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Research paper

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 (O_3) is one of the most toxic compounds for plants in the atmosphere. The large amount of anthropogenic O_3 precursors in the urban areas promote O_3 formation, thus making Mediterranean forests located in periurban areas particularly vulnerable to this pollutant. O_3 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 O_3 fluxes during seasons which are not commonly affected by drought stress. Overall, the forest canopy showed to be a net sink of O_3, with peak values of mean daily O_3 fluxes of -8.9 nmol $m^{-2}s^{-1}$ at the beginning of flowering season and -4.6 nmol $m^{-2}s^{-1}$ at the end of Fall. O_3 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, O_3, Holm oak, Mediterranean forest, Eddy Covariance, drought stress, pollution

Introduction

Tropospheric ozone (O_3) 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).

O_3 is produced in the atmosphere by photochemical reactions between anthropogenic and biogenic volatile organic compounds (VOC) and nitrogen oxide (NO_x), high irradiance and temperature occurring in the Mediterranean regions promote O_3 formation more than in other area (Paoletti 2006). O_3 removal from forest ecosystems is attributed to both stomatal and non-stomatal sinks, which include deposition on cuticles and soil surface as well as O_3 depleted by gas-phase reactions (Kurpius and Goldstein 2003, Cieslik 2004). The majority of O_3 deposition is often attributed to non-stomatal O_3 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 O_3 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. O_3 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 m^2leaf m^{-2}ground,

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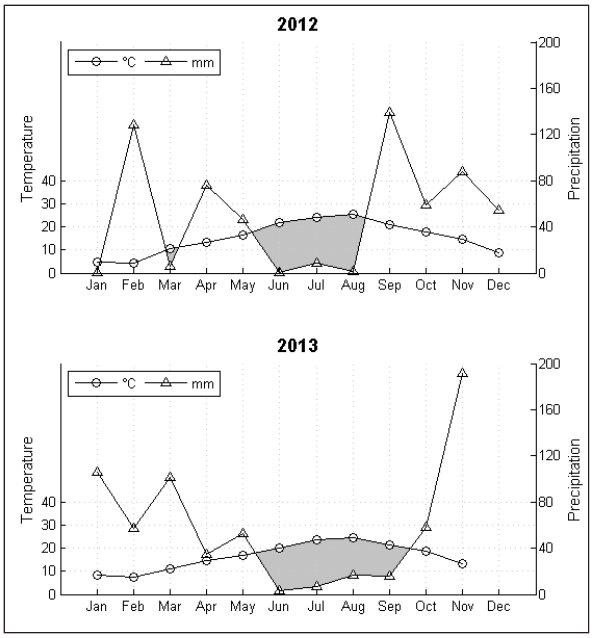

Figure 1 - Bagnouls-Gaussen diagrams for 2012 and 2013. Circles are monthly average temperature (°C) while triangles are monthly cumulated precipitation (mm). Shaded area represent drought period.

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 tridimensional sonic anemometer (Gill Windmaster) was used to measure instantaneous wind speed and temperature fluctuation. H_2O and CO_2 concentrations were measured with a closed-path infrared gas analyzer (LI-7200, Li-Cor, USA). O_3 fast measurements were performed by a chemiluminescence methods which uses coumarin dye reaction with O_3, 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 O_3 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).

H_2O, CO_2, O_3, latent and sensible heat fluxes were calculated according to the eddy covariance technique:

$$F_c = \overline{w' \cdot c'} \tag{1}$$

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).

O_3 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). O_3 stomatal conductance (G_{O3}) was calculated from G_{sto}, by correcting for the difference in diffusivity between O_3 and water vapor (Massman 1998). O_3 stomatal fluxes were calculated multiplying G_{O3} by O_3 concentration, assuming a constant vertical flux between the measurement height and the top of canopy and negligible intercellular O_3 concentration (Laisk et al. 1989). The remaining fraction of the O_3 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

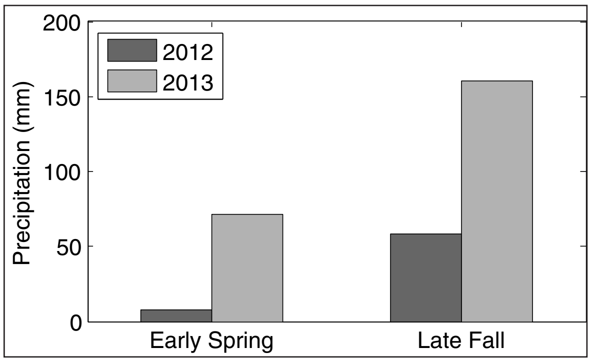

Figure 2 - Cumulated precipitation (mm) from March 20 to April 14 (Early Spring) and from November 11 to December 6 (Late Fall).

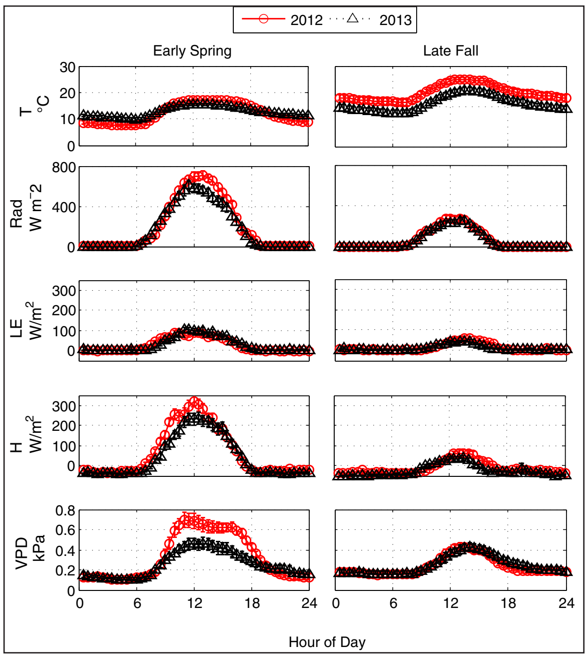

Figure 3 - Averaged daily values (± standard deviation) of temperature (a), net radiation (b), latent heat flux (c), sensible heat flux (d) and vapour pressure deficit (e) for the periods from March 20 to April 14 (Early Spring) and from November 11 to December 6 (Late Fall).

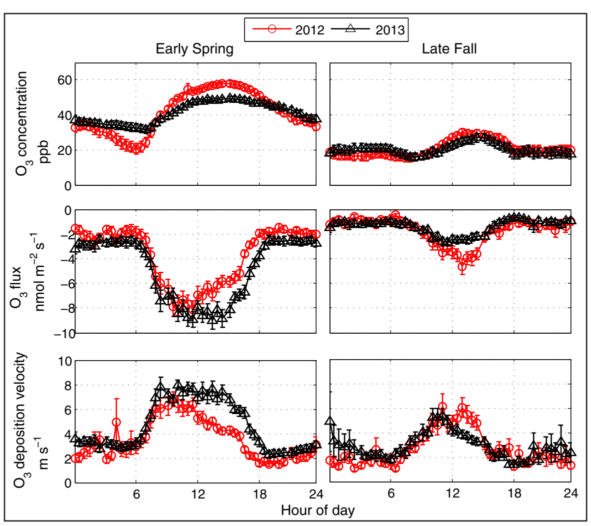

Figure 4 - Averaged daily values (± standard deviation) of ozone concentration (ppb), ozone fluxes (nmol m^{-2} s^{-1}) and deposition velocity (m s^{-1}) at the site in 2012 and 2013 early Spring and late Fall.

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.

O_3 concentration at the site

No significant differences were observed between mean O_3 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, O_3 concentration was higher in the warmest hours of the day and decreased during the night (Fig. 4). Overall, O_3 concentration was lower in the late Fall period according to the dependence of O_3 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 O_3 concentration. Figure 5 shows daytime (a) and nighttime (b) wind direction and O_3 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 O_3 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 O_3 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), O_3 concentration at night was higher, thus confirming that that air masses not directly coming from the urban areas are less depleted in O_3 concentration.

O_3 fluxes and deposition velocity

O_3 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 O_3 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 $m^{-2}s^{-1}$ and

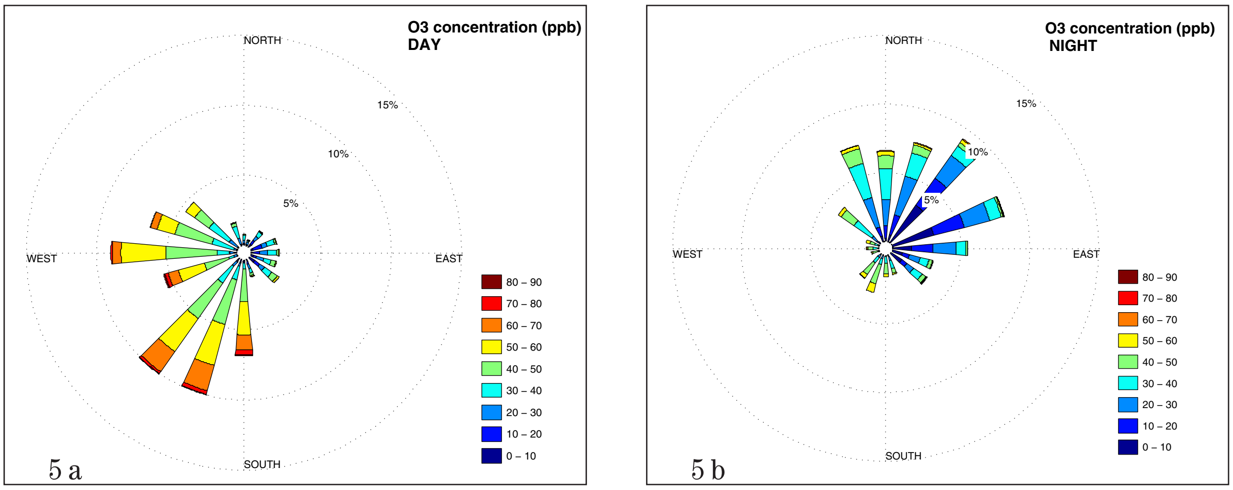

Figure 5 - Wind roses of daytime (a) and nighttime (b) wind directions and ozone concentration (ppb). The frequencies at which the wind blew from each direction is represented by the radial thickness of each slice, while ozone concentration is represented by the color of the filled area. Data are from February 2012 to November 2013.

Table 1 - Summary statistics of O_3 fluxes. For each periods is reported: mean O_3 flux ± standard error, 25th percentile, 75th percentile, skewness, number of observations (n) and percentage of valid observations (N).

Time period year	season	O_3 flux (nmol m^{-2} s^{-1}) mean±se	25th perc.	75th perc.	skewness	n	N (%)
2012	early Spring	-3.92±0.12	-5.88	-1.2	-1.14	991	81
	late Fall	-1.7±0.08	-2.80	-0.01	-1.7	1021	86
2013	early Spring	-4.92±0.10	-7.00	-2.29	-0.92	1123	99
	late Fall	-1.35±0.04	-1.95	-0.09	-1.69	1025	99

-2.5±0.3 nmol m^{-2}s^{-1} for 2012 and 2013, respectively. Late Fall O_3 fluxes for both years were about half of the fluxes measured in early Spring. A summary statistics of O_3 fluxes is reported in Table 1.

A strong correlation between O_3 fluxes and O_3 concentrations was observed in both study periods (Fig. 4), with the exception of the hottest hours of the day in 2012 early Spring. O_3 deposition velocity (flux normalized by concentration) in this period was reduced by 23.6%. We ascribe this behaviour to the reduction in stomatal O_3 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).

O_3 deposition velocities were lower in late Fall than in early Spring for both years (Fig. 4). This indicates that not only O_3 concentration controls the flux magnitude but also plant phenology, which determines low stomatal conductance in Fall, played a leading role in controlling O_3 flux. In order to better understand seasonal effects on O_3 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 O_3 flux was different during the two seasons, with higher stomatal fluxes in Spring, while non-stomatal O_3 fluxes were similar in the two seasons. This result confirmed the predominant role of stomatal control on O_3 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 O_3 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

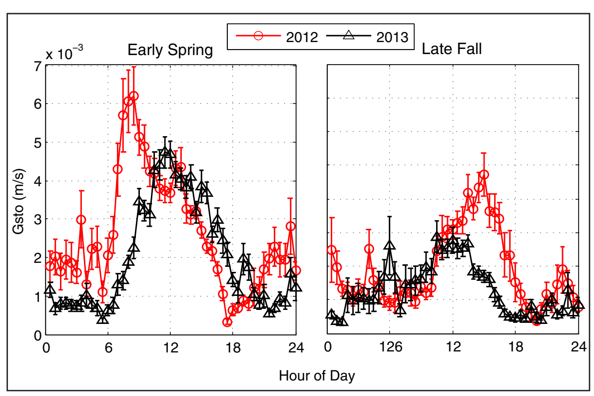

Figure 6 - Averaged daily values (± standard deviation) of stomatal conductance (Gsto, m/s) at the site in 2012 and 2013 early Spring (a) and late Fall (b).

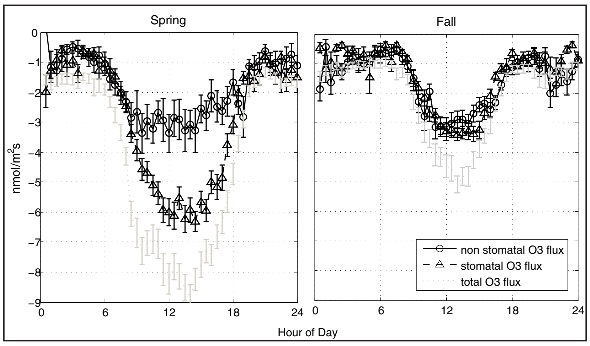

Figure 7 - Averaged daily values (± standard deviation) of total O_3 flux, stomatal O_3 flux and non stomatal O_3 flux measured during 2013 Spring (a) and Fall (b).

for the observed high nocturnal non-stomatal fluxes in Fall, when leaf surface wetness and air humidity have been shown to increase O_3 deposition (Zhang et al. 2002, Altimir et al. 2005).

Conclusion

O_3 fluxes were measured in an periurban 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, O_3 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 O_3. 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, O_3 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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References

Altimir N., Kolari P., Tuovinen J.-P., Vesala T., Bäck J., Suni T., Kulmala M., Hari P. 2005 - *Foliage surface ozone deposition: a role for surface moisture?* Biogeosciences Discussions 2: 1739–1793.

Anenberg S.C., Horowitz L.W., Tong D.Q. ,West J.J. 2010 - *An estimate of the global burden of anthropogenic ozone and fine particulate matter on premature human mortality using atmospheric modeling.* Environmental Health Perspective 118: 1189–1195.

Bauer M.R., Hultman N.E., Panek J.A., Goldstein A.H. 2000 - *Ozone deposition to a ponderosa pine plantation in the Sierra Nevada Mountains (CA): a comparison of two different climatic years.* Journal of Geophysical Research 105: 123-136.

Cieslik S. 2004 - *Ozone uptake at various surface types: a comparison between dose and exposure.* Atmospheric Environment 38: 2409–2420.

Fares S., Mereu S., Scarascia Mugnozza G., Vitale M., Manes F., Frattoni M., Ciccioli P., Gerosa G., Loreto F. 2009 - *The ACCENT-VOCBAS field campaign on biosphere-atmosphere interactions in a Mediterranean ecosystem of Castelporziano (Rome): site characteristics, climatic and meteorological condition and eco-physiology of vegetation.* Biogeosciences 6: 1043–1058.

Fares S., McKay M., Holzinger R., Goldstein A.H. 2010 - *Ozone fluxes in a Pinus ponderosa ecosystem are dominated by non-stomatal processes: evidence from long-term continuous measurements.* Agricultural and Forest Meteorology 150: 420-431.

Fares S., Weber R., Park J.H., Gentner D., Karlik J., Goldstein A.H. 2012 - *Ozone deposition to an orange orchard: Partitioning between stomatal and non-stomatal sinks.* Environmental Pollution 169: 258–266.

Fares S., Vargas R., Detto M., Goldstein A.H., Karlik J., Paoletti E., Vitale M. 2013a - *Tropospheric ozone reduces carbon assimilation in trees: estimates from analysis of continuous flux measurements.* Global Change Biology 19: 2427–2443.

Fares S., Schnitzhofer R., Jiang X., Guenther A., Hansel A., Loreto F. 2013b - *Observations of Diurnal to Weekly Variations of Monoterpene-Dominated Fluxes of Volatile Organic Compounds from Mediterranean Forests: Implications for Regional Modeling.* Environmental. Science and Technology 47 (19): 11073–11082.

Finlayson-Pitts B.J., Pitts J.N. 1997 - *Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles.* Science 276: 1045–1052.

Fowler D., Pilegaard K., Sutton M.A., Ambus P., Raivone M., Duyzer J., Simpson D., Fagerli H., Fuzzi S., Schjoerring J.K., Grainer C., Neftel A., Isaksen I.S.A., Laj P., Maione M., Monks P.S., Burkhardt J., Daemmgen U., Neirynck J., Personne E., Wichink-Kruit R., Butterbach-Bahl K., Flechard C., Tuovinen J.P., Coyle M., Gerosa G., Loubet B., Altimir N., Gruenhage L., Ammann C., Cieslik S., Paoletti E., Mikkelsen T.N., Ro-Poulsen H., Cellier P., Cape J.N., Horvath L., Loreto F., Niinemets U., Palmer P.I., Rinne J., Misztal P., Nemitz E., Nilsson D., Pryor S., Gallagher M.W., Vesala T., Skiba U., Brueggemann N., Zechmeister-Boltenstern S., Williams J., O'Dowd C., Facchini M.C., de Leeuw G., Flossman A., Chaumerliac N., Erisman J.W. 2009 - *Atmospheric Composition Change: Ecosystems-Atmosphere interactions.* Atmospheric Environment 43: 5193-5267.

Forster P., Ramaswamy V., Artaxo P., Berntsen T., Betts R. et al. 2007 - *Changes in atmospheric constituents and in radiative forcing. In: "Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change".* D. Qin, M. Manning, Z. Chen, M. Marquis et al., Cambridge ed. S Solomon, Cambridge Univ. Press 53: 129–234.

Gerosa G., Finco A., Mereu S., Vitale M., Manes F., Denti A.B. 2009 - *Comparison of seasonal variations of ozone exposure and fluxes in a Mediterranean Holm oak forest between the exceptionally dry 2003 and the following year.* Environmental Pollution 157: 1737–1744.

Goldstein A.H., Hultman N.E., Fracheboud J.M., Bauer M.R., Panek J.A., Xu M., Qi Y., Guenther A.B., Baugh W. 2000 - *Effects of climate variability on the carbon dioxide, water, and sensible heat fluxes above a ponderosa pine plantation in the Sierra Nevada (CA).* Agricultural and Forest Meteorology 101: 113–129.

Laisk A., Kull O., Moldau H. 1989 - *Ozone concentration in leaf intercellular air spaces is close to zero.* Plant Physiology 90: 1163-1167.

Manes F., Astorino G., Vitale M., Loreto F. 1997 - *Morpho-functional characteristics of Quercus ilex L. leaves of different age and their ecophysiological behaviour during different seasons.* Plant Biosystem 131 (2): 149-158.

Massman W.J. 1998 - *A review of the molecular diffusivities of H_2O, CO_2, CH_4, CO, O_3, SO_2, NH_3, N_2O, NO, and NO_2 in air, O2 and N2 near STP.* Atmospheric Environment 32: 1111-1127.

Monteith J.L. 1981 - *Evaporation and surface temperature.* Quarterly Journal of the Royal Meteorological Society 107: 1–27.

Kurpius M.R., Goldstein A.H. 2003 - *Gas-phase chemistry dominates O_3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere.* Geophysical Research Letters 30 (7): 1371.

Paoletti E. 2006 - *Impact of ozone on Mediterranean forests: a review.* Environmental Pollution 144: 463–474.

Zhang L., Brook J.R., Vet R. 2002 - *On ozone dry deposition, with emphasis on non- stomatal uptake and wet canopies.* Atmospheric Environment 36: 4787–4799.