Project Number 282910

ÉCLAIRE

Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems

Seventh Framework Programme

Theme: Environment

D11.4 Measurement and parameterization of the fraction of O3 that is taken up by leaves due to detoxification by constitutive BVOC, under associated environmental constraints and during leaf development

Due date of deliverable: **01/08/2014**

Actual submission date: **01/03/2015**

Start Date of Project: **01/10/2011**

Duration: **48 months**

Organisation name of lead contractor for this deliverable :
CNR

Project co-funded by the European Commission within the Seventh Framework		
Dissemination Level		
PU	Public	☐
PP	Restricted to other programme participants (including the Commission	☒
RE	Restricted to a group specified by the consortium (including the	☐
CO	Confidential, only for members of the consortium (including the Commission Services)	☐

1. Executive Summary

Concurrent measurements of stomatal ozone uptake, gross primary production and BVOC fluxes were carried out in a holm oak forest in Italy (two 2-week campaigns). The variability of BVOC emission was very elevated so that no significant correlation between ozone injury to gross primary production and BVOC emission was found. Thus, a literature survey was carried out to assess whether ozone injury to photosynthesis was affected by both ozone concentrations and BVOC emission. Here too, however, the variability of data was very high and no statistically significant effect was detected. We conclude that present knowledge is still imperfect for the parameterization of the fraction of O3 that is taken up by leaves due to detoxification by constitutive BVOC, and that BVOC thresholds of ozone damage cannot be assigned.

2. Objectives:

Measurement and parameterization of the fraction of O3 that is taken up by leaves due to detoxification by constitutive BVOC, under associated environmental constraints and during leaf development

3. Activities:

In a *Quercus ilex* forest where long-term measurements of ozone, carbon and water fluxes are carried out by an eddy covariance approach, a field campaign was carried out in Spring 2014 for concurrent measurements of stomatal ozone flux and BVOC fluxes at canopy level. Bad weather and technical issues affected this campaign, thus a new campaign (two weeks) was carried out in Summer 2014.

Using the Web of Science (Thompson-ISI), a survey of all peer-reviewed literature published between 1980 and 2014 was made on the basis of the keywords of “isoprene” or “monoterpene” and “ozone”. The literature was also checked for the words “elevated CO_2”, “nitrogen”, “drought” or “warming”; The experimental control was charcoal-filtered air (CF) or non-filtered air (NF) or ambient air for ozone treatments. Around 90 articles were used for a meta-analysis, but only 15 papers were about ozone.

4. Results:

The *Q. ilex* forest was a net sink of ozone (Figure 1), with higher fluxes at late spring, when stomatal conductance was high. Up to 8 g O3 m-2 were sequestered every year. Ozone concentrations showed the typical dome-shaped diurnal profile and were surprisingly high within and below the canopy (Figure 2 left). The partitioning of ozone sink distribution suggests a minor role for VOC as stomata explained almost the totality of ozone fluxes during the winter season, and <60% during the warm seasons under condition of drought stress (Figure 2 right). Soil removed up to 30% of ozone, suggesting the importance of this sink in this forest ecosystem. Monoterpenes like α-pinene, β-pinene and cis-ocimene were emitted by *Q. ilex*. Based on vertical wind velocity, we estimated the air retention time in the canopy to be less than 5 min in the daylight hours. Such a short retention time would not allow significant ozone losses by monoterpenes. Our hypothesis is also supported by the evidence that total ozone fluxes during summer were low and comparable to winter and fall. If temperature-dependent BVOC emission promoted chemical ozone fluxes, we would have expected to observe large fluxes in summer.

Monoterpene concentrations were higher in the morning, peaked right above the canopy and were significantly reduced below the canopy (Figure 3). Measured gradient concentrations and fluxes (Figure 4) confirmed that the canopy is a VOC source. Fluxes peak during the day because primary emitted VOC depend on light and temperature. Sesquiterpenes react with ozone in few seconds, therefore they disappear fast during the day when atmospheric ozone builds up (Figure 5). Non-stomatal ozone fluxes peak in coincidence with the highest concentration of Methyl-vynil-ketone + Metacrolein, two oxidation products from reaction between ozone and isoprene. The forest was a good carbon sink, with more than 600 g C m-2 sequestrated over the year (Figure 6). No relationship between stomatal ozone uptake by leaves and ozone detoxification by VOC was found.

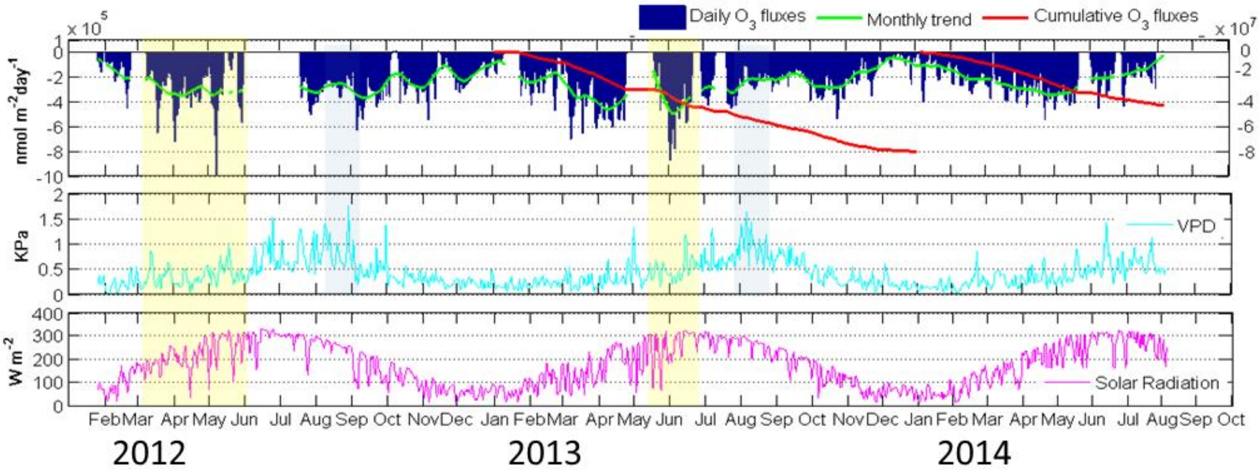


Figure 1. *Profiles of ozone fluxes, vapour pressure deficit and solar radiation over a Quercus ilex canopy*

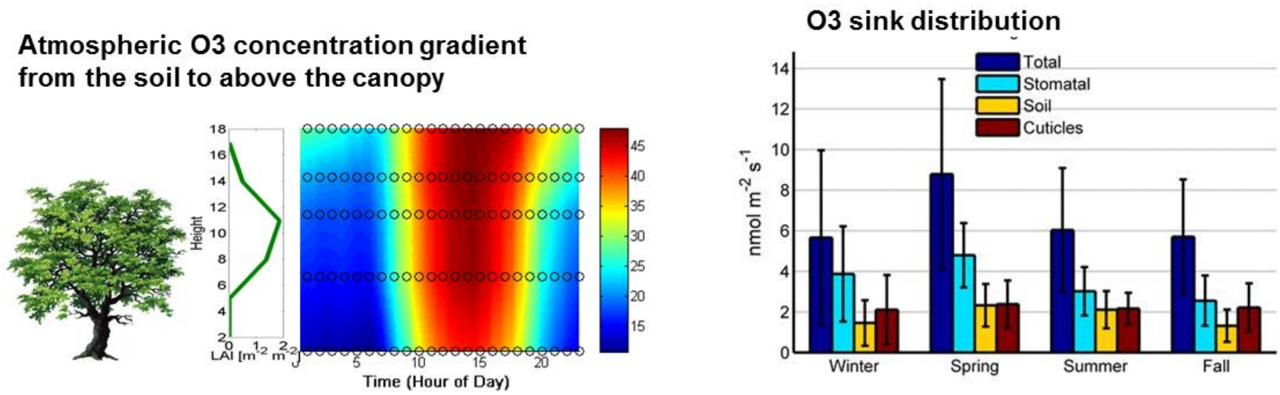


Figure 2. *Daily and vertical profile of ozone concentrations across a Quercus ilex canopy over the day (left) and partitioning of the ozone deposition among total, stomatal, cuticular and ground fluxes (right).*

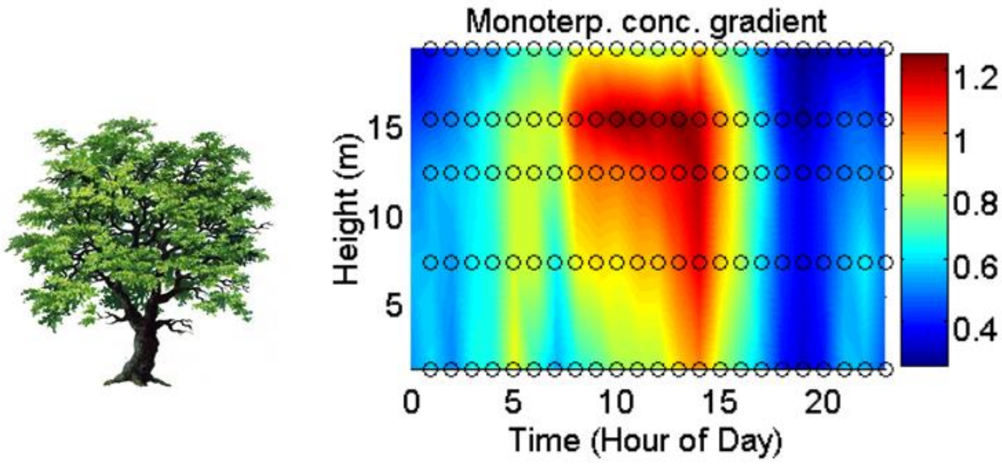
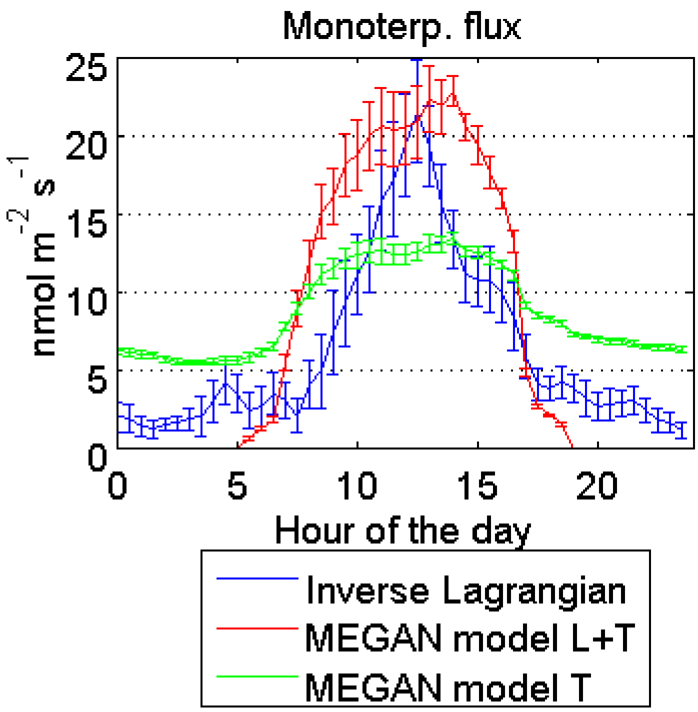


Figure 3. *Daily and vertical profile of monoterpene concentrations across a Quercus ilex canopy over the day*



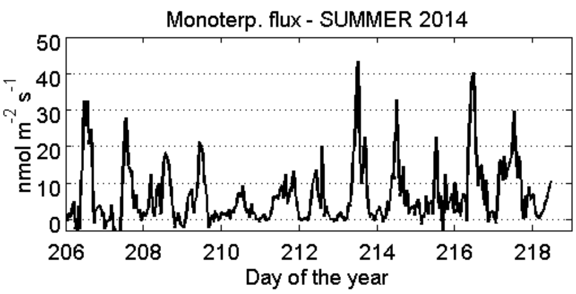


Figure 4. *Measured and modelled fluxes of monoterpenes from a Quercus ilex canopy over the day (left) and profile of monoterpenes fluxes over the two-week campaign (right)*

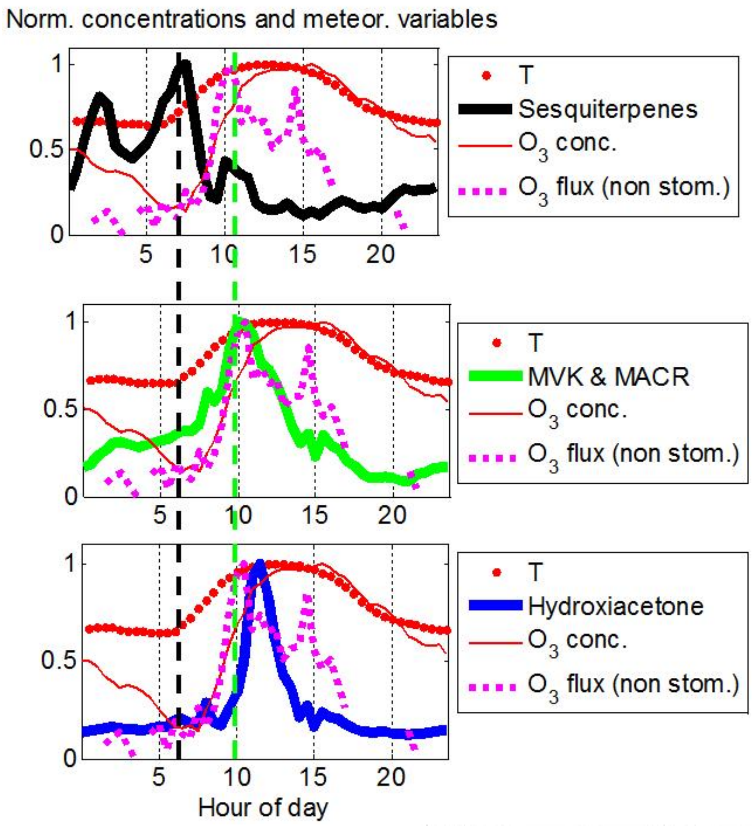


Figure 5. *Daily profiles of air temperature, ozone concentrations and non stomatal fluxes, sesquiterpenes, metyl vinil ketone and methacrolein (MVK & MACR) and hydroxiacetone*

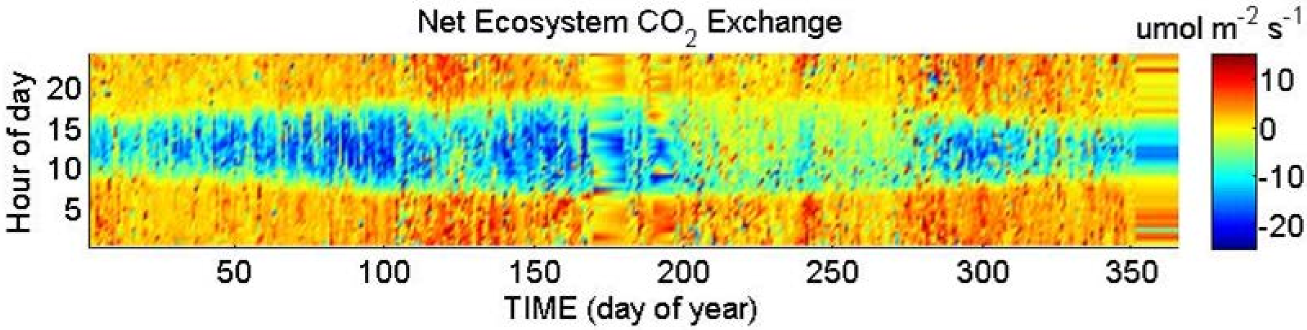


Figure 6. *Daily and annual profile of Net Ecosystem CO2 Exchange over a Quercus ilex forest*

In the literature review, the number of papers dealing with ozone and isoprene or monoterpenes was very limited (9 and 15, respectively) and not enough for conclusive statements about a role of BVOC in ozone detoxification and tolerance. Most of the responses, in fact, were not statistically significant, with the exception of the increase in α- and β-pinene (Figure 7).

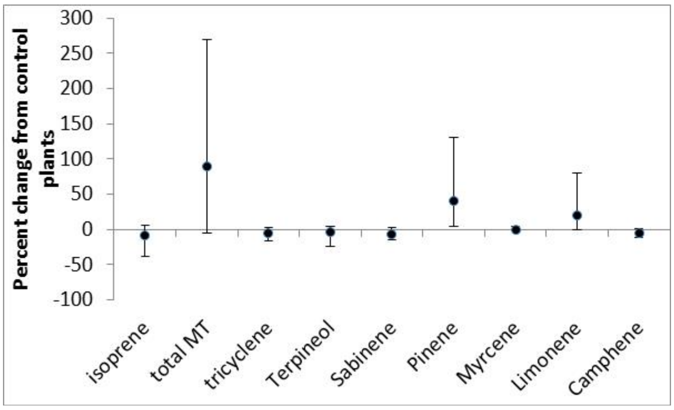


Figure 7. *Meta-analysis of the effects of ozone exposure on isoprenoids emission*

5. Milestones achieved:

MS52 Assignment of thresholds of O3 damage and BVOC-mediated O3 detoxification capacity

6. Deviations and reasons:

The submission of this deliverable was postponed due to bad weather and technical issues during the field measurement campaigns.

7. Publications:

Fares S., Savi F., Muller J., Matteucci G., Paoletti E.: 2014, **Simultaneous measurements of above and below canopy ozone fluxes help partitioning ozone deposition between its various sinks in a Mediterranean Oak Forest.** Agricultural and Forest Meteorology 198–199: 181–191.

8. Meetings:

ICP Vegetation Task Force in Rome, February 2015

9. List of Documents/Annexes: