



**Project Number 282910**

**ÉCLAIRE**

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

**Seventh Framework Programme**

**Theme: Environment**

**D 11.3 Quantification and parameterization of foliar O<sub>3</sub> deposition**

Due date of deliverable: **30/09/2013**

Actual submission date:

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

Duration:

Organisation name of lead contractor for this deliverable : **CNR**

Project co-funded by the European Commission within the Seventh Framework Programme		
Dissemination Level		
<b>PU</b>	Public	<input checked="" type="checkbox"/>
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	<input type="checkbox"/>
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	<input type="checkbox"/>
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	<input type="checkbox"/>

## 1. Executive Summary

In September 2011 we started an intensive field campaign aimed at investigating ozone deposition from a mixed Mediterranean forest (Castelporziano, central Italy), mainly composed by *Quercus suber*, *Quercus ilex*, *Pinus pinea*. Measurements at canopy level with the eddy covariance technique were supported by a vegetation survey and the measurement of all environmental parameters which allowed to calculate stomatal ozone fluxes. Leaf-level measurements were used to parameterize models to calculate stomatal conductance based on a Jarvis-type and Ball-Berry approach. Modeled stomatal ozone fluxes based on a Jarvis-type approach (DO3SE) correlated with measured fluxes better than using a Ball-Berry approach. Effects of drought, temperature and leaf phenology were investigated. We show changes in magnitude of ozone fluxes from a warm to a colder period. Stomata explained almost the totality of ozone fluxes during the colder days, but contributed only up to 50% to total ozone deposition during warm days, suggesting that other sinks (e.g. chemistry in the gas-phase) play a major role. Basal emission factors (BEFs) of biogenic volatile organic compounds (BVOCs) obtained by Eddy Covariance using a proton transfer reaction–time-of-flight–mass spectrometer (PTR-TOF-MS) were compared to BEFs reported in previous studies that could not measure fluxes in real-time. Globally, broadleaf forests are dominated by isoprene emissions, but these Mediterranean ecosystems are dominated by strong monoterpene emitters, as shown by the new BEFs.

### Objectives:

Quantification and parameterization of foliar O<sub>3</sub> deposition under drought and temperature stress and during leaf development and seasonal metabolic changes.

### 2. Activities:

At the start of the eclaire project, an eddy covariance tower located at Castelporziano, central Italy (41.74N, 12.40E, 80 m a.s.l., 7 km from the seashore) was equipped for stomatal ozone flux measurements. The climate is thermo-Mediterranean characterized by prolonged stress aridity during summer periods, and a moderate cold stress during winter. The soil has a sandy texture and low water-holding capacity. The mixed Mediterranean forest has an average height of 25 m, dominated by *Pinus pinea*, *Quercus ilex*, *Quercus suber* within the tower footprint. September to December months in this ecosystem represent a transition period from warm and dry to colder and wetter period. We identified a warm period (DOY 245-280) and a colder period (DOY 281-345).

Daily profiles of leaf-level gas exchange and leaf water potential as well as canopy-level meteorological variables, ozone, water and CO<sub>2</sub> concentrations were measured (see Fares et al., 2013a for details). Stomatal conductance from the eddy covariance measured evapotranspiration (G<sub>sto</sub>) was calculated using the Monteith equation also called Evaporative/Resistance. G<sub>sto</sub> was also modeled by the Jarvis multiplicative algorithm (DO3SE model) and the parameterizations of the UNECE mapping manual (UNECE, 2004 (2010 revision)), and by the Ball-Berry couple photosynthesis-stomatal conductance model. Fluxes of BVOCs were measured by a PTR-TOF-MS (for details see Fares et al., 2013b). Emission fluxes were calculated using algorithms parameterized with environmental parameters (PAR, temperature, and soil moisture) and BEF.

### 3. Results:

Ozone concentrations were obviously higher when temperatures and solar radiation were also higher. Ozone fluxes peaked during the central hours of the day, reaching values up to 9

$\text{nmol m}^{-2}\text{s}^{-1}$  during warm days and half of that during colder days. However, there was a mismatch between the hour of day where ozone concentrations was maximum (1 PM-3 PM) and hours when ozone fluxes were maximum (10 AM-2PM). This might be explained by stomatal and non-stomatal sinks having different dependencies on environmental variables. The non-stomatal ozone removal processes depend on surface deposition and gas-phase chemical reaction with BVOC. BVOC emission depends exponentially on air temperature, and in most cases is not linked to stomatal conductance. Reactive BVOC as sesquiterpenes and monoterpenes are emitted from the Mediterranean vegetation in Castelporziano. We hypothesize that during the central hours of the day a portion of non-stomatal ozone flux is due to reaction with BVOC emitted from leaves and soil. Moreover, in the early hours of the day, upon initiation of vertical mixing, a burst of BVOC emitted from soil and leaves at night may be involved in relevant ozone deposition. Early morning ozone deposition is also due to leaf wetness and dew deposition.

Stomatal ozone fluxes were of similar magnitude during warm and colder days, reaching values up to  $4 \text{ nmol m}^{-2}\text{s}^{-1}$ , about 50% of the total ozone fluxes during the warm days, and almost the totality of ozone fluxes during the coldest days, supporting again the conclusion that temperature-dependent gas-phase chemical reactions can significantly contribute to ozone fluxes in warm days. During these days, stomatal fluxes peaked in the morning around 10 AM, before light and VPD inhibited stomatal aperture and when predawn water potential suggested moderate water stress on several species. We thus suggest that a mid-day depression of stomatal conductance was motivated by a VPD effect rather than by limited water availability to the root system.

Leaf-level measurements were used to calculate the functions summarizing the effects of light, VPD, air temperature, and plant phenology on stomata.  $f_{\text{VPD}}$  was below 1 during warm days, supporting the previous conclusions on the VPD-limiting effect.  $f_{\text{phen}}$  was lower during the warm days (0.65), and became higher in the colder days (0.9), in agreement with the long vegetative period of mixed Oak Mediterranean forests.

When properly parameterized, the DO3SE model simulated well the stomatal conductance while the Ball-Berry model better captured the dynamics of stomatal conductance during the day, but underestimated stomatal conductance during the morning hours.

BEFs from Plant Functional Type (PFT)1, which included mainly stone pine, showed negligible isoprene emission, while total emission of monoterpenes was  $2082 \mu\text{g m}^{-2}\text{h}^{-1}$ , with predominance of linalool, limonene, and trans- $\beta$ -ocimene. PFT7 included the mixed Mediterranean forests and was confirmed to be a strong monoterpene emitter (total BEF of  $1747 \mu\text{g m}^{-2}\text{h}^{-1}$ ), while isoprene emission were 1 order of magnitude lower. Acetaldehyde, acetone and methanol emission were 125, 157,  $91 \mu\text{g m}^{-2}\text{h}^{-1}$ , respectively. PFT10 was associated with the shrubland ecosystem typical of the sand dunes of Mediterranean coasts. BVOC fluxes ranged 370 to  $440 \mu\text{g m}^{-2}\text{h}^{-1}$  for methanol,  $180\text{--}360 \mu\text{g m}^{-2}\text{h}^{-1}$  for acetaldehyde,  $180\text{--}450 \mu\text{g m}^{-2}\text{h}^{-1}$  for acetone,  $71\text{--}290 \mu\text{g m}^{-2}\text{h}^{-1}$  for isoprene, and  $240\text{--}860 \mu\text{g m}^{-2}\text{h}^{-1}$  for monoterpenes. We only used BEFs for isoprenoids ( $142$  and  $2008 \mu\text{g m}^{-2}\text{h}^{-1}$  for sum of isoprene and monoterpenes, respectively), since a clear dependence on light or just temperature was not found for oxygenated BVOC, therefore making it uncertain to calculate BEFs based on light and temperature or temperature only algorithm.

#### 4. Milestones achieved:

MS49 Completion of measurements of ozone uptake

MS50 Submission of data to database for modeling purposes

#### 5. Deviations and reasons:

Eddy covariance measurements are still in progress and will provide more results.

## 6. Publications:

Fares S., Matteucci, G., Scarascia Mugnozza, G., Morani A., Calfapietra C., Salvatori E., Fusaro L., Manes F., Loreto F., 2013a. Testing of models of stomatal ozone fluxes with field measurements in a mixed Mediterranean forest. *Atmospheric Environment*, 67:242-251.

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 & Technology*, 47 (19) , 11073-11082.

## 7. Meetings:

Results from the project were presented at the following international meetings:

IUFRO RG 7.01 International Conference 2012 'Biological Reactions of Forests to Climate Change and Air Pollution', Kaunas, Lithuania, 18-27 May, 2012.

ICP Vegetation workshop, Halmstad, Sweden, 28-31 January, 2013.

IUFRO RG 7.01 International Conference 2013 'Vegetation response to climate change and air pollution – unifying research and evidence across northern and southern hemisphere', Ilheus, Brasil, 1-6 September, 2013.

## 8. List of Documents/Annexes: