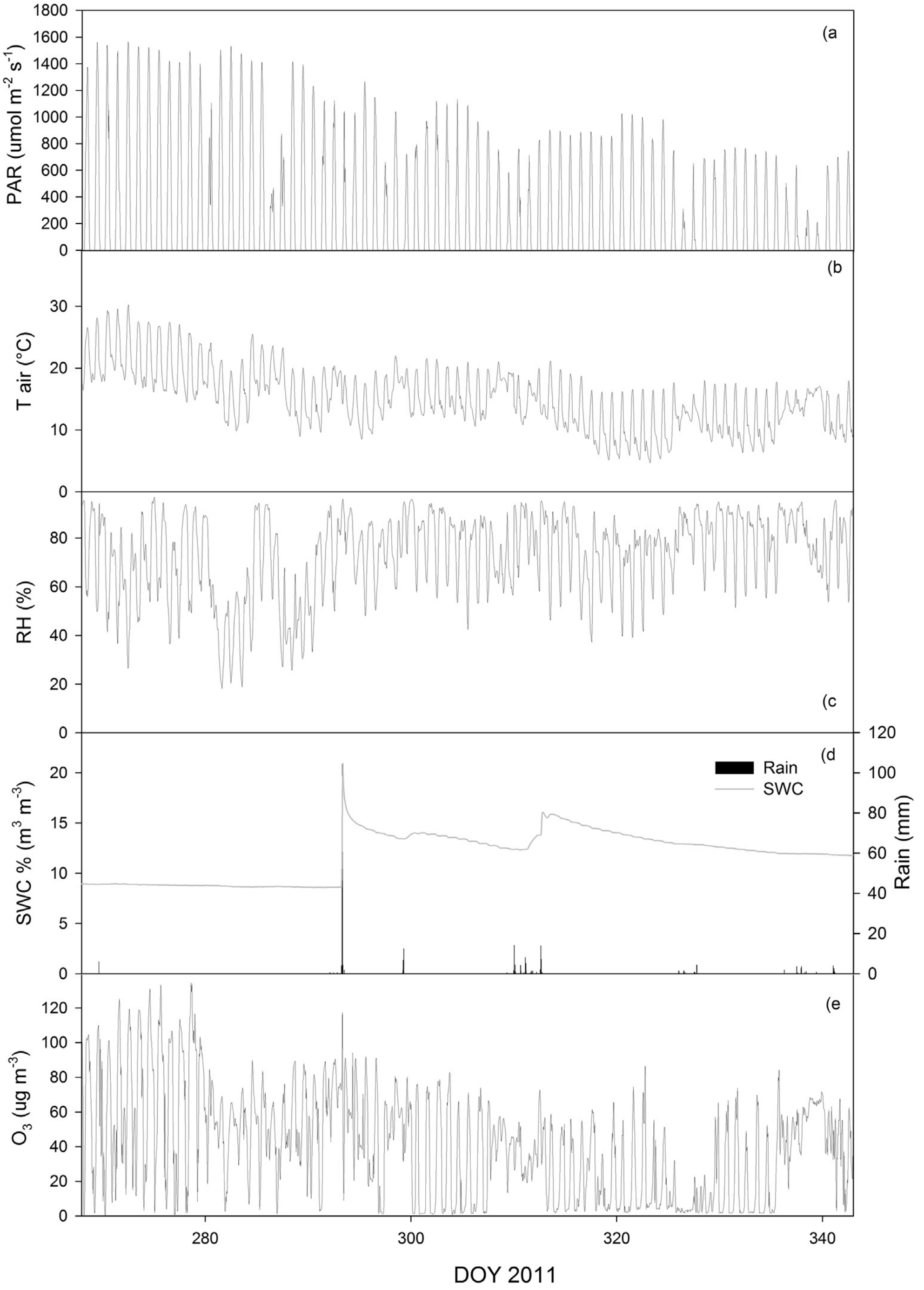

Fig. 1. Temporal course of Photosynthetic active radiation (PAR) (a), Temperature (b) relative humidity (RH) (c), soil water content SWC and precipitation (d) and O_3 concentration (e) during the sampling campaign measured by the monitoring station located in the Castelporziano estate.

Γ = CO_2 compensation point in the absence of dark respiration (ppm)
C_i = Internal CO_2 concentration (ppm)

If W_c is minimal, these coefficients correspond to

$$W_c = V_c - 0.5V_o = \frac{V_{cmax}(C_i - \Gamma)}{C_i + K_c\left(1 + \frac{[O_2]}{K_o}\right)} \qquad (8)$$

where

V_{cmax} = Maximum carboxylation rate when RuBP carboxylase/oxygenase is saturated
K_c = Michaelis–Menten coefficients for CO_2 (=333 μbars at 25 °C)
K_o = Michaelis–Menten coefficients for O_2 (=295 mbars at 25 °C)
Γ = CO_2 compensation point in the absence of dark respiration = $0.105^*K_c^*[O_2]/K_o$
$[O_2]$ = Partial pressures of O_2 in the intercellular air space (=210 μmol mol^{-1})

If W_j is minimal these coefficients correspond to

$$W_j = V_c - 0.5V_o = \frac{J(C_i - \Gamma)}{4C_i + 8\Gamma} \qquad (9)$$

where J is the potential rate of electron transport and expressed for sunlit leaves in the jth layer of the canopy as (Harley et al., 1992)

$$J = \frac{\alpha PAR_{sun,j}}{\sqrt{1 + \frac{\alpha^2 PAR^2_{sun,j}}{J^2_{\max}}}} \qquad (10)$$

and, for shaded leaves in the jth layer of the canopy

$$J = \frac{\alpha PAR_{shade,j}}{\sqrt{1 + \frac{\alpha^2 PAR^2_{shade,j}}{J^2_{\max}}}} \qquad (11)$$

α = Efficiency of light energy conversion on an incident light basis (=0.055 mol electrons/mol photons)
$PAR_{sun,j}$ = Flux density of PAR on sunlit leaves in the jth layer of canopy (μE m^{-2} s^{-1})
$PAR_{shade,j}$ = Flux density of PAR on shaded leaves in the jth layer of canopy (μE m^{-2} s^{-1})
$J_{\max}$ = Light-saturated rate of electron transport (=171 at 25 °C for trees)

The temperature dependencies of the $J_{\max}$ can be represented by Arrhenius Equation (Farquhar et al., 1980);

$$J_{\max} = J_{\max}(25\,^\circ\mathrm{C})\exp\left[\frac{(T-298)E}{298RT}\right] \qquad (12)$$

where

E = Relevant activation energy (kJ mol^{-1})
R = Universal gas constant (J mol^{-1} K^{-1})
T = Absolute leaf temperature (K)

More detailed information on the methods and code can be found in UFORE-D Model Descriptions at www.itreetools.org/resources/archives.php and Hirabayashi et al. (2011).

Based on the formulas above, three variables (V_{cmax}, $J_{\max}$ and m) involved in calculating g_s were chosen to test the sensitivity of the model and to improve the estimates agreement with the eddy covariance measurements. V_{cmax} and $J_{\max}$ are involved in the estimation of A in the model, while the coefficient m is directly involved in the Ball–Berry formula.

2.4. Model parameterization and validation

To parameterize the model, photosynthetic parameters as maximum rate of carboxylation (V_{cmax}) and maximum rate of electron transport ($J_{\max}$), were selected from literature for species found in the sampling area (Niinemets et al., 2002; Wullschleger, 1993). The coefficient m in the Ball–Berry formula was estimated by leaf physiological measurements performed in different moments along the campaign for the most important species found in the tower footprint area. The measurements were carried out with a portable infrared gas analyzer (LI-6400; Li-Cor, Lincoln, NE, USA) to determine photosynthesis, stomatal conductance, transpiration, and intercellular CO_2 concentration. Measurements were done under a PAR of 1000 μmol m^{-2} s^{-1}, at a leaf temperature of 30 °C, and at a relative humidity between 50 and 60%. To calculate a coefficient m representative for all species found in the footprint area, we calculated a weighted average of m according to the species-specific leaf area since in the model canopy cover is crucial to estimate pollutants removal. The calculated m value was 6.49.

A one-way sensitivity analysis to specific physiological parameters was performed to parameterize the model for the Mediterranean region. To test the sensitivity of the model to stomatal conductance for sunlit/shaded leaves in each layer, several paired values of V_{cmax} and $J_{\max}$ (30–54, 55–99, 76–137, 100–180 μmol m^{-2} s^{-1}, respectively) and values of m from 10 to 3 were used to run the model. V_{cmax} values were changed from 30 to 100 μmol m^{-2} s^{-1}, and $J_{\max}$ values were changed accordingly based on a constant $J_{\max}/V_{cmax}$ ratio of 1.798 (from Dreyer et al., 2001).

Hourly O_3 flux estimated by *i-Tree* model was compared with the O_3 flux measured by Eddy Covariance technique in Castelporziano. The Eddy Covariance data used for comparison were not gap-filled since the duration of flux measurements was not long enough to allow reliable estimates of missing data using conventional gap-filling methods (Moffat et al., 2007). After removing zero and negative values, the data used for the analysis performed in this study were 1609, representing the 83% of the 30-min samples recorded during the observation period. This work focused only on daytime hours (from 6 AM to 6 PM), because *i-Tree* considers the nocturnal O_3 stomatal flux equal to zero assuming stomata are closed. Moreover, during night-time hours, turbulence might be too low to attain eddy covariance principles (Aubinet, 2008), thus O_3 flux measurements at night might be subjected to high uncertainties.

Daily comparison between model estimates and eddy covariance measurements were performed because of the great daily variability of meteorological conditions that affects both estimations and measures. Tests were done for evaluating an agreement of model estimates with observed O_3 fluxes by setting m equal to 10 (the original model value), 6.49 (a weighted average of the different species measured in the field, as described above), and 3 (chosen analyzing least squares and cumulative O_3 fluxes for the whole campaign), while b was set to 0, C_a was set to 380 ppm indicated as constant and realistic by Gratani and Varone (2006).

Least squares estimates between observed and estimated O_3 fluxes were calculated to evaluate the agreement between modeled and observed O_3 fluxes over the 74-day measurement campaign. This method minimizes the sum of squares of the residuals: $\sum_{i=1}^{n}(xi - yi)^2$, where x_i is the observed value while y_i is the modeled value (Wang et al., 2001). Runs with lowest least squares values were used to determine the values that created the best fit between observed and estimated values.

3. Results and discussion

The beginning of the experimental campaign was characterized by a typical summer dry period (DOY 268–292), during which photosynthetic active radiation (PAR) and air temperature (Tair) were higher, while relative humidity (Rh) and relative soil water content (SWC) were lower (Fig. 1) as compared to the second part of

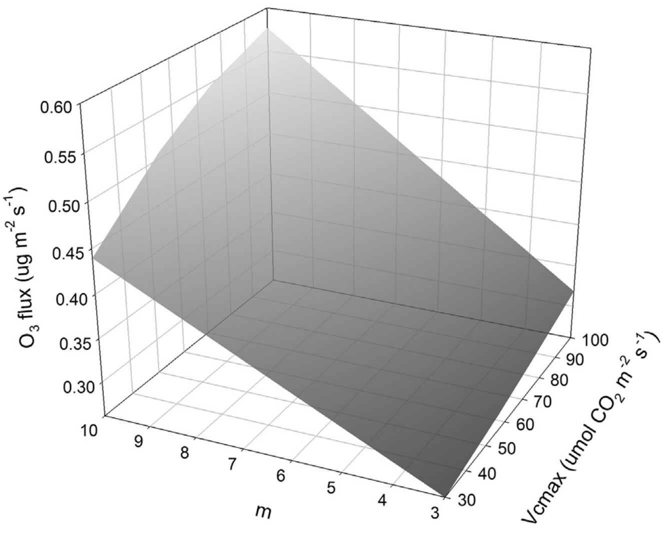

Fig. 2. Estimated O_3 flux rates (μg m^{-2} s^{-1}) at different V_{cmax} (μmol CO_2 m^{-2} s^{-1}) and m values. The coefficient m values varied from 10 to 3, while V_{cmax} values from 100 to 30.

Table 2
Agreement between observed and modeled O_3 fluxes using different m values.

Measure	Observed	$m = 10$	$m = 6.49$	$m = 3$
Cumulative flux ($g\ O_3\ m^{-2}$)	0.3461	0.5065	0.4186	0.3504
Least squares sum	na	0.000562736	2.06152E-11	2.17E-11
% overestimation	na	46.3	22.1	0.064

the campaign. After the rains occurred on DOY 293 SWC peaked, whereas PAR and Tair declined (Fig. 1). Along with PAR and Tair, O_3 concentration was higher during the warmer days with maximum hourly O_3 value recorded of 135 μg m^{-3} (Fig. 1). Observed O_3 concentrations followed patterns similar to Tair and PAR. Ozone concentrations were higher in Castelporziano when winds came from the seashore and lower when they came from the city area of Rome, because of O_3 reactivity with nitrogen monoxide and BVOCs that may have an important role in O_3 removal (Fares et al., 2013b; Gerosa et al., 2005). Averaging the entire campaign the observed O_3 flux was $1.19*10^{-7}$ g m^{-2} s^{-1}. Also for observed O_3 flux, the campaign can be distinguished in two main periods divided by the rain event of DOY 293: during the warmer days (before DOY 293) the mean observed O_3 flux was $1.61*10^{-7}$ g m^{-2} s^{-1} while in the second part (after DOY 293) $9.56*10^{-8}$ g m^{-2} s^{-1}. Although the first part was characterized by a stronger water limitation, higher temperature and solar radiation, higher O_3 removal by vegetation can be explained by higher O_3 concentration and thus higher flux (Fiscus et al., 1997).

Considering the most contrasting periods for soil water availability, the closest three days of data available before (DOY 290–292) and after (DOY 297–299) the rain event (DOY 293), show mean observed O_3 flux of $1.42*10^{-7}$ g m^{-2} s^{-1} before the rain and $1.90*10^{-7}$ g m^{-2} s^{-1} after the rain event. This increase is probably due to greater soil water availability, thus leading to higher stomatal conductance.

Overall, the model estimated an average O_3 flux 60% higher before the rain event than after the event. The progressive decrease in Tair and PAR, relevant after DOY 293, triggered a decrease in O_3 flux estimated by the model. Furthermore, since flux is calculated by multiplying O_3 concentration by V_d, higher O_3 concentration also means higher O_3 flux. Also as shown above, O_3 concentration was higher during the warm period (Fig. 1).

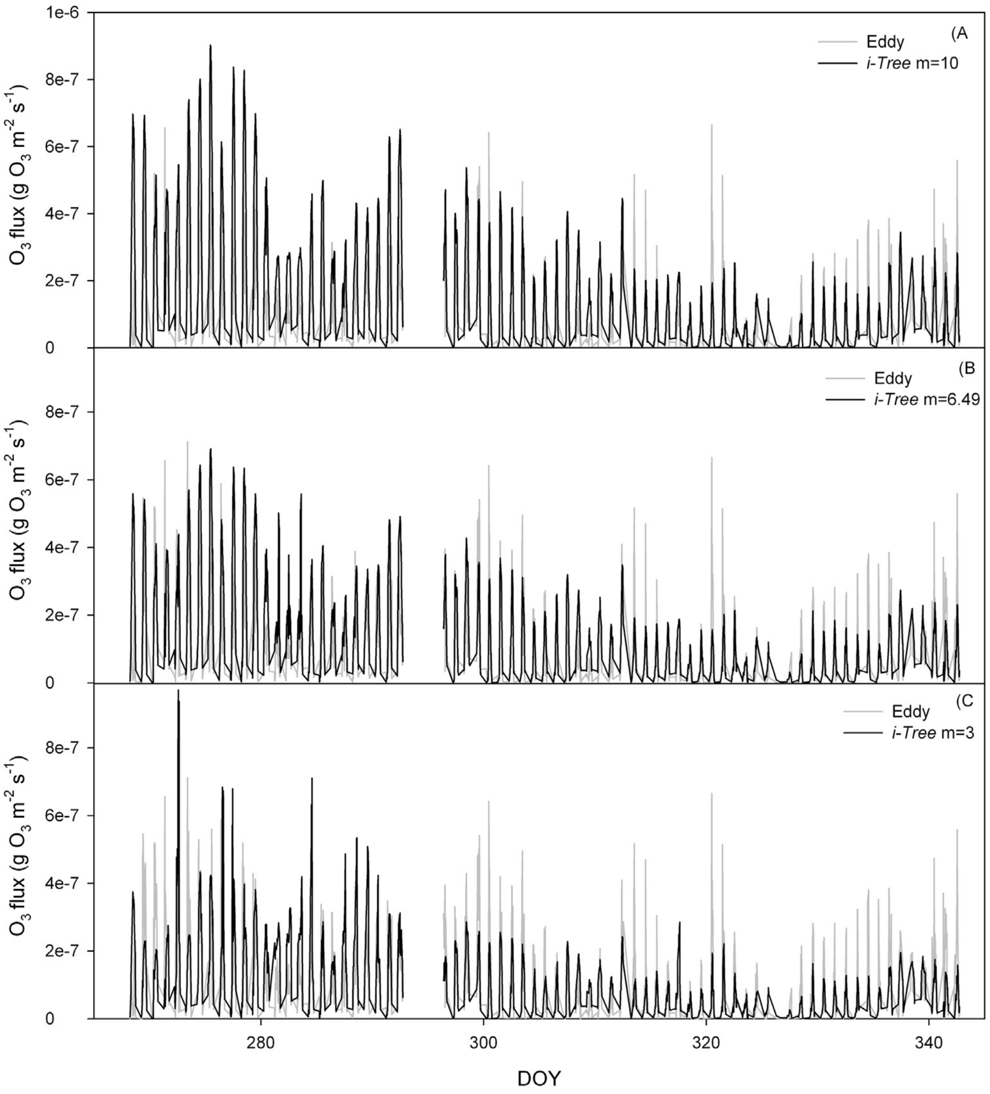

Fig. 3. Comparison between observed O_3 flux (gray lines) and estimated O_3 flux (black lines) with three different m values, respectively, 10 (A), 6.49 (B) and 3 (C), over the all measuring period.

The sensitivity analysis showed that the model is more sensitive to changes in the coefficient *m* rather than to variations of V_{cmax} and J_{max}. A decrease in the coefficient *m* from 10 to 3 produced a decrease in O_3 flux estimates of about 40%, while a decrease of V_{cmax} from 100 to 30 μmol m^{-2} s^{-1} produced a decrease in O_3 flux estimates of about 20% (Fig. 2). When increasing the value of *m*, the response of the model was linear. Increasing V_{cmax} or *m* led to increased O_3 flux. However, *m* had a greater effect on increasing O_3 flux than V_{cmax}. Based on this result, we focused on the coefficient *m* to improve an agreement between observed and estimated O_3 fluxes. This approach tested responses to parameters individually and did not account for compensating effects among parameters. Nevertheless, in the case of the Ball–Berry equation, all the main variables involved were taken into account. Tests of the sensitivity of *i-Tree*'s O_3 removal estimates to LAI (Leaf Area Index) and meteorological variables found that deposition velocity (V_d) was sensitive to temperature and LAI, while photosynthetic active radiation (PAR) and wind speed had limited effects on V_d (Hirabayashi et al., 2011).

Model estimates with $m = 10$, that is the originally set value, overestimated the observed O_3 flux by more than 40% (Table 2). Water supply is a critical factor influencing O_3 fluxes in Castelporziano (Cieslik, 2009). A wider stomatal aperture increases evapotranspiration, thus O_3 flux through stomata (Gerosa et al., 2009). Although *i-Tree* estimates total O_3 flux without distinguishing stomatal and non-stomatal removal, some studies (Fares et al., 2013b, 2012, 2010; Fowler et al., 2001; Kurpius and Goldstein, 2003) highlighted the importance of distinguishing the two components in O_3 uptake by trees, demonstrating that non-stomatal component might be as important as the stomatal one. Effectively a recent study in the experimental site explained with the non-stomatal removal and photochemical reactions with NO_x and BVOCs the slight uncoupling between the peaks of O_3 concentrations and the peaks in O_3 fluxes (Fares et al., 2013b).

With a reduction of the coefficient *m* in the Ball–Berry formula from 10 to 6.49, i.e. the *m* value calculated for Castelporziano from gas exchange measurements, the model overestimation decreased from 46% to 22% (Table 2). Decreasing the coefficient *m* from 6.49 to 3 basically canceled the overestimation of cumulated O_3 fluxes (0.06%) (Table 2) inducing an underestimation of the modeled O_3 flux during cooler days, after the rain event (Fig. 3). A decrease in the observed O_3 flux after DOY 293 was caused by a decrease in temperature, that decreases photochemistry, O_3 concentration, thus O_3 fluxes, and also stomata opening. However, the agreement between modeled and observed values changed considerably with changing time (Fig 3) and the environmental conditions, such as changing temperature, PAR and humidity (Figs. 1 and 3). Considering the period of 3 days (DOY 290–292) before the rains, the driest of all the measurement campaign (soil water content <9%), the estimated flux with $m = 3$ showed the best agreement with observed values (Fig. 4A). The model modified with $m = 3$ overestimated the observed O_3 flux only by 16.95% while the modified model with $m = 6.49$ and with $m = 10$ (*i-Tree* default value) overestimated by 57.44% and 94.18%, respectively. The best agreement between modeled and measured values with $m = 3$ was confirmed by least squares sum (7.18 E-13). After DOY 296, when maximum temperature was around 20 °C and PAR was about 900 μmol m^{-2} s^{-1}, with some cloudy days, and soil water content above the 15% we observed the best estimation by the modified model with $m = 6.49$, that overestimated the observed values of 0.68% with the lowest least squares sum (8.04 E-13). In the same period the modified model with $m = 3$ underestimated the observed flux by 21%, while the original model with $m = 10$ overestimated the observed flux by 22% (Fig. 4B). Those differences demonstrates that the model works quite well but needs parameterization for the climates such as the Mediterranean one often characterized by drought conditions.

Mean daily least squares were higher during the first period of the measuring campaign and decreased in the second part of the campaign characterized by lower temperatures. The least squares sum increased with increasing temperature, decreasing the agreement between observed and modeled O_3 fluxes (Fig. 5A). Even if there is not a relevant correlation between least squares and daily mean air temperature (*T*) ($R^2 = 0.19$ for $m = 10$; $R^2 = 0.35$ for $m = 6.49$, $R^2 = 0.32$ for $m = 3$), model performance decreased with high temperature as the overestimation increased. Therefore, the fit between observed and modeled O_3 fluxes decreased with high temperature and high PAR and limited rain events, thus likely drought periods. Observed O_3 flux showed a weak correlation with *T* ($R^2 = 0.43$) while estimated O_3 fluxes, both with $m = 6.49$ and $m = 3$ (respectively $R^2 = 0.70$ and $R^2 = 0.54$) showed a significant correlation ($p < 0.001$) (Fig. 5B). Estimated O_3 flux with $m = 10$ showed almost no correlation with temperature ($R^2 = 0.09$). These results suggest that the coefficient *m* can help to account for drought effects in the model by varying the *m* coefficient

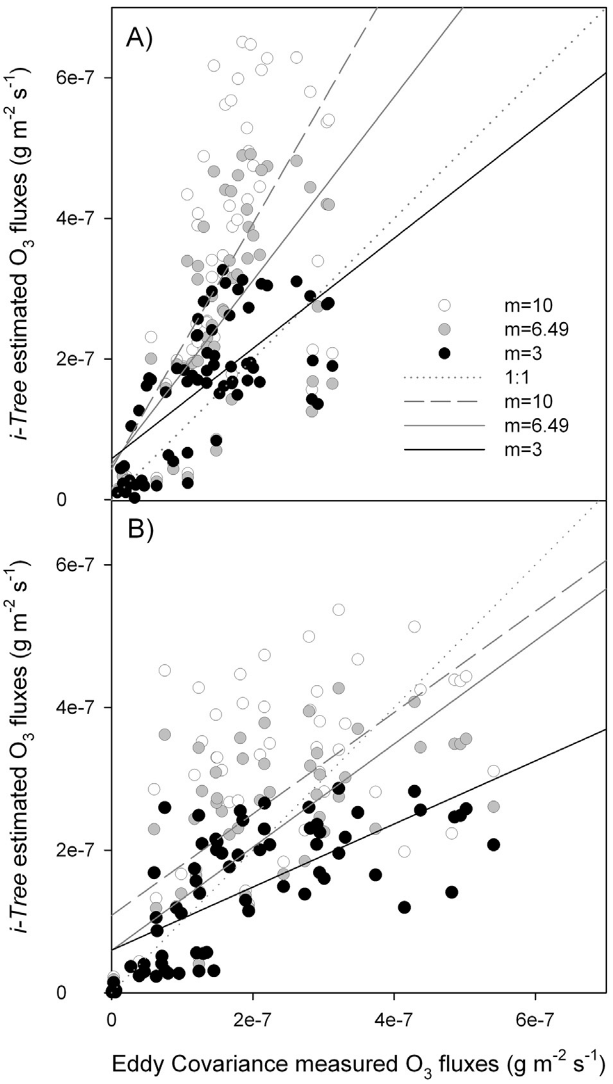

Fig. 4. Estimated vs. observed daily O_3 fluxes during A) driest period (DOY 290–292) and B) Wet period (DOY 297–300). White circles and dashed gray lines represent $m = 10$, gray circles and solid gray lines represent $m = 6.49$ and black circles and black lines represent $m = 3$. The dotted gray line represent the 1:1 line. Each correlation is significant at $p < 0.0001$.

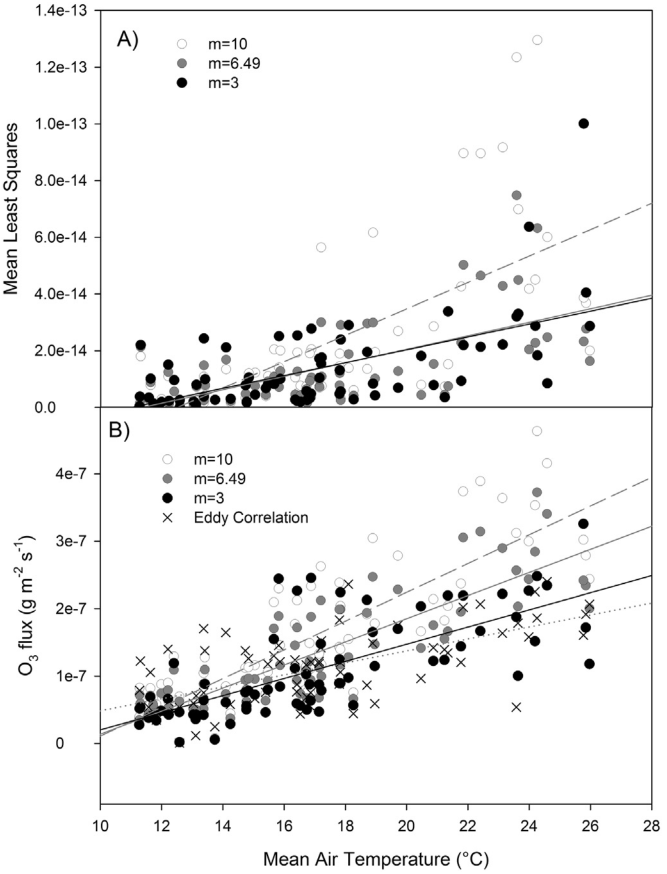

Fig. 5. A) Relationship between daily mean air temperature (°C) and daily mean least square. White circles and dashed gray lines represent $m = 10$, gray circles and solid gray lines represent $m = 6.49$ and black circles and black lines represent $m = 3$. Each correlation is significant at $p < 0.0001$. B) Relationship between daily mean air temperature (°C) and daily mean O_3 flux. White circles and dashed gray lines represent $m = 10$, gray circles and solid gray lines represent $m = 6.49$, black circles and black lines represent $m = 3$, black cross and gray dotted line represent the O_3 flux measured by eddy. Each correlation is significant at $p < 0.0001$.

depending upon meteorological conditions. The question of *m* being a constant or varying with soil water availability is still debated in the scientific community, with different studies showing controversial results: some researchers (Collatz et al., 1991; Harley and Tenhunen, 1991) considered *m* as a constant (10 ± 2) which is consistent when a plant has no water limitation, while under mild or severe drought conditions the value of *m* has been shown to change (Baldocchi, 1997; Sala and Tenhunen, 1996), similar to this study. However, detailed studies on how water stress affects *m* are still lacking (Xu and Baldocchi, 2003) and the effect of decreasing soil water availability on *m* is still discussed. Sala and Tenhunen (1996) assert that *m* decreases with drought, while Colello et al. (1998) state that it remains constant. Xu and Baldocchi (2003) showed how the Ball–Berry relationship can be applied under water stress conditions without modifications. Misson et al. (2004) showed how the parameter *m* varied significantly over the growing season, ranging from 4 to 18, but it did not show a significant relationship with soil water content. Further investigations are needed to unravel how the coefficient *m* varies with water stress.

4. Conclusions

i-Tree provided a good estimation of O_3 flux showing good agreement with measured flux by eddy covariance technique.

The sensitivity analysis of the model to specific parameters (V_{cmax}, J_{max} and *m*) involved in stomatal conductance calculation, showed that the model is more sensitive to changes in the coefficient *m* rather than to variations of V_{cmax} and J_{max}. The best fit between observed and modeled data was obtained with $m = 3$ during warmer days where overestimation was equal to 16.95% and with $m = 6.49$ during cooler days where overestimation was equal to 0.68%.

Results suggested that the coefficient *m* might not be a constant value, but it might change with soil water availability. Changing the coefficient *m* seems to account for stomatal limitation due to drought. Tree drought effects are not currently accounted for in *i-Tree*, but are crucial in the Mediterranean climate of Rome where plants are not commonly watered and summer is characterized by high temperature, high solar radiation and scarce precipitation. Changing *m* from a constant to a variable that changes depending on water availability may be a simple way to improve model performances in the Mediterranean climates and to account for drought effects on plant pollutant flux. Further investigations are necessary to verify whether these results are confirmed in the longer period (inter-annual variability) and also for other pollutants (e.g. SO_2 and NO_2).

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