Ozone dynamics in a Mediterranean Holm oak forest: comparison among transition periods characterized by different amounts of precipitation

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Abstract - Tropospheric ozone (O₃) is one of the most toxic compounds for plants in the atmosphere. The large amount of anthropogenic O₃ precursors in the urban areas promote O₃ formation, thus making Mediterranean forests located in periurban areas particularly vulnerable to this pollutant. O₃ flux measurements have been carried out using the Eddy Covariance technique over a Holm oak forest located 25 Km from Rome downtown, inside the Presidential Estate of Castelporziano (Italy). Two transition periods - early Spring and late Fall - in two consecutive years were examined. The uncommon low precipitation recorded in both transition periods in 2012 allowed to evaluate the influence of water availability on O₃ fluxes during seasons which are not commonly affected by drought stress. Overall, the forest canopy showed to be a net sink of O₃, with peak values of mean daily O₃ fluxes of -8.9 nmol m⁻²s⁻¹ at the beginning of flowering season and -4.6 nmol m⁻²s⁻¹ at the end of Fall. O₃ fluxes were partitioned between stomatal and non-stomatal sinks using the evaporative/resistive method based on canopy transpiration in analogy with an Ohm circuit. By comparison of the two years, water availability showed to be an important limiting factor during Spring, since in this season plants are more photosynthetically active and more sensitive to water availability, while in Fall, under conditions of low stomatal conductance, the dependence on water availability was less appreciated.

Keywords - ozone fluxes, O₃, Holm oak, Mediterranean forest, Eddy Covariance, drought stress, pollution

Introduction

Tropospheric ozone (O₃) is a significant environmental problem as it affects human health (Anenberg et al. 2010) and decreases carbon sequestration potentials of forest ecosystems (Fares et al. 2013a). It is also an important greenhouse gas, with a radiative forcing of 0.35–0.37 W m⁻², responsible for 5% - 16% of the global temperature increase since preindustrial time (Foster et al. 2007).

O₃ is produced in the atmosphere by photochemical reactions between anthropogenic and biogenic volatile organic compounds (VOC) and nitrogen oxide (NOₓ), high irradiance and temperature occurring in the Mediterranean regions promote O₃ formation more than in other area (Paolletti 2006). O₃ removal from forest ecosystems is attributed to both stomatal and non-stomatal sinks, which include deposition on cuticles and soil surface as well as O₃ depleted by gas-phase reactions (Kurpius and Goldstein 2003, Cieslik 2004). The majority of O₃ deposition is often attributed to non-stomatal O₃ sinks (Fowler et al. 2009), especially during the summer season when stomatal conductance is reduced under conditions of drought stress and high vapour pressure deficit (Gerosa et al. 2009).

The objective of this study is to quantify O₃ removal during two transition periods: before the beginning of the driest season, from March 20 to April 14 (early Spring) and before the coldest season, from November 11 to December 6 (late Fall) in a Mediterranean Holm oak forest. O₃ flux dynamics were compared between the uncommonly dry early Spring and late Fall of 2012 with the more wet periods of 2013 in order to highlight whether water availability can have a significant effect on ozone fluxes.

Materials and Methods

Study site description

The study site, named “Grotta di Piastra” (41°42' N, 12°21' E), is located within the Castelporziano Estate, 25 km SW from the centre of Rome, Italy. This site is a wild coastal rear dune ecosystem, 1.5 km from the seashore, covered almost prevalently by an even-aged evergreen Holm oak forest (Quercus ilex L.). The forest main height was 14 m and the Leaf Area Index (LAI) was 3.69 m²leaf m⁻²ground,
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measured using a LAI 2000 instrument (Li-Cor, USA). The soil has a sandy texture and low water-holding capacity. The climate is typically Mediterranean: precipitation occurred mainly in Fall and Winter, whereas Summers were hot and dry (Fig. 1). Averaged in the year 1999-2010, annual precipitation was 789.3±230.6 mm and mean monthly temperatures range between 7.3°C and 23.3°C. The wind regime was characterized by winds from the sea (S-SW) blowing during the morning, and winds from the inland (N-NE) in the afternoon.

Meteorology and flux measurement

Measurements were carried out in 2012 and 2013 in early Spring and late Fall, from day of the year 79 to 104 and 315 to 340 of each year.

Air temperature, precipitation, relative humidity, net solar radiation, wind direction, soil humidity and soil temperature were recorded every minute and averaged for 30 min intervals with a Davis vantage pro meteorological station (Davis Instruments Corp. CA, USA).

Flux measurement equipment was installed at 19.7 m height at the top of a scaffold tower. A tri-dimensional sonic anemometer (Gill Windmaster) was used to measure instantaneous wind speed and temperature fluctuation. H2O and CO2 concentrations were measured with a closed-path infrared gas analyzer (LI-7200, Li-Cor, USA). O3 fast measurements were performed by a chemiluminescence methods which uses coumarin dye reaction with O3, thanks to a customized instrument 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 O3 concentrations from a UV ozone monitor (Thermo Scientific, mod. 49i). Data were recorded at 10 Hz for all gases using a data logger (CR-3000, Campbell Scientific, Shepshed, UK).

H2O, CO2, O3, latent and sensible heat fluxes were calculated according to the eddy covariance technique:

\[
F_c = \overline{w'c'}
\]

where \(w'\) and \(c'\) are deviations from the 30 minute means of vertical wind velocity and gas concentration, respectively. The method is extensively described in Goldstein et al. (2000) and Fares et al. (2012).

O3 fluxes were partitioned between stomatal and non-stomatal trough several steps: first stomatal conductance for water (\(G_{sto}\)) was calculated from latent heat flux by inverting the Penmann–Monteith equation according to the evaporative/resistive method (Monteith 1981, Fares et al. 2013b, Gerosa et al. 2009). O3 stomatal conductance (\(G_{o3}\)) was calculated from \(G_{sto}\) by correcting for the difference in diffusivity between O3 and water vapor (Massman 1998). O3 stomatal fluxes were calculated multiplying \(G_{o3}\) by O3 concentration, assuming a constant vertical flux between the measurement height and the top of canopy and negligible intercellular O3 concentration (Laisk et al. 1989). The remaining fraction of the O3 flux is considered as non-stomatal deposition and includes all other deposition pathways.

Fluxes are expressed per unit of ground area per second, positive fluxes indicate upward transfer of mass and energy from the ecosystem to the atmosphere, and negative fluxes indicate transfer from the atmosphere into the ecosystem.

Results and discussion

Meteorology and energy fluxes

Periods examined in this work are both transition phases between a cold and wet season and a dry and warm season, when usually drought stressed does not occur: average in the year 1999-2010, mean precipitation were 61.3±24.6 mm in April and 130.1±54.4 mm in November. Early Spring and late Fall (2012) were dry respect to values collected in 2013 (Fig. 2): 8.0 mm in 2012 versus 58.4 mm of 2013 in the early Spring and 71.4 mm of 2012 versus 160.8 mm of 2013 in late Fall.

Figure 3 shows 2012 and 2013 mean daily course of temperature (°C), net radiation (W m⁻²), latent heat flux (LE, W m⁻²), sensible heat flux (H, W m⁻²) and vapour pressure deficit (VPD, kPa) for the two
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Figure 2 - Cumulated precipitation (mm) from March 20 to April 14 (Early Spring) and from November 11 to December 6 (Late Fall).

Figure 3 - Averaged daily values (± standard deviation) of temperature (a), net radiation (b), latent heat flux (c), sensible heat flux (d) and vapour pressure deficit (e) for the periods from March 20 to April 14 (Early Spring) and from November 11 to December 6 (Late Fall).

Figure 4 - Averaged daily values (± standard deviation) of ozone concentration (ppb), ozone fluxes (nmol m⁻² s⁻¹) and deposition velocity (m s⁻¹) at the site in 2012 and 2013 early Spring and late Fall.

periods. Early Spring mean temperature was similar across the two years (12.1±4.2°C and 12.6±2.9°C for 2012 and 2013, respectively) while 2013 late Fall was colder than the 2012 one (13.4±3.9°C and 10.6±4.2°C for 2012 and 2013, respectively). Late Fall night temperatures were higher than those recorded in early Spring 2012. Daytime cloudiness in 2013 early Spring was 19% higher than 2012. H reflected the solar radiation trend. During the early Spring hottest hours LE flux intensities were 16% lower in 2012 than 2013, as expected considering the scarcity of precipitation occurred in 2012. Interestingly, the relation is inverse in late Fall (LE fluxes were 23% minor in 2013 than 2012) suggesting that the water availability did not represent a limiting factor during Fall.

O₃ concentration at the site

No significant differences were observed between mean O₃ concentrations at the top of the canopy for the two years in early Spring (41.4±16.4 ppb and 41.5±10.8 ppb for 2012 and 2013, respectively) neither in late Fall (20.7±13.3 ppb and 20.3±12.8 ppb for 2012 and 2013, respectively). For both periods, O₃ concentration was higher in the warmest hours of the day and decreased during the night (Fig. 4). Overall, O₃ concentration was lower in the late Fall period according to the dependence of O₃ on air temperature (Kurpius and Goldstein 2003, Fares et al. 2010, Finlayson and Pitts 1997). The land-sea wind regime at the site also affected O₃ concentration. Figure 5 shows daytime (a) and nighttime (b) wind direction and O₃ concentration. During the day wind blew prevalently from the sea (S-W), carrying air masses to the forest, while during night wind blew from the city (N-E), transferring polluted air plumes to the forest site, as previously reported by Fares et al. (2009). Air coming from the city was previously characterized by low O₃ concentrations due to the fast reactions with anthropogenic pollutants like nitrogen oxides (NO_x, Finlayson and Pitts 1997). This may explain the average low concentrations of O₃ in Castelporziano as compared with periurban area north of Rome (Fares et al. 2009 and 2013b). Moreover, during the few times that wind circulation diverged from its typical pattern (Fig. 5 a, b), O₃ concentration at night was higher, thus confirming that that air masses not directly coming from the urban areas are less depleted in O₃ concentration.

O₃ fluxes and deposition velocity

O₃ fluxes to the forest reached the maximum values during the central hours of the day both in early Spring and in late Fall. The peak values of mean daily O₃ fluxes in early Spring were -8.1±0.7 nmol m⁻² s⁻¹ and -8.9±0.6 nmol/m²s for 2012 and 2013 respectively, while in late Fall they were -4.6±0.7 nmol m⁻²s⁻¹ and
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Figure 5 - Wind roses of daytime (a) and nighttime (b) wind directions and ozone concentration (ppb). The frequencies at which the wind blew from each direction is represented by the radial thickness of each slice, while ozone concentration is represented by the color of the filled area. Data are from February 2012 to November 2013.

Table 1 - Summary statistics of O₃ fluxes. For each periods is reported: mean O₃ flux ± standard error, 25th percentile, 75th percentile, skewness, number of observations (n) and percentage of valid observations (N).

<table>
<thead>
<tr>
<th>Time period</th>
<th>O₃ flux (nmol m⁻² s⁻¹) mean±se</th>
<th>25th perc.</th>
<th>75th perc.</th>
<th>skewness</th>
<th>n</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>early Spring</td>
<td>-3.92±0.12</td>
<td>-5.88</td>
<td>-1.2</td>
<td>-1.14</td>
<td>991</td>
<td>81</td>
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<tr>
<td>late Fall</td>
<td>-1.7±0.08</td>
<td>-2.80</td>
<td>-0.01</td>
<td>-1.7</td>
<td>1021</td>
<td>86</td>
</tr>
<tr>
<td>2013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>early Spring</td>
<td>-4.92±0.10</td>
<td>-7.00</td>
<td>-2.29</td>
<td>-0.92</td>
<td>1123</td>
<td>99</td>
</tr>
<tr>
<td>late Fall</td>
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<td>-1.95</td>
<td>-0.09</td>
<td>-1.69</td>
<td>1025</td>
<td>99</td>
</tr>
</tbody>
</table>

-2.5±0.3 nmol m⁻²s⁻¹ for 2012 and 2013, respectively. Late Fall O₃ fluxes for both years were about half of the fluxes measured in early Spring. A summary statistics of O₃ fluxes is reported in Table 1.

A strong correlation between O₃ fluxes and O₃ concentrations was observed in both study periods (Fig. 4), with the exception of the hottest hours of the day in 2012 early Spring. O₃ deposition velocity (flux normalized by concentration) in this period was reduced by 23.6%. We ascribe this behaviour to the reduction in stomatal O₃ fluxes, as previously hypothesized given the dependence of stomatal conductance on moisture content. Stomatal conductance was indeed lower in early Spring 2012 during the central hours of the day (Fig. 6).

O₃ deposition velocities were lower in late Fall than in early Spring for both years (Fig. 4). This indicates that not only O₃ concentration controls the flux magnitude but also plant phenology, which determines low stomatal conductance in Fall, played a leading role in controlling O₃ flux. In order to better understand seasonal effects on O₃ fluxes during Spring and Fall, these were partitioned between stomatal and non-stomatal fluxes (Fig. 7) for measurements performed in 2013 (data for 2012 not available).

In agreement with dynamics of stomatal conductance shown in Fig. 6, stomatal contribution to the total O₃ flux was different during the two seasons, with higher stomatal fluxes in Spring, while non-stomatal O₃ fluxes were similar in the two seasons. This result confirmed the predominant role of stomatal control on O₃ removal from the atmosphere in dependence on water availability in a photosynthetically active season (Spring). Therefore in Fall, under conditions of low stomatal conductance, the dependence on water availability was less appreciated.

Individual contribution of stomatal and non-stomatal sinks to total O₃ fluxes also varied during the day. Night values of non stomatal fluxes could have several contributors: gas-phase reaction with VOC and NOx (Finlayson and Pitts 1997), and surface deposition. The latter is probably responsible...
Figure 7 - Averaged daily values (a standard deviation) of total O₃ flux, stomatal O₃ flux and non-stomatal O₃ flux measured during 2013 Spring (a) and Fall (b).

for the observed high nocturnal non-stomatal fluxes in Fall, when leaf surface wetness and air humidity have been shown to increase O₃ deposition (Zhang et al. 2002, Altimir et al. 2005).

Conclusion

O₃ fluxes were measured in an perurban Mediterranean evergreen Holm oak forest during transition periods in two different years, characterized by different amount of precipitation.

During the measurement periods, not commonly affected by drought stress, O₃ flux was found to be reduced under conditions of low water availability, when stomatal sink contribution is typically higher. The non-stomatal ozone deposition proved to be an important sink of tropospheric ozone in this Holm oak ecosystem, current studies are aimed at partitioning these non-stomatal sinks between different contributors (e.g. NOx, VOCs, surface deposition).

Overall, our results indicate that the Castelporziano evergreen forest represents a net sink of O₃. This type of ecosystem service must be taken into account while evaluating the complex of the benefits that forest ecosystems can provide to urban and peri-urban areas.

Currently, O₃ fluxes are still measured at the site. A large temporal series will help to elucidate deeply the contribution of the environmental control factors on ozone dynamics.

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