

*The authors would like to thank the Editor and the Reviewers for very careful and detailed review of our manuscript and providing of comments and suggestions to improve the quality of the manuscript.*

**RC1: The manuscript discusses the light and temperature dependencies of several BVOC emissions from a Mediterranean oak species. This manuscript fits in the scope of the journal presenting a BVOC emission study on a relatively little studied tree species. The authors go through the methods they have used thoroughly, and the results are presented in the text and figures clearly. The discussion on the results and conclusions could, however, be deeper and underline how this study increases the understanding of BVOC emission dynamics. Though the manuscript is carefully written, some English language improvement would not be bad idea. My comments below are rather minor though their number is relatively high.**

**RC1: Line 13: You discuss many times about BVOC in singular form, though you actually mean plural BVOCs. Please check these throughout the text.**

AC: We did the modification in the manuscript.

**RC1: Line 23: You claim that the three sampling campaigns cover the entire seasonal cycle. However, note that there are likely sub-seasonal periods, which are not covered by your measurements. For example, the highest natural drought at the site is likely in late summer, when you did not measure. Do you think that your results from these three measurement periods are representative enough to model *Q. pubescens* BVOC emissions year around? If so, why? Could you describe with a few words the physiological state of the oaks during each of the campaigns, e.g. if the new leaf emergence or leaf size growth occurred during the spring measurement period?**

AC: We think that our measurement periods are well representative of *Q. pubescens* BVOCs emissions because they took place during the principal phenological stages of leaves. There was no leaf emergence during our spring period sampling, it was the end of leaf growth. We also performed an experiment during leaf emergence (in April 2013), not presented in this study, but there were very slight BVOCs emissions. During summer, leaves still matured and autumn was featured by the beginning of leaf senescence. We added a short comment on this part in the manuscript (lines 108-110).

**RC1: Line 24: Amplified drought impacted all studied BVOCs, but not necessarily all the minor compounds that the trees produce but you couldn't quantify.**

AC: Indeed, we added "studied" in this line.

**RC1: Line 32: Please use throughout the text the unit formatting as advised in the journal instructions.**

AC: We did the modification in the manuscript.

**RC1: Line 34: Please check the use of subscripts in the entire text.**

AC: We did the modification in the manuscript.

**RC1: Line 35: You likely mean tropospheric ozone concentration.**

AC: Yes, we changed this in the manuscript (line 35).

**RC1: Lines 72-74: In my mind, seven commas per a sentence is too much and makes the sentence hard to read. Please edit the sentence e.g.: However, there are still some misunderstandings at the level of emission mechanisms and consequently on model estimations for isoprene and, a fortiori, for highly volatile BVOCs under mild or severe water stress. In addition, you could open which misunderstandings you mean here.**

AC: We rewrote this sentence as suggested and we added some details on misunderstandings on isoprene emissions (lines 68-70).

**RC1: Line 80-81: Please correct: 2 million ha. Note that the study by Keenan et al. (2009) considers only forests, and there are other remarkable sources as well.**

AC: We did the modification in the manuscript (line 84).

**RC1: Line 86: The site may be free from direct human disturbance, but indirect disturbance through e.g. air pollution it certainly has experienced.**

AC: Indeed, we added “direct” in this sentence (line 90).

**RC1: Line 93: The plots were 200-300 m<sup>2</sup> in size. How many trees were growing in the plots? Can you be sure that the trees at the amplified drought plot did not uptake water by their vast root system from the non-drought area?**

AC: In natural drought plot, there is 145 stems and in amplified drought plot, there is 95 stems. We cannot be sure that trees at the amplified drought did not uptake water in natural drought plot. Indeed, we do not know where the trees roots are located. But, on our site, there is a buffer zone for each plot (2 meters). So, we only followed trees located in the heart of both plots. And, also, we observed effect of amplified drought on BVOC emissions and physiology parameters. We think that it a negligible phenomenon.

**RC1: Lines 96-97: I do not quite hit the idea of the latter part of the sentence: – corresponding for three years, to 2 months for natural treatment and 5 months for amplified treatment of drought period. Please rephrase.**

AC: We rephrased this sentence (lines 101-102).

**RC1: Line 100: You had five trees per treatment, but how many enclosures there were per tree and per sampling campaign? Did you move enclosures from tree to tree during one sampling campaign?**

AC: During each field campaigns, the five trees of each plot were sampled. We used 2 enclosure systems concomitantly which allowed us to analyze one tree under amplified drought and one tree under natural drought. The analyses was performed during 1 or 2 days, depending on the weather. And, every 1 or 2 days, we moved enclosures from tree to tree. We added a sentence about that in the manuscript (lines 114-115).

**RC1: Line 103: To be precise, BVOC exchange between the tree and the atmosphere is a part of tree gas exchange.**

AC: We did the modification in the manuscript.

**RC1: Line 104: How much biomass the enclosures enclosed? Please give some numbers (branch length, leaf area, leaf mass or equivalent).**

AC: We enclosed branches containing between 8 and 12 leaves which corresponded to 1.4g and 3.6g of dry matter. In terms of surface, we enclosed between 110 and 320 cm<sup>2</sup> of leaves. With these data, we calculated the relation between leaf mass and surface (LMA) and we found no significant difference between leaves from amplified and natural drought at any season. We added a sentence about that (lines 128-130).

**RC1: Line 106: A PTFE air generator sounds like it would produce PTFE in the air. Please rephrase.**

AC: We rephrased this sentence (line 116).

**RC1: Line 109: What do you mean by the excess of air humidity? Was the humidity inside the enclosure controlled (currently not stated in the text) and set to some range? If so, please make an addition in the text, as this is rather critical detail in the case of water-soluble compounds.**

AC: The humidity inside the enclosure was not controlled. However, we slightly removed some humidity from entering the chambers (before the air generator), especially in autumn to impede condensation of water vapor which would have disturb mass flow controller.

**RC1: Line 116: Rather say: made of PTFE.**

AC: We did the modification in the manuscript (line 116).

**RC1: Line 119: Is reference to chapter 2.2 correct or should it refer to 2.4 (BVOC analysis)?**

AC: Indeed, we did the modification in the manuscript (line 133).

**RC1: Line 120: Please edit: gas exchange values.**

AC: We did the modification in the manuscript (line 134).

**RC1: Line 125: Add s: parameters. Lyophilization is not familiar term to many readers of the journal, so say rather: –were lyophilized (freeze-dried) to assess the dry mass.**

AC: We did the modification in the manuscript (line 139).

**RC1: Line 140-141: You say that formaldehyde calculation took into account the humidity dependence. What about the other humidity-dependent compounds? Could the clearly visible steps methanol and acetone fluxes in the late evenings of natural drought (fig.4 and S3) be humidity-related? Anyhow, there seems to be something else happening simultaneously: net photosynthesis rises to positive values just before midnight (fig. 1, autumn, natural drought). Something wrong with the measurements or calculation?**

AC: We only took into account the humidity dependency of formaldehyde because for this compound, this dependency was very problematic compared to the others compounds (Vlasenko et al. 2010).

We do not think that the increase of methanol and acetone in late evening (in autumn) could come from the humidity because we analyzed a pair of trees at a time (one tree under natural drought and one tree under amplified drought). Moreover, the enclosure chambers were feed with the same inlet air (thus, with a similar humidity) and transpiration rate during the night was close to zero. If there was a humidity problem, with our set-up, we would have observed the same phenomenon on amplified drought and it was not the case. Moreover, it seems unlikely that there was a calculation problem because we always used the same calculation. It was probably a phenomenon linked to trees metabolisms but we cannot explain this yet.

**RC1: Line 145: Why did you choose to express the emission rates as C (carbon)?**

AC: We chose to express the emission rates in carbon because in many studies of dealing with BVOC modelling, they used this unit (Guenther et al. 2012; Guenther 2013). Also, in global scale, it is more convenient to express BVOC emissions in carbon to evaluate their impact on global change.

**RC1: Line 164-165: Please rephrase for example as follows: Afterwards, linear regression tests and slope tests (equal to 1) were also performed.**

AC: We did the modification in the manuscript (lines 181-182).

**RC1: Line 168: Have you any data how dry the soil actually was? Any soil volumetric water content measurements or equivalent throughout the seasons?**

AC: We have predawn water potential only for the summer campaign which can give a good idea of water availability in soil. During this season, there is a significant difference between both plots (-0.61MPa for natural drought and -0.85MPa for amplified drought,  $P < 0.05$ ). Moreover, we observed an effect of our treatments in physiology, especially on stomatal conductance.

**RC1: Line 171: Please correct spelling: other season and stomatal closure (the latter one in some following lines as well).**

AC: We did the modification in the manuscript.

**RC1: Line 177: I wonder if you have any tree growth data from the site ? In ceasing growth (height growth or lateral growth depending on timing) you might see drought effect earlier than in photosynthesis. The results are not discussed and compared to literature too much, so you could here e.g. refer to an earlier drought study (Damesin & Rambal1995) conducted with the same species.**

AC: Indeed, we have some data on tree growth (in terms of leaf biomass and lateral growth) but with no change in 2013 and 2014 and significant reduction of growth in 2016 (data showed on other publication) that is the fifth year of amplified drought. Photosynthesis is typically, is the first parameter to be impacted by drought (Chaves et al. 2002). That is exactly what occurred

in our study because we observed reduction of photosynthesis until 2012 (the first year of our experiment) whereas the first effect on growth appeared in 2016.

**RC1: Line 186-187: Reduced and increased emissions compared to what? And what is the reference for? In the discussion about isoprene emission dynamics during drought, you may also refer to Bruggemann & Schnitzler (2002), who have studied isoprene emissions of *Q. pubescens* saplings.**

AC: This experiment was conducted since 2012. In this paper, we only presented the results from the end of the second year to the beginning of the third year. In the first year, an increase of isoprene emissions was observed (data unpublished yet) whereas, we observed a decrease after 2-3 years of amplified drought. We added also a sentence on Bruggemann and Schnitzler's work (line 205).

**RC1: Line 193: You write here and in many other cases as well, that a compound responds to something. This reflects very much the modelling point of view. However, the plant responds to the changes in its environment, and that we see as a change in the plant volatile emissions. I would like to see in the discussion more of this plant-point-of-view: what does the plant do so that we see these kind of fluxes.**

AC: We added some part on plant-point of view throughout the discussion.

**RC1: Line 196-199: You write: “the daily cycle between natural and amplified drought was very different for each season.” If I look at the fig. 2 about isoprene emissions, I don't see very different daily cycles. Please clarify what you mean. Moreover, you write: “were not the only parameters driving isoprene emissions.” Please tell which other parameters you think were affecting at that time of the year.**

AC: Accordingly to the reviewer's comment, we change this sentence since indeed our description was confused. We should have written the daily cycle between natural and amplified drought was different. What was different but the intensity of isoprene emissions between amplified and natural drought. We suggest that plant likely needed to produce more isoprene with the aim to protect the photosystems apparatus in new leaves. We added this point in the manuscript (lines 220-221).

**RC1: Line 200: You discuss about MACR+MVK+ISOPROOH basically as a compound. Have you any data if all these three compounds really are present in the fluxes all the time or if one of them dominates the measured flux and thus masks the variations in the others?**

AC: We did not have data on these compounds separately. We only detected the ion 73 corresponding on the three compounds. Thus, we cannot say if one of these compounds dominated flux.

**RC1: Line 213: Turn the sign: <.**

AC: In this line, it is the good sign. It was just for specifying that the slope was not significantly different to 1. Maybe, it is confusing and we can remove this indication.

**RC1: Line 221: Please check spelling: phenomena.**

AC: We did the modification in the manuscript (line 248).

**RC1: Line 227: Please change to leaf elongation.**

AC: We did the modification in the manuscript (line 256).

**RC1: Line 230: You write that methanol emissions respond only to temperature in nighttime. Have you taken into account that in nighttime light intensity is basically zero if no artificial light is available and stays constant over the night? Moreover, in nighttime light intensity range is far smaller than in daytime, and this will be reflected in your modelling results.**

AC: We measured light during the night and used these data for modelling. The data on light during nighttime was close to zero and temperature was roughly constant. Thus, we attributed emissions of methanol during the nighttime to a temperature-driven response as already demonstrated by Smiatek and Steinbrecher (2006). We made some figures in the new version of the supplementary files, summarizing light and temperature conditions during our experiment.

**RC1: Line 254-255: Would this sentence need a reference?**

AC: These results were not published yet. Thus, we added personal communication from A.C. Génard-Zielinski, line 291).

**RC1: Line 261: Please change phenomenon to phenomena.**

AC: We did the modification in the manuscript (line 297).

**RC1: Line 263: Please check spelling: the calculation of ecophysiological parameters.**

AC: We did the modification in the manuscript (line 299).

**RC1: Line 278: Please check spelling: vapour.**

AC: We did the modification in the manuscript (313).

**RC1: Line 327-328: Here and in some other cases as well the italics of scientific names have been replaced with cryptic markings. Please check the reference list.**

AC: We did the modification in the manuscript.

**RC1: Table 1 caption: Please remove the abbreviation ER and add the explanations for ND and AD.**

AC: We did the modification in the manuscript.

**RC1: Figure 1: Please remove “ND: natural drought; AD: aggravated drought” as the information is in the figure. The various vertical scales make it hard to compare the seasons, so please consider unifying the scales. And please remove A from the lower right panel.**

AC: We did the modification in the manuscript.

**RC1: Figure 2-4 captions: Edit the last sentences: – emissions are presented –.**

AC: We did the modification in the manuscript.

Chaves M.M., Pereira J.S., Maroco J., Rodrigues M.L., Ricardo C.P.P., Osório M.L., Carvalho I., Faria T. & Pinheiro C. (2002). How plants cope with water stress in the field? Photosynthesis and growth. *Annals of botany*, 89, 907-916.

Guenther A. (2013). Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere. *International Scholarly Research Notices*, 2013.

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.

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.

**RC2:** This manuscript presents BVOC emission data from the drought tolerant *Quercus pubescens* using PTR-TOF-MS techniques. The authors study a suite of BVOCs (isoprene, methanol, acetone, acetaldehyde, formaldehyde and MACR+MVK+ISOPOOH) at 3 points over a year, under both natural and amplified drought conditions. They compare observations with model algorithms and report 2 types of emission responses: 1) light and temperature dependent and 2) it dependent during the day and only temperature dependent at night.

**RC2: General Comments** English grammar problems are numerous throughout the manuscript.

AC: The manuscript was corrected by a bilingual person.

**RC2:** Your two types of responses can be more easily summarized throughout the manuscript, “All six BVOCs monitored showed daytime light and temperature dependencies, while three BVOCs (methanol, acetone and formaldehyde) showed nighttime temperature dependencies as well.” Figures 4 and S3 show that the models do accurately simulate the emission burst for methanol as well as the formaldehyde deposition, albeit the models both show a slight lag in the hour of the day in just the autumn natural drought conditions.

AC: The burst of methanol is observed only in spring and summer between 6am and 8am. For example methanol emission reach almost  $0.8\mu\text{gC}\cdot\text{g}_{\text{DM}}^{-1}\cdot\text{h}^{-1}$  during the burst contrasting with the previous emission (less than 0.01). The graph shows that none of the model (yellow and dotted lines) fit this burst. Concerning formaldehyde deposition (S4), even if the models follow the same emission pattern than the observations, they don't show any negative emission and so can't accurately allow to estimate the deposition.

**RC2: Specific comments L13 and throughout manuscript: use plural form “BVOCs” when speaking about more than one compound.**

AC: We did the modifications throughout the manuscript.

**RC2: L19: “. . .especially in the Mediterranean. . .”**

AC: We did the modifications throughout the manuscript (line 18).

**RC2: L22: “. . .a drought tolerant. . .”**

AC: We already deleted this point as suggested by the other reviewer.

**RC2: L51 – 53: You write: “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.” Please separate references for accuracy. For example, MEAGAN models (Guenther 2006 and 2012 references) do not include vegetation species specific emission factors nor account for leaf age or biomass density.**

AC: We did the modification (line 52).

**RC2: L70: “. . .IPCC predicts. . .”**

AC: We did the modification (line 76).

**RC2: L85: “60 km North of Marseille, France. . .”**

AC: We did the modification (line 89).



**RC2: L93: You write, “. . .drought (300m<sup>2</sup> ) and an amplified drought (232m<sup>2</sup> ).” Better indicate what the values in parentheses represent.**

AC: We have corrected this point as follows: “A rainfall exclusion device (an automated monitored roof deployed during selected rain events) was set up over part of the O<sub>3</sub>HP canopy (232m<sup>2</sup> surface) to exclude 30% of raining according to the worst scenario of climate change (Giorgi & Lionello 2008; IPCC 2013). This surface, thus, formed the amplified drought plot which was compared to natural drought plot (300m<sup>2</sup> surface) where trees grew under natural conditions with no rain exclusion.”

**RC2: L93 – 101: This wording was difficult to understand. How did you determine the extent of drought? How do you know this was indeed a drought stress?**

AC: To answer to this point, we have added a new graph showing the ombrothermic diagrams for the 2 plots used. The drought periods were presented in this graph showing the recurrence and length of drought periods for every years. Drought stress occurs when the temperature line is above the precipitation bars in ombrothermic diagrams (Emberger *et al.* 1963).

**RC2: L95 – 97: “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.” This text should be rewritten to clearly describe the differences between the natural and amplified drought treatments in terms of rainfall exclusion and periods of application, i.e. what 2 month period? What 5 month period?**

AC: We have rewritten the paragraph to be clearer. Together with the ombrothermic diagram, we hope that the experimental precipitation exclusion is better explained (lines 93-105).

**RC2: Was there any sampling conducted prior to the experiment or during the experiment on non-drought stressed trees for comparison?**

AC: There was no sampling conducting prior to the experiment on non-drought stress trees. Indeed, we have two treatments: one where trees are submitted to natural rain (and so natural Mediterranean summer drought) and a second one where trees are submitted to amplified drought (more or less 30% according to climatic models) during the tree growth period.

**RC2: L229 - 231: Nevertheless, our results suggested that methanol emissions responded strongly to light and temperature during the day whereas, during the night, they responded to temperature. See General Comments for suggested clarification.**

AC: We better structured the manuscript by introducing: “All six BVOCs monitored showed daytime light and temperature dependencies while three BVOCs (methanol, acetone and formaldehyde) also showed emissions during the night despite the absence of light under constant temperature. » in the beginning result section (lines 212-215).

**RC2: L261 – 262: “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.” Figures 4 and S3 show that the models do accurately simulate the emission burst for methanol as well as the formaldehyde deposition, albeit the models both show a slight lag in the hour of the day in just the autumn natural drought conditions.**

AC: As we said above: “the burst of methanol is observed only in spring and summer between 6am and 8am. For exemple, methanol emission reach almost 0.8μgC.g<sub>DM</sub><sup>-1</sup>.h<sup>-1</sup> during the burst contrasting with the previous emission (less than 0.01). The graph shows that none of the model (yellow and dotted lines) fit this burst. Concerning formaldehyde deposition (S4), even if the models follow the

same emission pattern than the observations, they don't show any negative emission and so can't accurately allow to estimate the deposition".

Emberger L., Gaussen H., Kasas M. & DePhilippis A. (1963). Carte bioclimatique de la zone méditerranéenne. *UNE SC OF AO, Paris, carte et annexes.*

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

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

# 1 **Effect of mid-term drought on *Quercus pubescens* BVOCs** 2 **emissions seasonality and their dependence to light and/or** 3 **temperature**

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12 **Key words:** BVOCs, natural and amplified drought, season, light and temperature

13 **Abstract.** Biogenic volatile organic compounds (BVOCs) emitted by plants represent a large source of carbon  
14 compounds released into the atmosphere where they account for precursors of tropospheric ozone and secondary  
15 organic aerosols. Being directly involved in air pollution and indirectly in climate change, understanding what  
16 factors drive BVOCs is a prerequisite for modelling their emissions and predict air pollution. The main  
17 algorithms currently used to model BVOCs emissions are mainly light and/or temperature dependent. Additional  
18 factors such as seasonality and drought also influence isoprene emissions, especially in the Mediterranean region  
19 which is characterized by a rather long drought period in summer. These factors are increasingly included in  
20 models but only for the principal studied BVOC, namely isoprene but there are still some discrepancies in  
21 estimations of emissions. In this study, the main BVOCs emitted by *Quercus pubescens*: isoprene, methanol,  
22 acetone, acetaldehyde, formaldehyde, MACR MVK and ISOPOOH (these 3 last compounds detected under the  
23 same ion), were monitored with a PTR-ToF-MS over an entire seasonal cycle, under both in situ natural and  
24 amplified drought which is expected with climate change. Amplified drought impacted all studied BVOCs by  
25 reducing emissions in spring and summer while increasing emissions in autumn. All six BVOCs monitored  
26 showed daytime light and temperature dependencies while three BVOCs (methanol, acetone and formaldehyde)  
27 also showed emissions during the night despite the absence of light under constant temperature. Moreover,  
28 methanol and acetaldehyde burst in the early morning and formaldehyde deposition/uptake were also punctually  
29 observed which were not assessed by the classical temperature and light models.

## 30 **1 Introduction**

31 Plants contribute to global emissions of volatile organic compounds (VOCs) with an estimated emission rate of  
32  $10^{15}$  gC<sub>yr</sub><sup>-1</sup> (Guenther *et al.* 1995; Harrison *et al.* 2013). The large variety of compounds released by plants  
33 represents, at the global scale, 2-3% of the total carbon released in the atmosphere (Kesselmeier & Staudt 1999).  
34 Under strong photochemical conditions, BVOCs, together with NO<sub>x</sub>, can significantly contribute to tropospheric  
35 ozone concentration (Xie *et al.* 2008; Papiez *et al.* 2009). In addition to its greenhouse effect, O<sub>3</sub> has strong  
36 effects on plant metabolism (Reig-Armiñana *et al.* 2004; Beauchamp *et al.* 2005) as well as on human health  
37 (Lippmann 1989). BVOCs are also rapidly oxidized by OH radical and NO<sub>3</sub> (Hallquist *et al.* 2009; Liu *et al.*  
38 2012), which account for an important fraction of the total mass of secondary organic aerosols (SOA, Jimenez *et al.*  
39 2009). Methanol and acetone are, after isoprene, the principal BVOCs released to the atmosphere. Isoprene  
40 emissions represent between 400-600 TgC yr<sup>-1</sup> at the global scale (Arnth *et al.* 2008) whereas methanol  
41 emissions vary between 75 and 280 TgC yr<sup>-1</sup> (Singh *et al.* 2000; Heikes *et al.* 2002, respectively) and acetone  
42 emissions represent only 33 TgC yr<sup>-1</sup> (Jacob *et al.* 2002). Other compounds such as acetaldehyde, methacrolein  
43 (MACR), methyl vinyl ketone (MVK), isoprene hydroxy hydroperoxides (ISOPOOH) and formaldehyde, whose  
44 biogenic origin has been poorly investigated, are better known to be anthropogenic and/or secondary VOCs  
45 issued from atmospheric oxidations (Hallquist *et al.* 2009). However, acetaldehyde is also a by-product of plant  
46 metabolism and its emissions represent 23 Tg yr<sup>-1</sup> at the global scale (Millet *et al.* 2010). Formaldehyde, MACR,  
47 MVK and ISOPOOH are released by plants through oxidations of methanol and isoprene, respectively, within  
48 leaves but they can have other leaf precursors (Oikawa & Lerdau 2013). Thus, it is thereby important to model  
49 all this panel of BVOCs emissions with the aim of predicting their effect on secondary atmospheric chemistry.  
50 Current models allow to predict BVOCs emissions according to the type of vegetation, biomass density, leaf age,  
51 specific emission factor for many vegetal species, as well as the impact of some environmental factors. Models,  
52 such as the MEGAN (Guenther *et al.* 2006; Guenther *et al.* 2012) or CHIMERE (Menuet *et al.* 2014) model,  
53 include at least two main algorithms that allow to model light and temperature emissions dependence (called  
54 L+T algorithm afterwards) and a temperature dependent algorithm (called T algorithm afterwards), both  
55 described in Guenther *et al.* (1995). The L+T algorithm is typically used for BVOCs emissions whose synthesis  
56 rapidly relies on photosynthesis, and hence include *de novo* emissions. The T algorithm is used for BVOCs  
57 emissions that do not directly rely on BVOCs synthesis when, for example, they originate from permanent large  
58 storage pools (Ormeno *et al.* 2011). The dependence to light and/or temperature is well documented for  
59 isoprenoids (Owen *et al.* 2002; Rinne *et al.* 2002; Dindorf *et al.* 2006) but there is still a lack of knowledge about  
60 highly volatile BVOCs (e.g. methanol, acetone, acetaldehyde). However, many of these compounds are very  
61 reactive in the atmosphere (Hallquist *et al.* 2009) and, could be emitted in large quantities to the atmosphere at  
62 global scale. The characterization of their emissions and sensitivity to light and/or temperature is, thus, necessary  
63 in order to obtain reliable predictions of atmospheric processes in order not to miss this important part of the  
64 atmospheric reactivity.

65 Other factors than light and temperature can drive BVOCs emissions such as water stress. Most studies dealing  
66 with BVOCs response to water stress have, however, focused on terpene-like compounds and have been carried  
67 out after weeks of watering restriction or removal under controlled conditions (for a review, see studies cited in  
68 Peñuelas and Staudt 2010). These studies reveal that there are still some misunderstandings at the level of  
69 emission mechanisms since some works showed increases (Funk *et al.* 2004; Monson *et al.* 2007) or decreases  
70 of isoprene emissions (Brüggemann & Schnitzler 2002; Fortunati *et al.* 2008) and there is a lack of knowledge

71 on the impact of water stress on highly BVOCs emissions. Moreover, the sensitivity of isoprene and highly  
72 volatile BVOCs emissions to recurrent water stress (few years) under in situ conditions is clearly missing.  
73 Likewise, the capacity of current L+T and T algorithms to predict emission shifts under different drought  
74 scenarios in the context of climate change needs to be addressed for isoprene and highly volatile compounds.  
75 This is of especial interest for the Mediterranean area where the most severe climatic scenario of the IPCC  
76 predicts an intensification of summer drought consisting on a rain reduction that can locally reach 30%, an  
77 extension of the drought period as well as a temperature rise of 3.4°C, (Giorgi & Lionello 2008; IPCC 2013;  
78 Polade *et al.* 2014) for 2100.

79 In the present investigation, we aimed (i) to study the standard emission factors of each studied BVOC released  
80 by *Q. pubescens*, including isoprene and highly volatile compounds that originate from plant metabolism under  
81 water stress (ii) to test the performance of the L+T and T algorithms to predict isoprene and highly volatile  
82 BVOCs emissions over the seasonal cycle and under two recurrent water stress treatments. *Q. pubescens* was  
83 chosen as vegetal model because this species is highly resistant to drought and well widespread in the Northern  
84 Mediterranean area occupying 2 million ha (Quézel & Médail 2003). It also represents the major source of  
85 isoprene emissions in the Mediterranean area and the second one at the European scale (Keenan *et al.* 2009).

## 86 2 Material and methods

### 87 2.1 Experimental site

88 Our study was performed at the O<sub>3</sub>HP site (Oak Observatory at OHP, Observatoire de Haute Provence), located  
89 60 km North of Marseille, France (5°42'44" E, 43°55'54" N), at an elevation of 650m above the sea level. The  
90 O<sub>3</sub>HP (955m<sup>2</sup>), free from direct human disturbance for 70 years, consists of a homogeneous forest mainly  
91 composed of *Q. pubescens* (≈ 90 % of the biomass and ≈ 75 % of the trees) with a mean diameter of 1.3 m. The  
92 remaining 10 % of the biomass is mainly represented by *Acer monspessulanum* trees, a very low isoprene-  
93 emitter species (Genard-Zielinski *et al.* 2015). The O<sub>3</sub>HP site was created in 2009 in order to study the impact of  
94 climate change on a Q. pubescens forest. Using a rainfall exclusion device (an automated monitored roof  
95 deployed during rain events) set up over part of the O<sub>3</sub>HP canopy, it was possible to reduce natural rain by 30%  
96 and to extend the drought period in an attempt to mimic the current climatic model projections for 2100 (Giorgi  
97 & Lionello 2008; IPCC 2013; Polade et al. 2014). Two plots were considered in the site; a plot receiving natural  
98 precipitation where trees grew under natural drought (300m<sup>2</sup> surface, used as control plot) and a second plot  
99 submitted to amplified drought (232m<sup>2</sup> surface, used as amplified drought plot). Rain exclusion on this latter plot  
100 started on April 2012 and was continuously applied every year, principally, during the growth period.  
101 Ombrothermic diagrams indicated that the drought period was extended for 2 months in 2012, 4 months in 2013  
102 and 3 months in 2014 for amplified drought relative to natural drought (Fig 1). Data on cumulative precipitation  
103 showed that 35% of rain was excluded in 2012 (from 29 April from to 27 October), 33.5% in 2013 (from 7 July  
104 from to 29 December), 35.5% in 2014 (from 8 April to 8 December). This experimental set up involved a  
105 recurrent drought in the amplified drought plot. Sampling was performed at the branch-scale at the top of the  
106 canopy during three campaigns from October 2013 to July 2014, covering an entire seasonal cycle: in autumn  
107 (14 to 28 October 2013, 2nd year of amplified drought), in spring (12 to 19 May 2014, 3rd year of amplified  
108 drought) and in summer (13 to 25 July 2014, 3rd year of amplified drought). Spring, summer and autumn

109 campaigns corresponded to the end of leaf growth, leaf maturation and the beginning of the leaf senescence,  
110 respectively. The same five trees per plot were selected and investigated throughout the study.

## 111 2.2 Branch scale-sampling methods

112 Two identical dynamic branch enclosures were used for sampling gas exchange (in terms of CO<sub>2</sub>, H<sub>2</sub>O and  
113 BVOCs) as fully described in Genard-Zielinski *et al.* (2015) with some modifications. Branches were enclosed  
114 in a  $\approx$  30L PTFE (polytetrafluoroethylene) frame closed by a 50 $\mu$ m thick PTFE film. One tree from natural and  
115 one tree from amplified drought plot were analysed concomitantly during 1 or 2 days. Inlet air was introduced at  
116 9L.min<sup>-1</sup>, controlled by mass flow controllers (MFC, Bronkhorst), using an air generator made, inside, by PTFE  
117 (KNF N840.1.2FT.18®, Germany) allowing for air renewal inside the chamber every  $\sim$  3min. Ozone was  
118 removed from inlet air by placing PTFE filters impregnated with sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) as described by  
119 Pollmann *et al.* (2005), so that oxidation of BVOCs due to ozone within the enclosed atmosphere is negligible.  
120 The excess of air humidity was removed using drierite. A PTFE fan ensured a rapid mixing of the chamber air  
121 and a slight positive pressure within the enclosure enabled the PTFE film to be held away from leaves to  
122 minimise biomass damage. Microclimate (temperature, relative humidity and photosynthetically active radiation  
123 or PAR) was continuously (every minute) monitored by a data logger (LI-COR 1400®; Lincoln, NE, USA) with  
124 a relative humidity and temperature probe placed inside the chamber (RHT probe, HMP60, Vaisala, Finland) and  
125 a quantum sensor (PAR, LI-COR, PAR-SA 190®, Lincoln, NE, USA) placed outside the chamber. The climatic  
126 conditions in terms of PAR and temperatures are summarized in Fig. S1 (in supplementary files) for each field  
127 campaigns. All air flow rates were controlled by mass flow controllers (MFC, Bronkhorst) and all tubing lines  
128 were made of PTFE. Chambers were installed the day before measurements and flushed overnight. Enclosed  
129 branches contained 8 to 12 leaves corresponding to a range of 1.4 to 3.6g of dry matter and 110 to 320cm<sup>2</sup> of leaf  
130 surface, respectively.

## 131 2.3 Ecophysiological parameters

132 Exchanges of CO<sub>2</sub> and H<sub>2</sub>O from the enclosed branches were continuously (every min) measured using infrared  
133 gas analysers (IRGA 840A®, LI-COR) concomitantly with BVOCs emission measurements (cf. 2.4). Gas  
134 exchange values were averaged by taking into account all the data measured between 12h and 15h (local time).  
135 Net photosynthesis ( $P_n$ ,  $\mu$ molCO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>) and stomatal conductance to water ( $G_w$ , mmolH<sub>2</sub>O m<sup>-2</sup> s<sup>-1</sup>) were  
136 calculated using equations described by Von Caemmerer and Farquhar (1981) as used in Genard-Zielinski *et al.*  
137 (2015) (for more details, see Appendix A, equations A1 to A4). Leaves from enclosed branches were directly  
138 collected after gas exchange sampling to accurately measure leaf surface with a leaf area meter. Gas exchange  
139 were hence expressed in a leaf surface basis. After that, leaves were freeze-dried to assess their dry mass.

## 140 2.4 BVOCs analysis

141 A PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was used for online  
142 measurements of BVOCs emitted by the enclosed branches. A multi-position common outlet flow path selector  
143 valve system (Vici) and a vacuum pump were used to sequentially select air samples from: amplified drought,  
144 inlet air, natural drought, ambient air and catalyser. Each sample was analysed every hour, with 15min of

145 analysis. Mass spectra in the range 0-500amu were recorded at 1min integration time. The reaction chamber  
146 pressure was fixed at 2.1mbar, the drift tube voltage at 550V and the drift tube temperature at 313 K  
147 corresponding to an electric field strength applied to the drift tube (E) to a buffer gas density (N) ratio of 125Td  
148 (1Td =  $10^{-17}$  V cm<sup>2</sup>). A calibration gas standard (TO-14A Aromatic Mix, Restek Corporation, Bellefonte, USA,  
149  $100 \pm 10$ ppb in Nitrogen) was used to experimentally determine the ion relative transmission efficiency. BVOCs  
150 targeted in this study and their corresponding ions include formaldehyde (m/z 31.018), methanol (m/z 33.033),  
151 acetaldehyde (m/z 45.03), acetone (m/z 59.05), isoprene (m/z 41.038, 69.069) and MACR+MVK+ISOPOOH  
152 (m/z 71.049, these three compounds were detected with the same ion with PTR-MS). The signal corresponding  
153 to protonated VOCs was converted into mixing ratios by using the proton transfer rate constants k given by  
154 Cappellin *et al.* (2012). Formaldehyde concentrations were calculated according to the method described by  
155 Vlasenko *et al.* (2010) to account for its humidity dependent sensitivity.

156 BVOCs emissions rates (ER) were calculated by considering the BVOCs concentrations in the inlet and outlet  
157 air as follows (equation 1):

$$158 \quad ER = \frac{Q_0 * (C_{out} - C_{in})}{B} \quad (1)$$

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

## 162 2.5 Emission algorithms

163 The light and/or temperature dependence of *Q. pubescens* BVOCs (isoprene and highly volatile compounds)  
164 under natural and amplified drought was tested using both the *L+T* and *T* algorithms. Emission rates calculated  
165 according to the se algorithms (called afterwards  $ER_{L+T}$  and  $ER_T$ , respectively) were calculated using the equation  
166 described in Guenther *et al.* (1995) (for more details, see Appendix B, equations B1 to B5). The empirical  
167 coefficient  $\beta$  (used in the *T* algorithm) was determined for each compound according to the season and the  
168 treatment through the slope of correlation between the natural logarithm of emissions rates (measured emissions,  
169  $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ ) and experimental temperature (K). Standardised emissions rates (EF, emissions rates at standard  
170 conditions of light and temperature,  $1000\mu\text{mol m}^{-2} \text{s}^{-1}$  and  $30^\circ\text{C}$ ), were used to calculate modelled emissions. EF  
171 were determined for each compound according to the season and the treatment and corresponded to the slope of  
172 the correlation between experimental emission rates and values of  $C_i * C_t$  when using the *L+T* algorithm or  $C_T$   
173 when using the *T* algorithm (see Appendix B for a full description of  $C_i * C_t$  and  $C_T$ ). All parameters used for the  
174 calculation of modelled emissions are presented in supplementary files (Table S1).

## 175 2.6 Data treatment

176 Data treatment was performed with the software STATGRAPHICS® centurion XV (Statpoint, Inc). After  
177 having checked the normality of the data set, two-way repeated measures ANOVA were performed to evaluate  
178 the variability of  $P_n$ ,  $G_w$  and BVOCs emission rates according to the drought treatment and the season.  
179 Pearson's correlations between measured and modelled emissions were performed to evaluate the algorithm  
180 (*L+T* or *T*) that better predicted *Q. pubescens* emissions under the different drought conditions and over the

181 seasonal cycle. Afterwards, linear regressions tests and slope comparison tests (equal to 1, referred to “sl”  
182 afterwards) were also performed to evaluate the good fit of tested algorithms with BVOCs emissions rates.

### 183 3. Results and discussion

#### 184 3.1 Ecophysiological parameters

185 The physiology of *Q. pubescens* was slightly impacted by amplified drought (Fig. 2), over the whole study, with  
186 a decrease of  $G_w$  under amplified drought compared to natural drought, by 44 % in spring ( $P < 0.1$ ) and 55 % in  
187 summer ( $P < 0.01$ , Table 1). In autumn, there was no significant difference between both treatments.  $P_n$  was  
188 only reduced in summer by 36 % ( $P < 0.1$ ) and there was no difference for the others season. Thus, the stomatal  
189 closure observed had a slight impact on carbon assimilation. Indeed, *Q. pubescens* has a high stem hydraulic  
190 efficiency (Nardini & Pitt 1999) which compensates the stomatal closure since it allows to use water more  
191 efficiently, thus, maintaining  $P_n$ . Moreover, it must be noted that an increase of  $P_n$  was observed in autumn and  
192 could likely be attributed to the autumnal rains. These results showed that the amplified drought artificially  
193 applied to *Q. pubescens* at O<sub>3</sub>HP led to a moderate drought for this species, based on a moderate reduction of the  
194 physiological performances (Niinemets 2010).

#### 195 3.2 Effect of drought on BVOCs emissions

196 The emissions of all BVOCs followed during this experimentation were reduced under amplified drought  
197 compared to natural drought, especially in spring and summer (Table 1) except for acetaldehyde emissions.  
198 Indeed, for this compound, there was no significant difference between both treatments probably due to a large  
199 variability of the data set. In autumn, for all BVOCs, there was no difference between both plots. The decrease of  
200 oxygenated BVOCs in spring and summer under amplified drought (e.g. methanol, MACR+MVK+ISOPOOH,  
201 formaldehyde, acetone) could be explained by the concomitant stomatal closure in spring and summer under  
202 amplified drought. Indeed, the emissions of these compounds are strongly bound to  $G_w$  (Niinemets *et al.* 2004).  
203 Isoprene emissions were also reduced in spring and summer during the third year of this experiment whereas an  
204 increase was observed in the first year (personal communication from A.C Génard-Zielinski) as well as what had  
205 been shown by Brüggemann and Schnitzler (2002) but this work was conducted with potted plants. The isoprene  
206 decrease observed in our experiment cannot be explained by the stomatal closure because this compound could  
207 also be emitted through the cuticle (Sharkey & Yeh 2001). It could rather be due to the decrease of  $P_n$  which  
208 reduced the carbon availability to produce isoprene. Moreover, carbon assimilated through  $P_n$  can be also  
209 invested into the synthesis of other defense compounds leading to a decrease of isoprene production and  
210 emission.

#### 211 3.3 Effect of drought on light and/or temperature dependence through a seasonal cycle

212 All six BVOCs monitored showed daytime light and temperature dependencies (isoprene, degradation products  
213 of isoprene and acetaldehyde), while three BVOCs (methanol, acetone and formaldehyde) also showed  
214 emissions during the night despite the absence of light under constant temperature.

215



216 Regarding the light and temperature dependencies, the daily cycle of isoprene emissions (Fig. 3) showed that this  
217 compound responds strongly to light and temperature as already known (Guenther *et al.* 1993) and that this  
218 response was not impacted by amplified drought. Isoprene can protect thylakoids from oxidative damage  
219 (Velikova *et al.* 2011) occurring mainly during the day which can explain this kind of dependence. Yet, our  
220 results showed the importance to take into account the effect of amplified drought on emission factors because  
221 the intensity of isoprene emissions between natural and amplified drought was very different independently of  
222 the season. The modelled emissions were very representative of measured emissions except in spring for natural  
223 drought when we obtained a slight underestimation of emissions ( $sl = 0.84$ ,  $P < 0.05$ ) maybe, because light and  
224 temperature, in spring, were not the only parameters driving isoprene emissions. At this season, plants likely  
225 needed to produce more isoprene to protect the establishment of photosystems in the new leaves.  
226 MACR+MVK+ISOPOOH emissions, as isoprene, seemed to respond better to light and temperature than to only  
227 temperature (Fig. S2 in supplementary files) since correlations between measured emissions and  $ER_{L+T}$  were  
228 always better than correlations with  $ER_T$ . Since MACR+MVK+ISOPOOH are oxidation products of isoprene  
229 (Oikawa & Lerdau 2013), it is not surprising that these compounds followed the same pattern than isoprene in  
230 terms of dependence to light and temperature. The estimations of  $ER_{L+T}$  were quite good except in spring under  
231 natural drought where a slight underestimation was observed ( $sl = 0.87$ ,  $P < 0.05$ ).

232 The dependence of acetaldehyde emissions to light and/or temperature is very contrasted; studies have shown  
233 that they are bound to both light and temperature (Jardine 2008; Fares *et al.* 2011) or to temperature only  
234 (Hayward *et al.* 2004). Our results suggested that acetaldehyde emissions were mainly bound to light and  
235 temperature (Fig. 4). Indeed, correlations between measured and  $ER_{L+T}$  were always better than with  $ER_T$ .  
236 However, some discrepancies were observed. Under natural drought, underestimations were observed in spring  
237 and summer ( $sl = 0.72$ , and  $sl = 0.57$ ,  $P < 0.05$ , respectively) whereas in autumn, there was a good estimation ( $sl$   
238  $= 0.86$ ,  $P > 0.05$ ). Under amplified drought, underestimation was only observed in summer ( $sl = 0.80$ ,  $P < 0.05$ ).

239 Daily cycles of acetaldehyde emissions presented also an emissions burst in the morning (at 7h, local time) in  
240 spring (under both treatments) and in summer (only under natural drought). Acetaldehyde can be produced due  
241 to an overflow of pyruvic acid during light-dark transitions. Cytosolic pyruvic acid levels rise rapidly and it can  
242 be converted into acetaldehyde by pyruvate decarboxylase (Fall 2003). This mechanism could explain the  
243 morning burst for this compound and the fact that no emissions during the night was observed-  
244

245 We observed emissions of methanol, acetone and formaldehyde during the night under no light and constant  
246 temperature (around 20°C, see supplementary files S1). Correlations between  $ER_{L+T}$  or  $ER_T$  and measured  
247 methanol emissions were very similar especially in spring and summer (Fig. 5). However, some observed  
248 phenomena suggested that methanol emissions was sustained by temperature alone at certain moment of the day.  
249 Indeed, the burst in the early morning (at 7h, local time), similar to acetaldehyde, was observed when stomata  
250 opened in spring and summer, independently of the drought treatment although it was clearer under natural than  
251 amplified drought. This burst can be explained by a strong release of this compound that has been accumulated  
252 in the intercellular air space and leaf liquid pools (due to the relative high polarity of methanol) at night when  
253 stomata are closed (Hüve *et al.* 2007). Moreover, for both drought treatments, methanol emissions during the  
254 night were observed at any seasons (especially autumn) which could be explained by nocturnal temperatures  
255 (roughly constant) that sufficed to maintain the biochemical processes involved in methanol formation. Methanol

emissions, which result from the demethylation of pectin during the leaf elongation, has already been described to be temperature dependent alone (Hayward *et al.* 2004; Folkers *et al.* 2008). However, our results suggest that methanol emissions respond strongly to light and temperature during the day. This kind of diurnal emissions cycle has already been described by Smiatek and Steinbrecher (2006).

Our results about daily cycles of acetone emissions (Fig. S3 in supplementary files) showed that this compound responded better to light and temperature than only temperature since correlations were better with  $ER_{L+T}$ . 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 ( $sl = 1.27$ ,  $P < 0.05$ ). Previous studies have shown that acetone rather depends on temperature alone (Fares *et al.* 2011) or to light and temperature (Jacob *et al.* 2002), indicating that its dependence to light and/or temperature remains unclear. During the day, acetone emissions were dependent to light and temperature and emissions still occurred during the night, especially in autumn. Alike methanol, nocturnal temperatures could allow to maintain acetone formation (Smiatek & Steinbrecher 2006). Acetone is a by-product of plant metabolism (Jacob *et al.* 2002) and its production can be enzymatic and non-enzymatic (Fall 2003) which can explain these observed differences through the day. We can suppose that acetone emissions observed during the day could come from the enzymatic activity and, on the contrary, during the night, they could come from the non-enzymatic production.

Formaldehyde emissions followed the same pattern than methanol and acetone emissions (Fig. S4 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 (mainly through oxidations) within leaves leading to CO<sub>2</sub> formation (Oikawa & Lerdau 2013). Emissions during the night suggest that formaldehyde came from another source than oxidation within leaves since oxidations occur mainly during the day due to an excess of light in chloroplasts, principal place of reactive oxygen species production (Asada 2006). Thus, formaldehyde emissions observed during the night could result from, for example, the glyoxylate decarboxylation or the dissociation of 5,10-methylene-THF (Oikawa & Lerdau 2013).

#### 4 Conclusion

After 3 years of amplified drought, all BVOCs emissions were reduced in spring and summer compared to natural drought 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 (2012), especially for isoprene, where an increase was observed for this compound (personal communication from A.C. Génard-Zielinski).

292 Amplified drought did not seem to shift the dependence to light and/or temperature which remained unchanged  
293 between treatments.

294 Moreover, two different dependence behaviours were found: (i) all six BVOCs monitored showed daytime light  
295 and temperature dependencies while (ii) only three BVOCs (methanol, acetone and formaldehyde) also showed  
296 that their emissions were maintained during the night with no light at rather constant nocturnal temperatures.

297 Moreover, some phenomena, such as methanol and acetaldehyde emissions bursts in early morning or the  
298 formaldehyde deposition/uptake (formaldehyde), were not assessed by either  $L+T$  or  $T$  algorithm.

## 299 Appendix A: calculation of ecophysiological parameters

300 Net photosynthesis ( $P_n$ ,  $\mu\text{molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ) was calculated using equations described by Von Caemmerer and  
301 Farquhar (1981) as follows:

$$302 \quad P_n = \frac{F*(Cr-Cs)}{S} - CS * E \quad (\text{A1})$$

303 Where  $F$  is the inlet air flow ( $\text{mol s}^{-1}$ ),  $C_s$  and  $C_r$  are the sample and reference  $\text{CO}_2$  molar fraction respectively  
304 (ppm),  $S$  is the leaf surface ( $\text{m}^2$ ),  $C_s * E$  is the fraction of  $\text{CO}_2$  diluted in water evapotranspiration and  $E$  ( $\text{molH}_2\text{O}$   
305  $\text{m}^{-2} \text{ s}^{-1}$  then transformed in  $\text{mmolH}_2\text{O m}^{-2} \text{ s}^{-1}$ , afterward) is the transpiration rate calculated as follow:

$$306 \quad E = \frac{F*(Ws-Wr)}{S*(1-Ws)} \quad (\text{A2})$$

307 where  $W_s$  and  $W_r$  are the sample and the reference  $\text{H}_2\text{O}$  molar fraction respectively ( $\text{molH}_2\text{O mol}^{-1}$ ).

308 Stomatal conductance to water ( $G_w$ ,  $\text{molH}_2\text{O m}^{-2} \text{ s}^{-1}$  then transformed in  $\text{mmolH}_2\text{O m}^{-2} \text{ s}^{-1}$ ) was calculated using  
309 the following equation:

$$310 \quad G_w = \frac{E*(1-\frac{Wl-Ws}{2})}{Wl-Ws} \quad (\text{A3})$$

311 where  $W_l$  is the molar concentration of water vapour within the leaf ( $\text{molH}_2\text{O mol}^{-1}$ ) calculated as follows:

$$312 \quad W_l = \frac{V_{psat}}{P} \quad (\text{A4})$$

313 where  $V_{psat}$  is the saturated vapour pressure (kPa) and  $P$  was the atmospheric pressure (kPa).

## 314 Appendix B: Modelled emissions calculation

315 The modelled emissions rates according to light and temperature ( $ER_{L+T}$ ) or the temperature algorithm ( $ER_T$ )  
316 were calculated according to algorithms described in Guenther *et al.* (1995) as follows :

$$317 \quad ER_{L+T} = EF_{L+T} * Cl * Ct \quad (\text{B1})$$

318 where  $EF_{L+T}$  is the emission factor at  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  of photosynthetically active radiation (PAR) and  $30^\circ\text{C}$   
319 of temperature (obtained with the slope of the correlation between experimental emissions and  $Cl * Ct$ ),  $Cl$  and  
320  $Ct$  correspond to light and temperature dependence factors respectively and were calculated with the following  
321 formulae:

$$322 \quad Cl = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L}} \quad (\text{B2})$$

$$Ct = \frac{\exp\left(\frac{C_{T1}(T-T_s)}{RT_sT}\right)}{1 + \exp\left(\frac{C_{T2}(T-T_M)}{RT_sT}\right)} \quad (\text{B3})$$

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

Modelled emissions according to temperature alone that is  $ER_T$ , was calculated as follows:

$$ER_T = EF_T * C_T \quad (\text{B4})$$

where  $EF_T$  is the emission factor at 30°C of temperature (obtained with the slope of the correlation between experimental emissions and  $C_T$ ) and  $C_T$  is a temperature dependence factor calculated as follows:

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

where  $\beta$  is an empirical coefficient (with a standard variation value of  $0.09\text{K}^{-1}$  used in literature when not measured) determined, in this study, for each compound according to the season and the treatment through the slope of the correlation between the natural logarithm of measured emissions rates ( $ER$ ,  $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ ) and experimental temperature (expressed in K),  $T$  is the leaf experimental temperature (K) and  $T_s$  is the standard temperature (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.

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**Table:**

**Table 1:** Net photosynthesis ( $P_n$ ,  $\mu\text{molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ ), stomatal conductance to water ( $G_w$ ,  $\text{mmolH}_2\text{O m}^{-2} \text{ s}^{-1}$ ) and emission rates ( $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$ ) according to treatment and season. Values represent an average of all data measured between 12h and 15h (local time). Letters denote the difference between drought treatments with  $a > b$  ( $P < 0.05$ ) and values showed represent the mean  $\pm$  SE,  $n=5$ . ND: natural drought and AD: amplified drought.

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



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### Figure legends

**Figure 1:** Ombrothermic diagram for natural and amplified drought in 2012, 2013 and 2014. Bars represent mean monthly precipitation (mm) and curves represent mean monthly temperature (°C). On each amplified drought graph, the percentage represents the proportion of excluded rain compared to natural drought plot.

**Figure 2:** Diurnal pattern of stomatal conductance ( $G_w$ ) and net photosynthesis ( $P_n$ ) according to drought treatment and season. Values showed represent means  $\pm$  SE, n=5.

**Figure 3:** Diurnal pattern of isoprene emissions rates, where points represent measured emissions, and the yellow line correspond to modelled emissions rates according to the  $L+T$  algorithm ( $ER_{L+T}$ ). Values are mean  $\pm$  SE, n=5.  $R^2$  and slope (sl) of correlations between measured and modelled emissions are presented in the yellow frame. Correlations were obtained without forcing data through the origin.

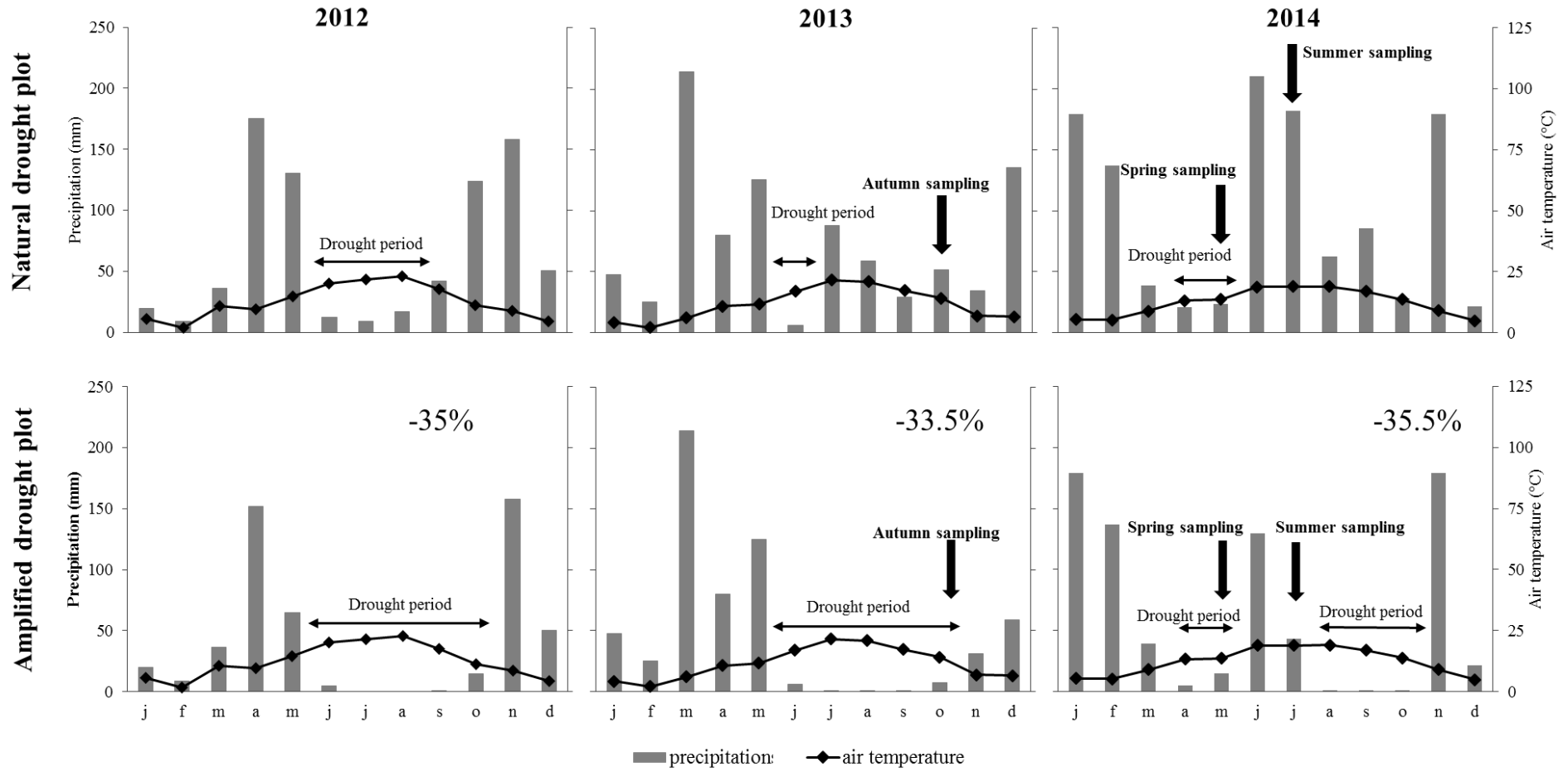
**Figure 4:** Diurnal pattern of acetaldehyde emissions rates, where points represent measured emissions, the yellow line correspond to modelled emissions rates according to the  $L+T$  algorithm ( $ER_{L+T}$ ) and dotted line is modelled emissions rates according to  $T$  algorithm ( $ER_T$ ). Values are mean  $\pm$  SE, n=5.  $R^2$  and slope (sl) of correlations between measured and modelled emissions are presented in the yellow frame for  $L+T$  and in the white frame for  $T$ . Correlations were obtained without forcing data through the origin.

**Figure 5:** Diurnal pattern of measured methanol emissions rates. Points (means  $\pm$  SE, n=5) represent measured emissions, yellow line correspond to modelled emissions rates according to the  $L+T$  algorithm ( $ER_{L+T}$ ) and dotted line is modelled emissions rates according to  $T$  algorithm ( $ER_T$ ). Values are mean  $\pm$  SE, n=5.  $R^2$  and slope (sl) of correlations between measured and modelled emissions are presented in the yellow frame for  $L+T$  and in the white frame for  $T$ . Correlations were obtained without forcing data through the origin.

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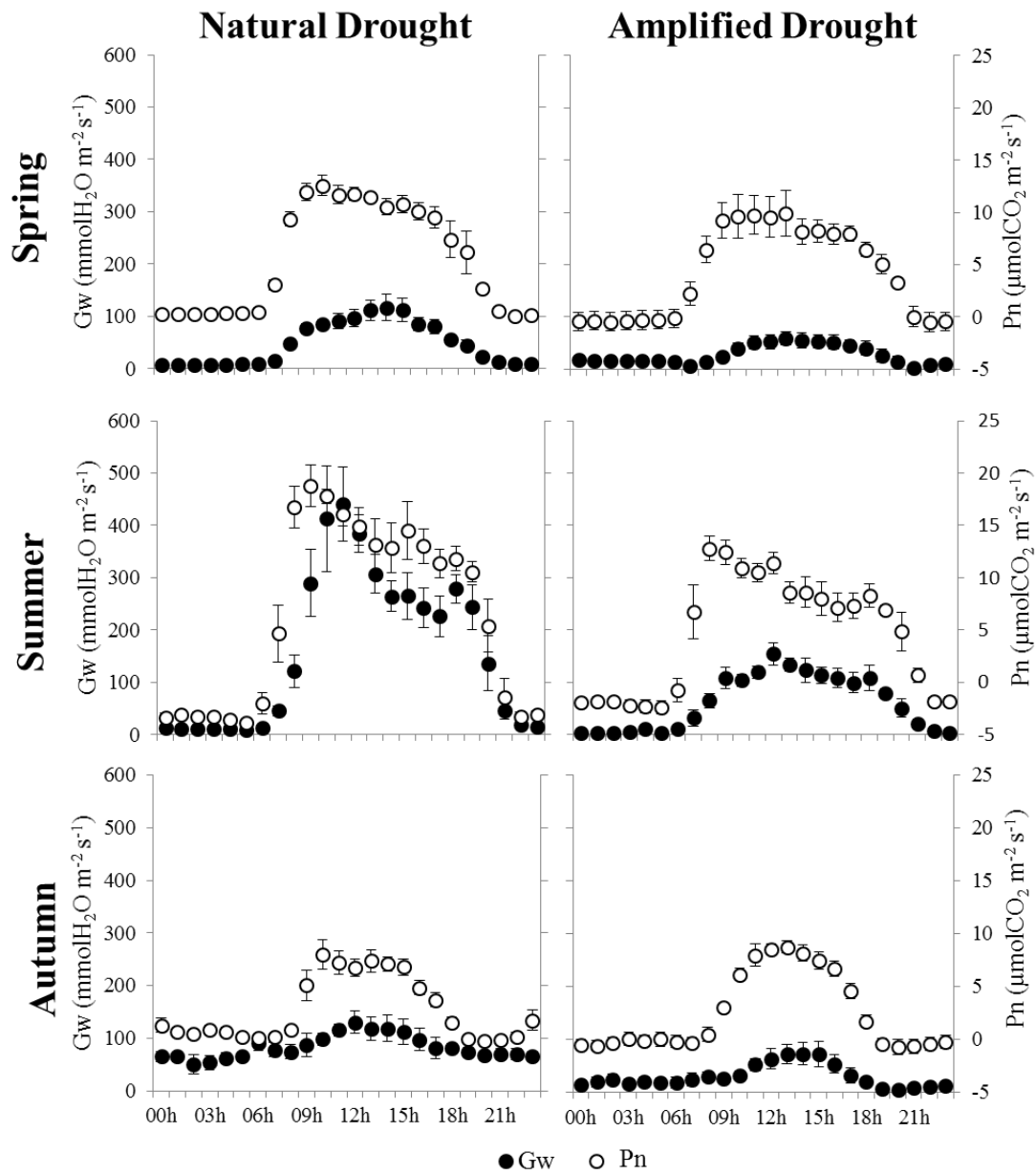


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574 **Figure 1:**

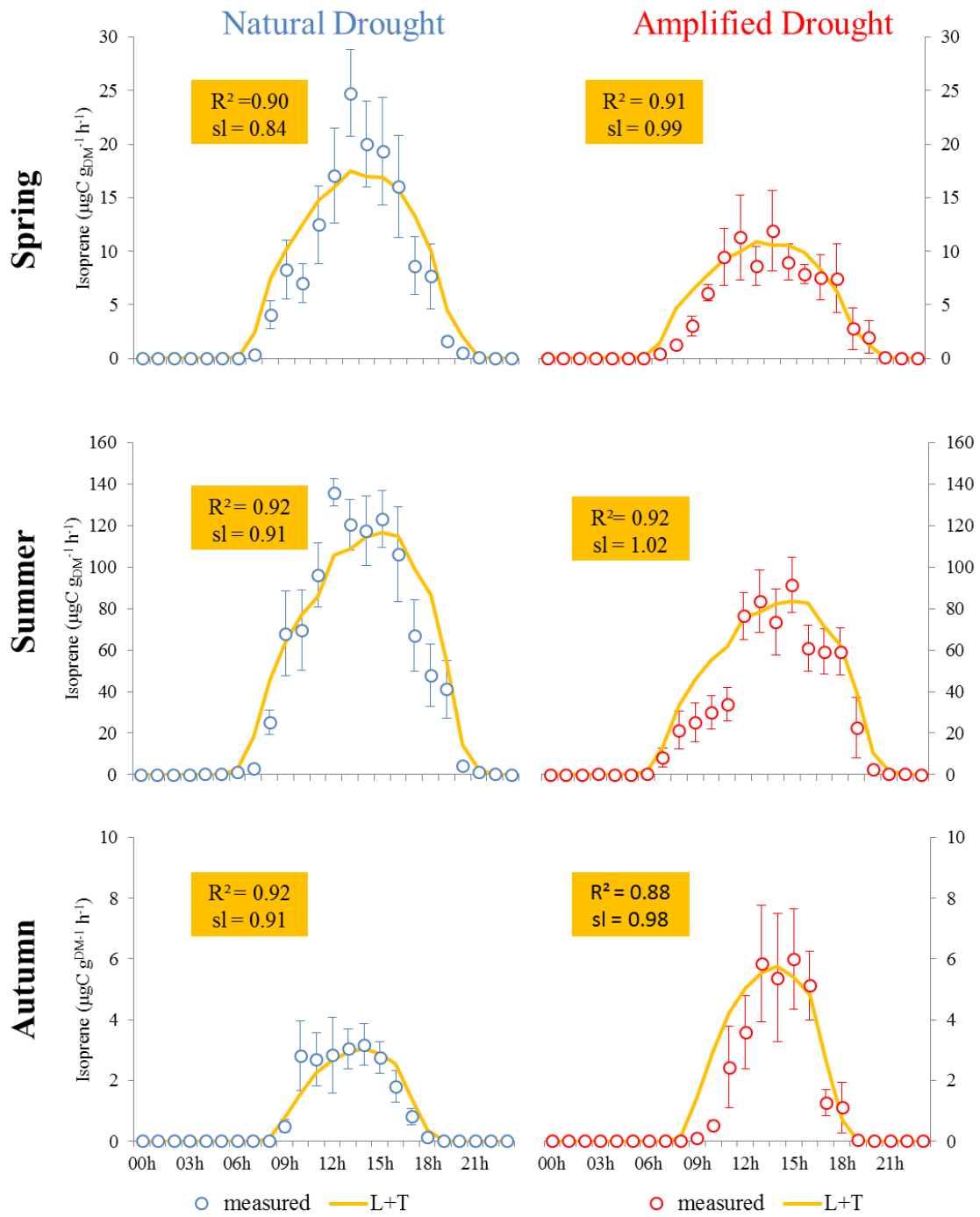
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579 **Figure 2:**

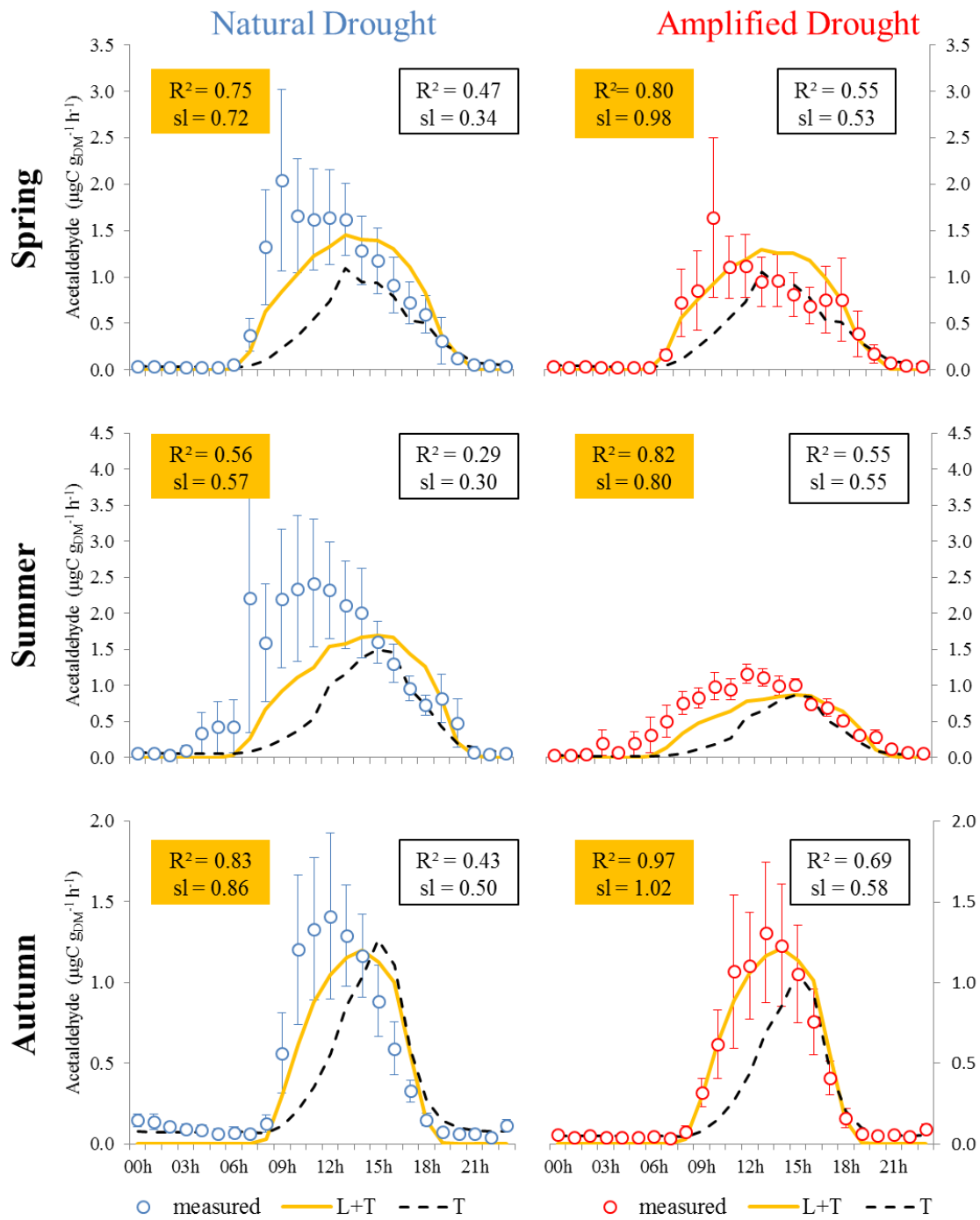


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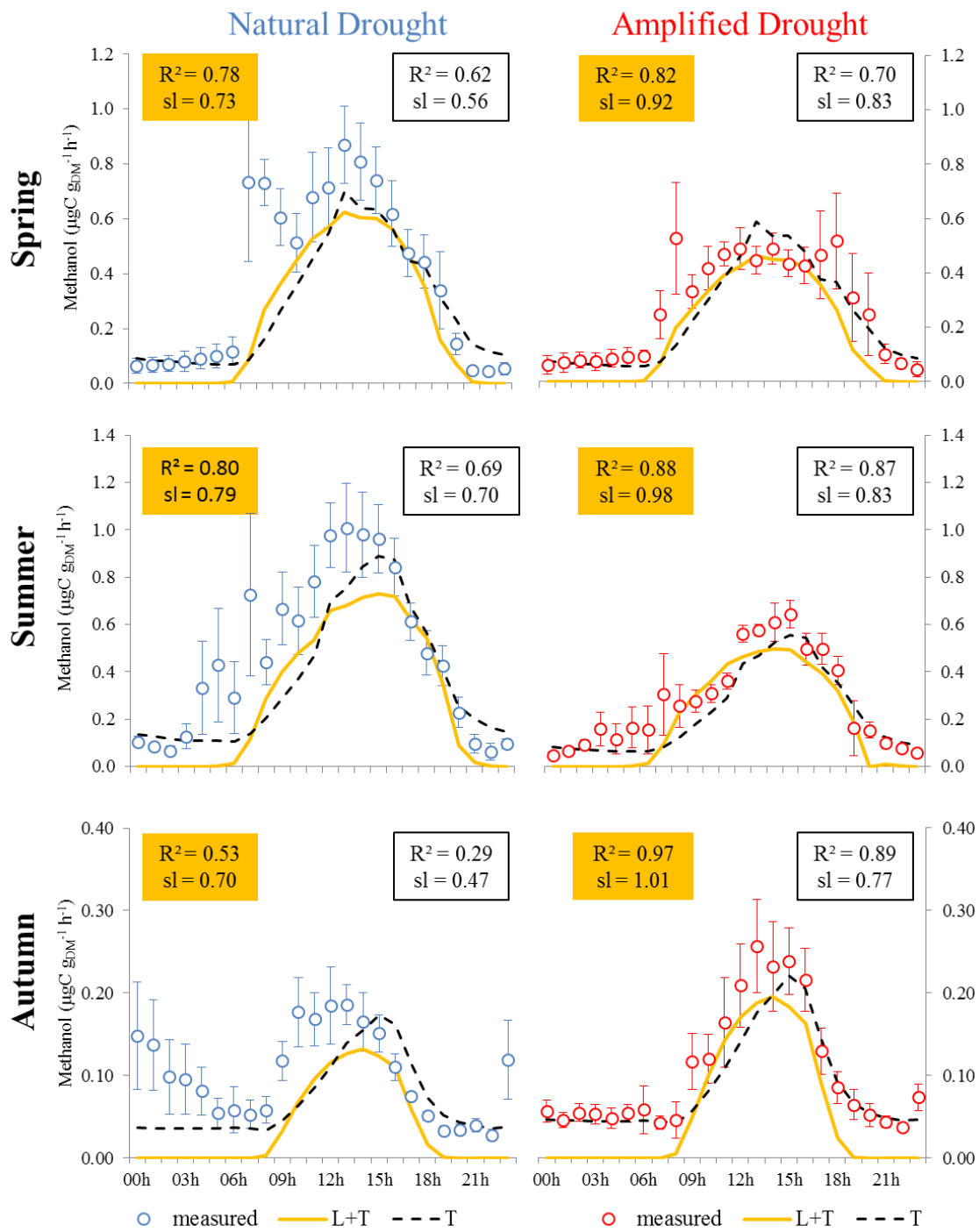
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