Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

Effect of mid-term drought on *Quercus pubescens* BVOC emissions seasonality and their dependence to light and/or temperature

Amélie Saunier[1], Elena Ormeño[1], Christophe Boissard[2], Henri Wortham[3], Brice Temime-Roussel[3], Caroline Lecareux[1], Alexandre Armengaud[4], Catherine Fernandez[1].

[1]Aix Marseille Univ, Univ Avignon, CNRS, IRD, IMBE, Marseille, France.
[2]Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
[3]Aix Marseille Univ, CNRS, LCE, Laboratoire de Chimie de l'Environnement, Marseille, France
[4] Air PACA, 146 rue Paradis, Bâtiment Le Noilly Paradis, 13294 Marseille, Cedex 06

Correspondence to: Amélie Saunier (amelie.saunier@imbe.fr)

Key words: BVOC, natural and amplified drought, season, light and temperature

Abstract. Biogenic volatile organic compounds (BVOC) emitted by plants are a large source of carbon compounds released into the atmosphere where they are precursors of ozone and secondary organic aerosols. Being directly involved in air pollution and indirectly in climate change, it is very important to understand what factors drive the BVOC emissions in order to characterize the atmospheric composition through models. The main algorithms currently used to predict BVOC emissions are mainly light and/or temperature dependent. Additional factors such as seasonality and drought have been also found to influence isoprene emissions, especially in Mediterranean region which is characterized by its drought period in summer. These factors are increasingly included in models but only for the principal studied BVOC which is isoprene but there are still some discrepancies in estimations of emissions. In this study, the main BVOC (isoprene, methanol, acetone, acetaldehyde, formaldehyde and MACR+MVK+ISOPOOH), emitted by *Quercus pubescens* a tolerant drought Mediterranean species, were monitored with a PTR-ToF-MS over an entire seasonal cycle, under both natural and amplified drought which is expected with climate change. Amplified drought impacted all BVOC by reducing emissions in spring and summer and, in the contrary, by increasing emissions in autumn. Two types of dependence were found: light and temperature dependence (isoprene, MACR+MVK+ISOPOOH and acetaldehyde), and light and temperature dependence during the day and only temperature dependence during the night (methanol, acetone and formaldehyde). Moreover, a methanol burst in early morning and formaldehyde deposition/uptake were also punctually observed which were not assessed by model.

1 Introduction

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

Plants contribute to global emissions of volatile organic compounds (VOC) with an estimated emission rate of 10^{15} gC.yr^{-1} (Guenther *et al.* 1995; Harrison *et al.* 2013). The large variety of compounds released by plants represents, at the global scale, 2-3% of the total carbon released in the atmosphere (Kesselmeier & Staudt 1999). Under strong photochemical conditions, BVOC, together with NOx, can significantly contribute to tropospheric ozone (Xie *et al.* 2008; Papiez *et al.* 2009). In addition to its greenhouse effect, O_3 has strong effects on plant metabolism (Reig-Armiñana *et al.* 2004; Beauchamp *et al.* 2005) as well as on human health (Lippmann 1989). BVOC are also rapidly oxidized by OH radical and NO_3 (Hallquist *et al.* 2009; Liu *et al.* 2012), which account for an important fraction of the total mass of secondary organic aerosols (SOA, Jimenez *et al.* 2009). Methanol and acetone are, after isoprene, the principal BVOC released to the atmosphere. Isoprene emissions represent, at the global scale, between 400-600 TgC.yr^{-1} (Arneth *et al.* 2008) whereas methanol emissions vary between 75 and 280 TgC.yr^{-1} (Singh *et al.* 2000; Heikes *et al.* 2002, respectively) and acetone emissions represent only 33 TgC.yr^{-1} (Jacob *et al.* 2002). Other compounds such as acetaldehyde, methacrolein (MACR), methyl vinyl ketone (MVK), isoprene hydroxy hydroperoxides (ISOPOOH) and formaldehyde, whose biogenic origin has been poorly investigated, are better known to be anthropogenic and/or secondary VOCs issued from atmospheric oxidations (Hallquist *et al.* 2009). However, acetaldehyde is also a by-product of plant metabolism and its emissions represent 23 Tg.y^{-1} at the global scale (Millet *et al.* 2010). Formaldehyde, MACR, MVK and ISOPOOH are released by plants through the oxidations of methanol and isoprene, respectively, within leaves but they can have other leaf precursors (Oikawa & Lerdau 2013). These compounds could have a strong impact on climate change. Thus, it is thereby important to model BVOC emissions with the aim of predicting the effect of these emissions on secondary atmospheric chemistry.

Several models, already existing (Guenther *et al.* 2006; Guenther *et al.* 2012; Menut *et al.* 2014), predict BVOC emissions according to the type of vegetation, biomass density, leaf age, specific emission factor for many vegetal species, as well as the impact of environmental factors. Two major emission algorithms which come from MEGAN model, are mainly considered: a light and temperature dependent algorithm (called L+T afterward) and a temperature dependent algorithm (called T afterward) both described in Guenther *et al.* (1995). The L+T algorithm is typically used for BVOC, such as isoprene, whose emissions rapidly rely on photosynthesis and thus, there are *de novo* emissions. The T algorithm corresponds to BVOC whose emissions do not directly rely on BVOC synthesis since they originate from permanent large storage pools. The dependence to light and/or temperature is well documented for isoprenoids (Owen *et al.* 2002; Rinne *et al.* 2002; Dindorf *et al.* 2006) but there is still a lack of knowledge about highly volatile BVOC (e.g. methanol, acetone, acetaldehyde). However, many of these compounds are very reactive in the atmosphere (Hallquist *et al.* 2009) and, at global scale, could be emitted in large quantities to the atmosphere. The characterization of their emissions and sensitivity to light and/or temperature is, thus, necessary in order to obtain reliable predictions of atmospheric processes in order not to miss this important part of the atmospheric reactivity. Nevertheless, other factors than light and temperature can drive BVOC emissions such as water stress. Indeed, numerous studies have shown an impact of water stress on BVOC emissions, especially on terpenes (Pegoraro *et al.* 2004; Peñuelas & Staudt 2010; Genard-Zielinski *et al.* 2014). Thus, it is necessary to investigate mid term (few years) effect of *in situ* water stress conditions on isoprene and highly volatile BVOC emissions and if current algorithms are able to predict the potential emission shifts, especially in a context of climate change. Indeed, the most severe climatic scenario of IPCC plans an intensification of summer drought in the Mediterranean area that

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

can locally reach 30% rain reduction, an extension of a drought period and a temperature rise of 3.4°C, (Giorgi & Lionello 2008; IPCC 2013; Polade *et al.* 2014) for 2100. However, there is still some misunderstandings at the level of emissions mechanisms and, consequently, on models estimations, for isoprene and, *a fortiori*, for highly volatile BVOC, under mild or severe water stress.

The aims of this study were (i) to measure, at the branch level, the specific emission factors of BVOC released by *Q. pubescens*, including isoprene and highly volatile compounds that originate from plant metabolism under water stress (ii) to test the performance of the L+T and T algorithms to predict isoprene and highly volatile BVOC emissions over the seasonal cycle and under water stress. *Q. pubescens* was chosen as vegetal model because this species is highly resistant to drought and well widespread in the Northern Mediterranean area occupying two millions ha (Quézel & Médail 2003). It also represents the major source of isoprene emissions in the Mediterranean area and the second one at the European scale (Keenan *et al.* 2009).

2 Material and methods

2.1 Experimental site

Experiments were performed at the O_3HP site (Oak Observatory at OHP, Observatoire de Haute Provence), located 60 km North of Marseille (5°42'44" E, 43°55'54" N), at an elevation of 650m above sea level. The O_3HP (955m^2), free from human disturbance for 70 years, consists of a homogeneous forest mainly composed of *Q. pubescens* (≈ 90 % of the biomass and ≈ 75 % of the trees) with a mean diameter of 1.3 m. The remaining 10 % of the biomass is mainly represented by *Acer monspessulanum* trees, a very low isoprene-emitter species (Genard-Zielinski *et al.* 2015). The O_3HP site was created in 2009 in order to study the *Q. pubescens* forest ecosystem at soil and tree scale. A rainfall exclusion device (an automated monitored roof deployed during rain events) was set up over part of the O_3HP canopy allowing to reduce natural rain of 30% according to climatic models in using the worst scenario of climate change (Giorgi & Lionello 2008; IPCC 2013) to have a natural drought (300m²) and an amplified drought (232m²). Amplified drought started on April 2012 and continued the years after with an exclusion during the growth period (April to October). During the first year of experiments (2012), 35 % of natural rain was excluded and, afterward, 33.5 and 35.5 % were excluded (2013 and 2014, respectively) corresponding for three years, to 2 months for natural treatment and 5 months for amplified treatment of drought period. Sampling was performed at the branch-scale at the top of the canopy during three campaigns from October 2013 to July 2014, during an entire seasonal cycle: in autumn (14 to 28 October 2013, 2nd year of amplified drought), in spring (12 to 19 May 2014, 3nd year of amplified drought) and in summer (13 to 25 July 2014, 3nd year of amplified drought). The same five trees per plot were selected and investigated throughout the study.

2.2 Branch scale-sampling methods

Dynamic branch enclosures were used for sampling gas exchanges and BVOC as fully described in Genard-Zielinski *et al.* (2015) with some modifications. Branches were enclosed in a ≈ 30L PTFE (polytetrafluoroethylene) frame closed by a 50µm thick PTFE film. Inlet air was introduced at 9L.min^{-1} using a PTFE air generator (KNF N840.1.2FT.18®, Germany) allowing for air renewal inside the chamber every ~

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

3min. Ozone was removed from inlet air by placing PTFE filters impregnated with sodium thiosulfate ($Na_2S_2O_3$) as described by Pollmann *et al.* (2005), so that oxidation within the enclosed atmosphere is negligible. The excess of air humidity was removed using drierite. A PTFE fan ensured a rapid mixing of the chamber air and a slight positive pressure within the enclosure enabled the PTFE film to be held away from the leaves to minimise biomass damage. Microclimate (temperature, relative humidity and photosynthetically active radiation or PAR) was continuously (every minute) monitored by a data logger (LI-COR 1400®; Lincoln, NE, USA) with a relative humidity and temperature probe placed inside the chamber (RHT probe, HMP60, Vaisala, Finland) and a quantum sensor (PAR, LI-COR, PAR-SA 190®, Lincoln, NE, USA) placed outside the chamber. All air flow rates were controlled by mass flow controllers (MFC, Bronkhorst) and all tubing lines were PTFE-made. Chambers were installed on the day before the measurement and flushed overnight.

2.3 Ecophysiological parameters

Exchanges of CO_2 and H_2O from the enclosed branches were also continuously (every minute) measured using infrared gas analysers (IRGA 840A®, LI-COR) concomitantly with BVOC emission measurements (cf. 2.2). Gas exchanges values were averaged by taking into account all the data measured between 12h and 15h (local time). Net photosynthesis (Pn, $\mu molCO_2.m^{-2}.s^{-1}$) and stomatal conductance to water (Gw, $mmolH_2O.m^{-2}.s^{-1}$) were calculated using equations described by Von Caemmerer and Farquhar (1981) as used in Genard-Zielinski *et al.* (2015) (for more details, see Appendix A). Leaves from enclosed branches were directly collected after the sampling. Then, the surface of this leaves was assessed with a leaf area meter to calculate physiological parameter. After that, leaves were lyophilized to assess the dry mass.

2.4 BVOC analysis

A PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was used for online measurements of BVOC emitted by the enclosed branches. A multi-position common outlet flow path selector valve system (Vici) and a vacuum pump were used to sequentially select a sample (amplified drought - inlet air – natural drought - ambient air - catalyser) every hour for analysis during 15min over a 1-2 day period. Mass spectra in the range 0-500amu were recorded at 1min integration time. Reaction chamber pressure was fixed at 2.1mbar, the drift tube voltage at 550V and the drift tube temperature at 313 K corresponding to an electric field strength applied to the drift tube (E) to a buffer gas density (N) ratio of 125Td (1Td = 10^{-17} V cm^2). A calibration gas standard (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA, 100 ± 10ppb in Nitrogen) was used to determine experimentally the ion relative transmission efficiency. BVOC targeted in this study and their corresponding ions include formaldehyde (m/z 31.018), methanol (m/z 33.033), acetaldehyde (m/z 45.03), acetone (m/z 59.05), isoprene (m/z 41.038, 69.069) and MACR+MVK+ISOPOOH (m/z 71.049, these three compounds were detected with the same ion with PTR-MS).The signal corresponding to protonated VOCs was converted into mixing ratio by using the proton transfer rate constants k given by Cappellin *et al.* (2012). Formaldehyde concentrations were calculated according to the method described by Vlasenko *et al.* (2010) to account for its humidity dependent sensitivity.

BVOC emissions rates (ER) were calculated by considering the BVOC concentrations in the inlet and outlet air as follows:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

$$ER = \frac{Q_0 * (C_{out} - C_{in})}{B} \quad (1)$$

where ER was expressed in $\mu gC.g_{DM}^{-1}.h^{-1}$, Q_0 was the flow rate of the air introduced into the chamber ($L.h^{-1}$), C_{out} and C_{in} were the concentrations in the inflowing and outflowing air ($\mu gC.L^{-1}$), respectively, and B was the total dry biomass matter (g_{DM}). Daily cycle were made by averaging measured emissions of all trees and by hour.

2.5 Emission algorithms

The light and/or temperature dependence of *Q. pubescens* BVOC (isoprene and highly volatile compounds) under natural and amplified drought was tested using both the L+T and T algorithms. Emission rates according to the L+T and T algorithms (called afterward ER_{L+T} and ER_T, respectively) were calculated using the equation described in Guenther *et al.* (1995) (for more details, see Appendix B). The empirical coefficient β (used in T algorithm) was determined for each compounds according to the season and the treatment through the correlation between experimental temperature (K) and the logarithm of emissions rate (measured emissions, $\mu gC.g_{DM}^{-1}.h^{-1}$). Specific standardised emissions factors (EF) at 30°C and 1000µmol.$m^{-2}.s^{-1}$, were used to calculate modelled emissions; they were determined, for each compound, according to the algorithm used, the season and the treatment using the slope of the correlation between emissions rate and values of ClCt (L+T) or T. All parameters used for the calculation of modelled emissions are presented in supplementary files (Table S1).

2.6 Data treatment

Data treatment was performed with the software STATGRAPHICS® centurion XV (Statpoint, Inc). After having checked the normality of the data set, two-ways repeated ANOVA were performed for Pn, Gw and the BVOC emissions according to the treatment and the season. Pearson's correlations between measured and modelled emissions were performed. This procedure allowed to evaluate the algorithm that better predicted *Q. pubescens* emissions under the different drought conditions and over the seasonal cycle. Afterward, linear regressions tests, slope tests (equal to 1) were also performed.

3. Results and discussion

3.1 Ecophysiological parameters

The physiology of *Q. pubescens* was slightly impacted by amplified drought (Fig. 1), over the whole study, with a decrease of Gw under amplified drought compared to natural drought, by 44 % in spring ($P < 0.1$) and 55 % in summer ($P < 0.01$, Table 1). In autumn, there was no significant difference between both treatments. Pn was only reduced in summer by 36 % ($P < 0.1$) and there was no difference for the others seasons. Thus, the stomata closure observed had a slight impact on the carbon assimilation. Indeed, *Q. pubescens* had a high stem hydraulic efficiency (Nardini & Pitt 1999) which allowed to compensate the stomata closure in using more efficiently the available water and, thus, maintaining Pn. Moreover, it must be noted that an increase of Pn was observed in autumn. This improvement of Pn could come from the autumnal rains. These results showed that the amplified drought artificially applied to *Q. pubescens* at O_3HP led to a moderate drought for this species, based on a moderate slowing down of the physiological performances (Niinemets 2010).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

3.2 Effect of drought on BVOC emissions

The emissions of all BVOC followed during this experimentation were reduced with amplified drought compared to natural drought in spring and summer (Table 1) except for acetaldehyde emissions. Indeed, for this compound, there was no significant difference between both treatments probably due to a large variability of the data set. In autumn, for all BVOC, there was no difference between both plots. The decrease of oxygenated BVOC in spring and summer under amplified drought (e.g. methanol, MACR+MVK+ISOPOOH, formaldehyde, acetone and acetaldehyde) could be explained through the stomata closure observed, at the same time, in spring and summer under amplified drought. Indeed, the emissions of these compounds were strongly bound to stomatal conductance (Niinemets *et al.* 2004). Isoprene emissions were also reduced in spring and summer in the third year of this experiment whereas an increase was observed in the first year (Genard-Zielinski *et al.* 2015). The isoprene decrease cannot be explained by the stomata closure because this compound could also be emitted through the cuticle (Sharkey & Yeh 2001). It could rather be due to the decrease of Pn which reduced the carbon availability to produce isoprene. Moreover, carbon assimilated through Pn can be also invested into other defense compounds and, consequently, decreased the isoprene production.

3.3 Effect of drought on light and/or temperature dependence through a seasonal cycle

Daily cycle of isoprene emissions (Fig. 2) showed that this compound responds strongly to light and temperature as demonstrated by Guenther *et al.* (1993). Moreover, this dependence was not impacted by amplified drought. But it was very important to take into account the effect of amplified drought on emission factors because the daily cycle between natural and amplified drought was very different for each season. The modelled emissions were very representative of measured emissions except in spring for natural drought, with a slight underestimation (sl = 0.84, $P < 0.05$) maybe, because light and temperature, at this precise time, were not the only parameters driving isoprene emissions.

MACR+MVK+ISOPOOH emissions, as isoprene, seemed to respond better to light and temperature than to only temperature (Fig. S1 in supplementary files). Indeed, correlations between measured emissions and L+T modelled emissions were always better than correlations with T modelled emissions. Since MACR+MVK+ISOPOOH are oxidation products of isoprene (Oikawa & Lerdau 2013), it is not surprising that these compounds followed the same pattern than isoprene in terms of dependence to light and temperature. The estimations of L+T modelled emissions were quite good except in spring with natural drought where a slight underestimation was observed (sl = 0.87, $P < 0.05$).

The dependence of acetaldehyde emissions to light and/or temperature is very contrasted; studies have shown that they were bound to both light and temperature (Jardine 2008; Fares *et al.* 2011) or to temperature only (Hayward *et al.* 2004). Our results suggested that acetaldehyde emissions were mainly bound to light and temperature (Fig. 3). Indeed, correlations between measured and L+T modelled emissions were always better than with T modelled emissions. However, some discrepancies were observed. Under natural drought, underestimations were observed in spring and summer (sl = 0.72, and sl = 0.57, $P < 0.05$, respectively) whereas in autumn, there was a good estimation (sl = 0.86, $P > 0.05$). Under amplified drought, underestimation was only observed in summer (sl = 0.80, $P < 0.05$). Daily cycles of acetaldehyde emissions presented also an emissions burst in the morning (7h, local time) in spring (for both treatment) and in summer (only for natural drought).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

Acetaldehyde can be produced under light-dark transitions by a pyruvic acid overflow mechanism. Indeed, under these transitions, cytosolic pyruvic acid levels rise rapidly and it can be converted into acetaldehyde by pyruvate decarboxylase (Fall 2003). This mechanism could explain the morning burst for this compound.

Correlations between modelled with L+T or T and measured methanol emissions were very similar especially in spring and summer (Fig. 4). But some observed phenomenon suggested that methanol responded only to temperature at certain moment of the day. Indeed, the burst in the early morning (7h, local time), similar to acetaldehyde, was observed when stomata opened in spring and summer under natural drought and in a lesser extent under amplified drought. This burst can be explained by a strong release of this compound that has been accumulated in the intercellular air space and leaf liquid pool at night with closed stomata (Hüve *et al.* 2007). Moreover, for both treatments, methanol emissions during the night were observed for all seasons. Methanol emissions, which result from the demethylation of pectin occurring during the leaves elongation, has already been described to be temperature dependent (Hayward *et al.* 2004; Folkers *et al.* 2008). Nevertheless, our results suggested that methanol emissions responded strongly to light and temperature during the day whereas, during the night, they responded to temperature. This kind of pattern emissions have been already described by Smiatek and Steinbrecher (2006).

Our results about daily cycles of acetone emissions (Fig. S2 in supplementary files) showed that this compound seemed to respond better to light and temperature than only temperature. Indeed, correlations were better with L+T modelling. Under natural drought, the modelled emissions were well representative of measured emissions in summer. By contrast, in spring and in autumn, slight underestimations were observed (sl = 0.88, $P < 0.05$ and sl = 0.69, $P < 0.05$, respectively). Under amplified drought, good estimations were observed in summer and autumn but in spring, there was an overestimation of modelled emissions (sl = 1.27, $P < 0.05$). Nevertheless, acetone emissions were observed during the night, especially in autumn. This indicated that this compound could respond to temperature at this moment of the day. Acetone is a by-product of plant metabolism (Jacob *et al.* 2002) and its dependence to light and/or temperature was very contrasted. Indeed, different studies have shown that acetone was dependent to only temperature (Fares *et al.* 2011) or to light and temperature (Jacob *et al.* 2002). Our results suggested that during the day, acetone emissions were dependent to light and temperature whereas during the night, like methanol, emissions responded to temperature (Smiatek & Steinbrecher 2006).

Formaldehyde emissions followed the same pattern than methanol and acetone emissions (Fig. S3 in supplementary files), especially in autumn. By considering only the daytime (correlation with L+T modelled emissions), there were good estimations in summer and autumn and a slight underestimation was observed in spring (sl = 0.89, $P < 0.05$) for natural drought. Under amplified drought, correlations indicated that L+T modelled emissions were well representative of measured emissions, but some negative emissions were observed in summer which suggested a deposition or an uptake of this compound by leaves as already highlighted by Seco *et al.* (2008). This phenomenon could have a role in stress tolerance, since formaldehyde can be catabolised within leaves in CO_2 (Oikawa & Lerdau 2013).

4 Conclusion

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

After 3 years of amplified drought, all BVOC emissions were reduced in spring and summer whereas, in autumn, an increase was observed for some compounds. These results are in opposition with the results obtained after only one year of amplified drought, especially for isoprene, where an increase was observed for this compound. Amplified drought did not seem to shift the dependence to light and/or temperature which remained unchanged between treatments.

Moreover, two different dependence behaviours were found: (i) isoprene, MACR+MVK+ISOPOOH and acetaldehyde emissions were strongly bound to light and temperature during the all daily cycle (ii) methanol, acetone and formaldehyde emissions were observed to depend on light and temperature during daytime and to temperature during the night. Moreover, some phenomenon, such as the burst in early morning (methanol and acetaldehyde) or the deposition/uptake (formaldehyde), were not modelled by L+T or T algorithm.

Appendix A: Ecophysilogical parameters calculation

Net photosynthesis (Pn, µmolCO_2.m^{-2}.s^{-1}) were calculated using equations described by Von Caemmerer and Farquhar (1981) as follows:

$$\mathrm{Pn} = \frac{F*(Cr-Cs)}{S} - CS*E \quad \text{(A1)}$$

Where *F* was the inlet air flow (mol.s^{-1}), *Cs* and *Cr* were the sample and reference CO_2 molar fraction respectively (ppm), *S* was the leaf surface (m^2), *Cs* * *E* was the fraction of CO_2 diluted in water evapotranspiration and *E* (molH_2O.m^{-2}.s^{-1} then transformed in mmolH_2O.m^{-2}.s^{-1}, afterward) was the transpiration rate calculated as follow:

$$\mathrm{E} = \frac{F*(Ws-Wr)}{S*(1-Ws)} \quad \text{(A2)}$$

where *Ws* and *Wr* were the sample and the reference H2O molar fraction respectively (molH_2O.mol^{-1}). Stomatal conductance (Gw, molH_2O.m^{-2}.s^{-1} then transformed in mmolH_2O.m^{-2}.s^{-1}, afterward) was calculated using the following equation:

$$\mathrm{Gw} = \frac{E*(1-\frac{Wl-Ws}{2})}{Wl-Ws} \quad \text{(A3)}$$

where *Wl* was the molar concentration of water vapour within the leaf (molH_2O.mol^{-1}) calculated as follows:

$$Wl = \frac{Vpsat}{P} \quad \text{(A4)}$$

where Vpsat was the saturated vaour pressure (kPa) and P was the atmospheric pressure (kPa).

Appendix B: Modelled emissions calculation

The modelled emissions (ER_{L+T} and ER_T) were calculated according to algorithms described in Guenther *et al.* (1995) as follows :

$$ER_{L+T} = EF_{L+T} * Cl * Ct \quad \text{(B1)}$$

$$ER_T = EF_T * T \quad \text{(B2)}$$

where Cl and Ct were calculated with the following formulae:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

$$Cl = \frac{\alpha C_{L1} L}{\sqrt{1+\alpha^2 L}} \quad \text{(B3)}$$

$$Ct = \frac{exp\frac{C_{T1}(T-T_S)}{RT_S T}}{1+exp\frac{C_{T2}(T-T_M)}{RT_S T}} \quad \text{(B4)}$$

where α = 0.0027, C_{L1} = 1.066, C_{T1} = 95000J.mol^{-1}, C_{T2} =230000J.mol^{-1}, T_M = 314K are empirically derived constants, L is the photosynthetically active radiation (PAR) flux (µmol$_{photon}$m^{-2}.s^{-1}), T is the leaf experimental temperature (K) and T_S is the leaf temperature at standard condition (303K).

T was calculated as follows:

$$T = \exp[\beta(T - T_S)] \quad \text{(B5)}$$

where β is the empirical coefficient determined for each compounds according to the season and the treatment through the correlation between experimental temperature (K) and the logarithm of emissions rate (measured emissions, µgC.g$_{DM}$$^{-1}$.h^{-1}), T is the leaf experimental temperature (K) and T_S is the leaf temperature at standard condition (303K).

Author contribution

AS, EO and CF designed the research and the experimental design. AS, BTR, EO and CF conducted the research. AS, CB, BTR, and CL collected and analyzed the data. AS, EO, CB, HW, BTR, AA and CF wrote the manuscript

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgment

This work was supported by the French National Agency for Research (ANR) through the SecPriMe² project (ANR-12-BSV7-0016-01); Europe (FEDER) and ADEME/PACA for PhD funding. We are grateful to FR3098 ECCOREV for the O_3HP facilities (https://o3hp.obs-hp.fr/index.php/fr/). We are very grateful to J.-P. Orts, I. Reiter. We also thank all members of the DFME team from IMBE and particularly: S. Greff, S. Dupouyet and A. Bousquet-Melou for their help during measurements and analysis. We thank also, the Université Paris Diderot-Paris7 for its support. The authors thank the MASSALYA instrumental platform (Aix Marseille Université, lce.univ-amu.fr) for the analysis and measurements used in this publication.

References

Arneth A., Monson R., Schurgers G., Niinemets Ü. & Palmer P. (2008). Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)? *Atmospheric Chemistry and Physics*, 8, 4605-4620.

Beauchamp J., Wisthaler A., Hansel A., Kleist E., Miebach M., NIINEMETS Ü., Schurr U. & WILDT J. (2005). Ozone induced emissions of biogenic VOC from tobacco: relationships between ozone uptake and emission of LOX products. *Plant, Cell & Environment*, 28, 1334-1343.

Cappellin L., Karl T., Probst M., Ismailova O., Winkler P.M., Soukoulis C., Aprea E., Märk T.D., Gasperi F. & Biasioli F. (2012). On quantitative determination of volatile organic compound concentrations using

proton transfer reaction time-of-flight mass spectrometry. *Environmental science & technology*, 46, 2283-2290.

Dindorf T., Kuhn U., Ganzeveld L., Schebeske G., Ciccioli P., Holzke C., Köble R., Seufert G. & Kesselmeier J. (2006). Significant light and temperature dependent monoterpene emissions from European beech (Fagus sylvatica L.) and their potential impact on the European volatile organic compound budget. *Journal of Geophysical Research: Atmospheres*, 111.

Fall R. (2003). Abundant oxygenates in the atmosphere: a biochemical perspective. *Chemical reviews*, 103, 4941-4952.

Fares S., Gentner D.R., Park J.-H., Ormeno E., Karlik J. & Goldstein A.H. (2011). Biogenic emissions from< i> Citrus</i> species in California. *Atmospheric Environment*, 45, 4557-4568.

Folkers A., Hüve K., Ammann C., Dindorf T., Kesselmeier J., Kleist E., Kuhn U., Uerlings R. & Wildt J. (2008). Methanol emissions from deciduous tree species: dependence on temperature and light intensity. *Plant biology*, 10, 65-75.

Genard-Zielinski A.-C., Boissard C., Fernandez C., Kalogridis C., Lathière J., Gros V., Bonnaire N. & Ormeño E. (2015). Variability of BVOC emissions from a Mediterranean mixed forest in southern France with a focus on Quercus pubescens. *Atmospheric Chemistry and Physics Discussions*, 14, 17225-17261.

Genard-Zielinski A.-C., Ormeño E., Boissard C. & Fernandez C. (2014). Isoprene Emissions from Downy Oak under Water Limitation during an Entire Growing Season: What Cost for Growth? *PloS one*, 9, e112418.

Giorgi F. & Lionello P. (2008). Climate change projections for the Mediterranean region. *Global and Planetary Change*, 63, 90-104.

Guenther A., Hewitt C.N., Erickson D., Fall R., Geron C., Graedel T., Harley P., Klinger L., Lerdau M., McKay W.A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J. & Zimmerman P. (1995). A global model of natural volatile organic compound emissions. *Journal of Geophysical Research: Atmospheres*, 100, 8873-8892.

Guenther A., Jiang X., Heald C., Sakulyanontvittaya T., Duhl T., Emmons L. & Wang X. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions.

Guenther A., Karl T., Harley P., Wiedinmyer C., Palmer P. & Geron C. (2006). Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics*, 6, 3181-3210.

Guenther A.B., Zimmerman P.R., Harley P.C., Monson R.K. & Fall R. (1993). Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 98, 12609-12617.

Hallquist M., Wenger J., Baltensperger U., Rudich Y., Simpson D., Claeys M., Dommen J., Donahue N., George C. & Goldstein A. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics*, 9, 5155-5236.

Harrison S.P., Morfopoulos C., Dani K., Prentice I.C., Arneth A., Atwell B.J., Barkley M.P., Leishman M.R., Loreto F. & Medlyn B.E. (2013). Volatile isoprenoid emissions from plastid to planet. *New Phytol.*, 197, 49-57.

Hayward S., Tani A., Owen S.M. & Hewitt C.N. (2004). Online analysis of volatile organic compound emissions from Sitka spruce (Picea sitchensis). *Tree Physiology*, 24, 721-728.

Heikes B.G., Chang W., Pilson M.E., Swift E., Singh H.B., Guenther A., Jacob D.J., Field B.D., Fall R. & Riemer D. (2002). Atmospheric methanol budget and ocean implication. *Global Biogeochemical Cycles*, 16, 80-1-80-13.

Hüve K., Christ M., Kleist E., Uerlings R., Niinemets Ü., Walter A. & Wildt J. (2007). Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata. *Journal of experimental botany*, 58, 1783-1793.

IPCC (2013). In: *Contribution of working group I to the fith assessment report of the intergovernmental panel on climate change*. Cambridge Univeristy Press Cambridge.

Jacob D.J., Field B.D., Jin E.M., Bey I., Li Q., Logan J.A., Yantosca R.M. & Singh H.B. (2002). Atmospheric budget of acetone. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 107, ACH 5-1-ACH 5-17.

Jardine J. (2008). Plant physiological and environmental controls over the exchange of acetaldehyde between forest canopies and the atmosphere. *Biogeosciences*, 5.

Jimenez J., Canagaratna M., Donahue N., Prevot A., Zhang Q., Kroll J.H., DeCarlo P.F., Allan J.D., Coe H. & Ng N. (2009). Evolution of organic aerosols in the atmosphere. *Science*, 326, 1525-1529.

Keenan T., Niinemets Ü., Sabate S., Gracia C. & Peñuelas J. (2009). Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties. *Atmospheric Chemistry and Physics Discussions*, 9, 6147-6206.

Kesselmeier J. & Staudt M. (1999). Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry*, 33, 23-88.
Lippmann M. (1989). Health effects of ozone a critical review. *Japca*, 39, 672-695.
Liu Y., Siekmann F., Renard P., El Zein A., Salque G., El Haddad I., Temime-Roussel B., Voisin D., Thissen R. & Monod A. (2012). Oligomer and SOA formation through aqueous phase photooxidation of methacrolein and methyl vinyl ketone. *Atmospheric Environment*, 49, 123-129.
Menut L., Bessagnet B., Khvorostyanov D., Beekmann M., Blond N., Colette A., Coll I., Curci G., Foret G. & Hodzic A. (2014). CHIMERE 2013: a model for regional atmospheric composition modelling. *Geoscientific Model Development*, 6, 981-1028.
Millet D.B., Guenther A., Siegel D.A., Nelson N.B., Singh H.B., de Gouw J.A., Warneke C., Williams J., Eerdekens G. & Sinha V. (2010). Global atmospheric budget of acetaldehyde: 3-D model analysis and constraints from in-situ and satellite observations. *Atmospheric Chemistry and Physics*, 10, 3405-3425.
Nardini A. & Pitt F. (1999). Drought resistance of Quercus pubescens as a function of root hydraulic conductance, xylem embolism and hydraulic architecture. *New Phytol.*, 143, 485-493.
Niinemets Ü. (2010). Mild versus severe stress and BVOCs: thresholds, priming and consequences. *Trends in plant science*, 15, 145-153.
Niinemets Ü., Loreto F. & Reichstein M. (2004). Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in plant science*, 9, 180-186.
Oikawa P.Y. & Lerdau M.T. (2013). Catabolism of volatile organic compounds influences plant survival. *Trends in plant science*, 18, 695-703.
Owen S., Harley P., Guenther A. & Hewitt C. (2002). Light dependency of VOC emissions from selected Mediterranean plant species. *Atmospheric environment*, 36, 3147-3159.
Papiez M.R., Potosnak M.J., Goliff W.S., Guenther A.B., Matsunaga S.N. & Stockwell W.R. (2009). The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada. *Atmospheric Environment*, 43, 4109-4123.
Pegoraro E., Rey A., Greenberg J., Harley P., Grace J., Malhi Y. & Guenther A. (2004). Effect of drought on isoprene emission rates from leaves of< i> Quercus virginiana</i> Mill. *Atmospheric Environment*, 38, 6149-6156.
Peñuelas J. & Staudt M. (2010). BVOCs and global change. *Trends in plant science*, 15, 133-144.
Polade S.D., Pierce D.W., Cayan D.R., Gershunov A. & Dettinger M.D. (2014). The key role of dry days in changing regional climate and precipitation regimes. *Scientific reports*, 4.
Pollmann J., Ortega J. & Helmig D. (2005). Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences. *Environmental science & technology*, 39, 9620-9629.
Quézel P. & Médail F. (2003). *Ecologie et biogéographie des forêts du bassin méditerranéen*. Elsevier Paris.
Reig-Armiñana J., Calatayud V., Cerveró J., Garcıa-Breijo F., Ibars A. & Sanz M. (2004). Effects of ozone on the foliar histology of the mastic plant (Pistacia lentiscus L.). *Environmental Pollution*, 132, 321-331.
Rinne H., Guenther A., Greenberg J. & Harley P. (2002). Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmospheric Environment*, 36, 2421-2426.
Seco R., Penuelas J. & Filella I. (2008). Formaldehyde emission and uptake by Mediterranean trees< i> Quercus ilex</i> and< i> Pinus halepensis</i>. *Atmospheric Environment*, 42, 7907-7914.
Sharkey T.D. & Yeh S. (2001). Isoprene emission from plants. *Annual review of plant biology*, 52, 407-436.
Singh H., Chen Y., Tabazadeh A., Fukui Y., Bey I., Yantosca R., Jacob D., Arnold F., Wohlfrom K. & Atlas E. (2000). Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 105, 3795-3805.
Smiatek G. & Steinbrecher R. (2006). Temporal and spatial variation of forest VOC emissions in Germany in the decade 1994–2003. *Atmospheric Environment*, 40, 166-177.
Vlasenko A., Macdonald A., Sjostedt S. & Abbatt J. (2010). Formaldehyde measurements by Proton transfer reaction–Mass Spectrometry (PTR-MS): correction for humidity effects. *Atmospheric Measurement Techniques*, 3, 1055-1062.
Von Caemmerer S.v. & Farquhar G. (1981). Some relationships between the biochemistry of photosynthesis and the gas exchange of leaves. *Planta*, 153, 376-387.
Xie X., Shao M., Liu Y., Lu S., Chang C.-C. & Chen Z.-M. (2008). Estimate of initial isoprene contribution to ozone formation potential in Beijing, China. *Atmospheric Environment*, 42, 6000-6010.

Table legends:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

436 **Table 1: N**et photosynthesis (Pn, $\mu molCO_2.m^{-2}.s^{-1}$), stomatal conductance to water (Gw, $mmolH_2O.m^{-2}.s^{-1}$) and
437 emission rates (ER, $\mu gC.g_{DM}^{-1}.h^{-1}$) according to treatment and season. Values represent an average of all data
438 measured between 12h and 15h (local time) when branches were the most active. Errors represent the SE.

Season	**Spring**		**Summer**		**Autumn**	
Treatment	**ND**	**AD**	**ND**	**AD**	**ND**	**AD**
Pn	10.6 ± 0.7	9.1 ± 1.7	13.6 ± 2.3	8.7 ±1.2	7.2 ±0.8	9.1 ± 1.0
Gw	107.7 ± 18.6	56.6 ± 13.1	285.4 ± 37.7	125.9 ± 17.4	122.5 ± 23.4	74.1 ± 21.1
Isoprene	20.3 ± 3.8	10.2 ± 2.3	124.3± 10.2	81.1 ± 11.0	3.0 ± 0.6	5.2 ± 1.5
MACR+MVK +ISOPOOH	0.12 ± 0.03	0.06 ± 0.01	0.4 ± 0.05	0.2 ± 0.02	0.04 ± 0.01	0.06 ± 0.01
Methanol	0.8 ± 0.1	0.5 ±0.04	1.0 ± 0.2	0.6 ± 0.03	0.2 ± 0.03	0.2 ± 0.05
Acetaldehyde	1.4 ± 0.4	0.9 ± 0.3	2.0 ± 0.5	1.1 ± 0.1	1.2 ± 0.3	1.2 ± 0.3
Acetone	0.5 ± 0.1	0.2 ± 0.02	1.1 ± 0.2	0.5 ± 0.04	0.4 ± 0.1	0.4 ± 0.1
Formaldehyde	0.2 ± 0.05	0.1± 0.01	0.4 ± 0.07	0.1 ± 0.02	0.2 ± 0.05	0.3 ± 0.06

439

440

441

442

443

444

445

446

447

448

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

Atmospheric Chemistry and Physics Discussions

449 **Figure legends**

450 **Figure 1**: Diurnal pattern of stomatal conductance (Gw, mmolH2O.m^{-2}.s^{-1})) and net photosynthesis (Pn,
451 µmolCO2.m^{-2}.s^{-1}) according drought and seasons**.** Means ± SE, n=5. ND: natural drought; AD: aggravated
452 drought.
453
454 **Figure 2**: Diurnal pattern of measured isoprene emissions rates (µgC.g$_{DM}^{-1}$.h^{-1}). Points (means ± SE, n=5)
455 represent measured emissions, yellow line is ER_{L+T} according treatment and season. R^2 and slope (sl) of
456 correlations between measured and modelled emissions were presented in yellow frame.
457
458 **Figure 3**: Diurnal pattern of measured acetaldehyde emissions rates (µgC.g$_{DM}^{-1}$.h^{-1}). Points (means ± SE, n=5)
459 represent measured emissions, yellow line is ER_{L+T} and dotted line is ER_T according to treatment and season. R^2
460 and slope (sl) of correlations between measured and modelled emissions were presented in yellow frame for L+T
461 and in white frame for T.
462
463 **Figure 4**: Diurnal pattern of measured methanol emissions rates (µgC.g$_{DM}^{-1}$.h^{-1}). Points (means ± SE, n=5)
464 represent measured emissions, yellow line is ER_{L+T} and dotted line is ER_T according to treatment and season. R^2
465 and slope (sl) of correlations between measured and modelled emissions were presented in yellow frame for L+T
466 and in white frame for T.
467
468

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

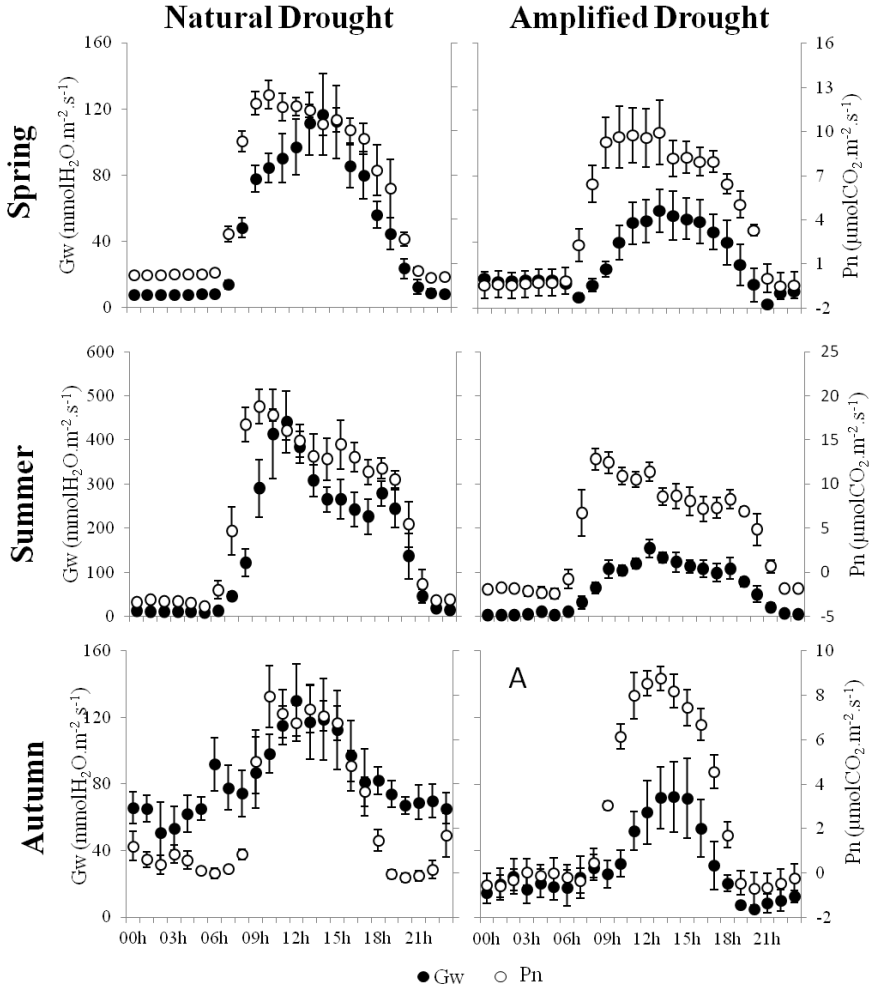
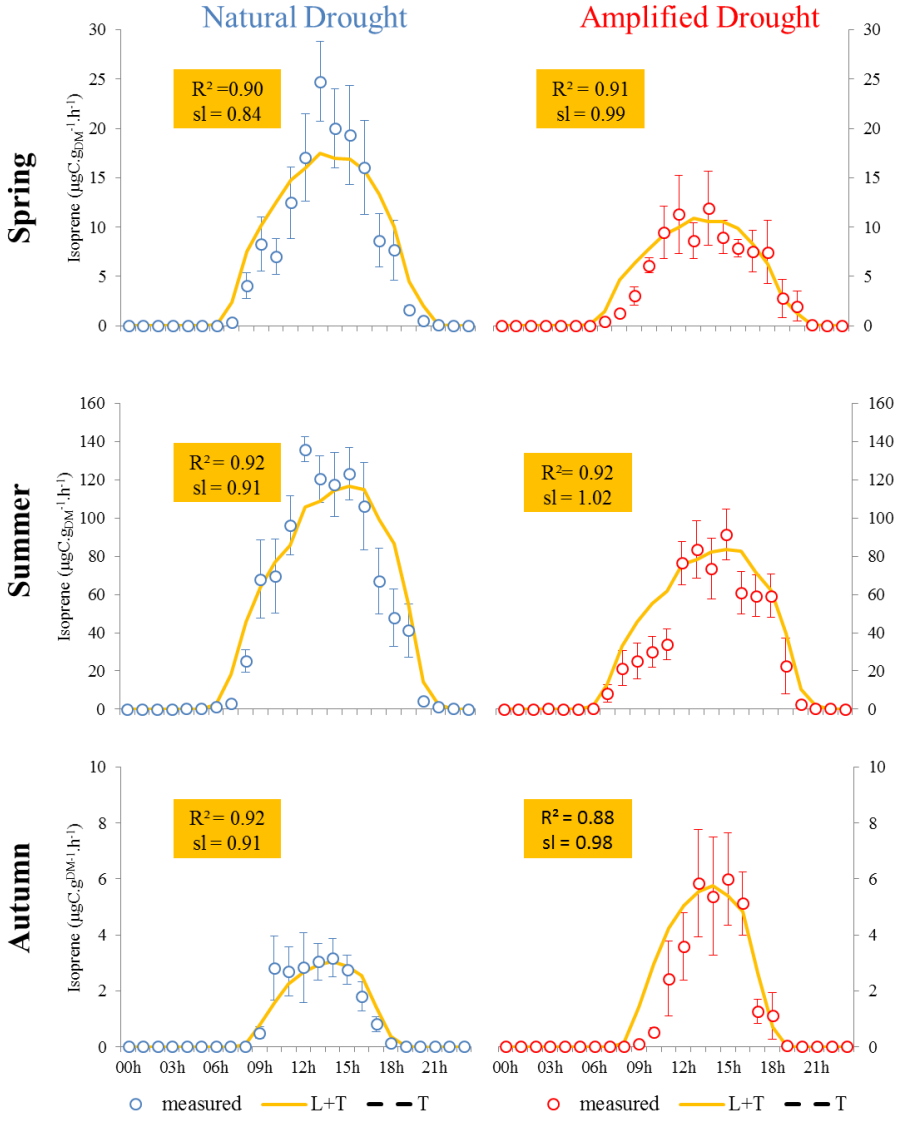


Figure 1:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016



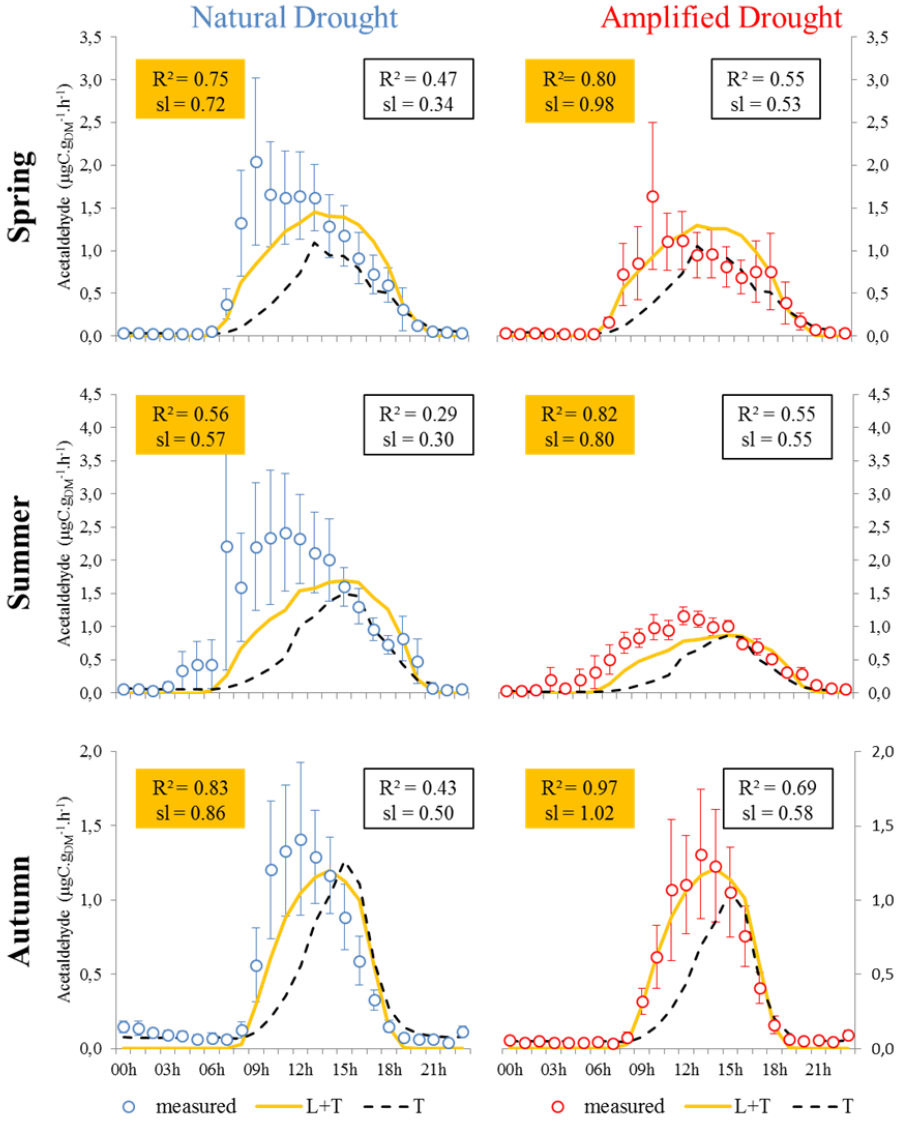
471

472 **Figure 2:**

473

474

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016



475

476 **Figure 3:**

477

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-836, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 7 October 2016

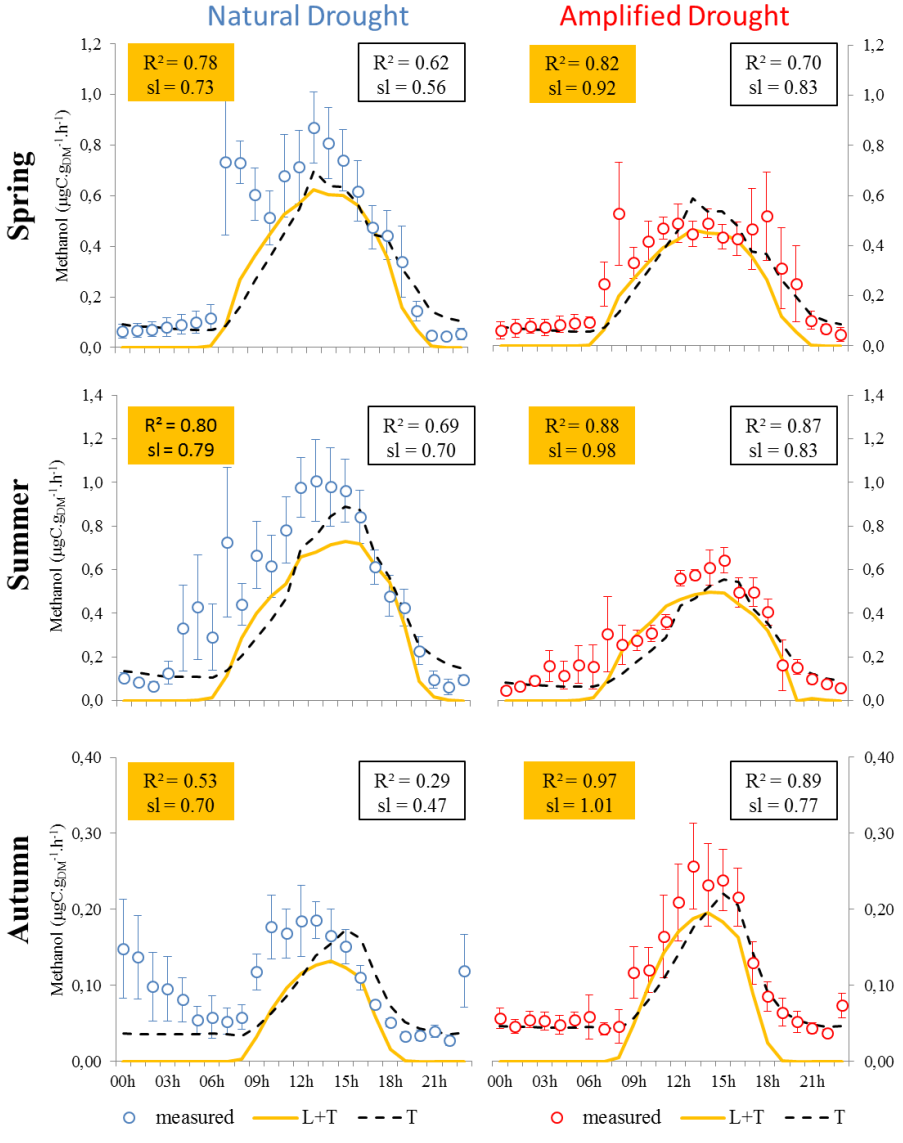


Figure 4: