Variability of BVOC emissions from a Mediterranean mixed forest in southern France with a focus on *Quercus pubescens*

A.-C. Genard-Zielinski[1,2], C. Boissard[2], C. Fernandez[1], C. Kalogridis[2], J. Lathière[2], V. Gros[2], N. Bonnaire[2] and E. Ormeño[1].

[1] IMBE, Aix Marseille Université – CNRS – IRD – Univ. Avignon 3 Place Victor Hugo, F-13331 Marseille cedex 3, France

[2] Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL), Unité Mixte CEA-CNRS-UVSQ (Commissariat à l'Energie Atomique, Centre National de la Recherche Scientifique, Université de Versailles Saint-Quentin-en-Yvelines), F-91198 Gif-sur-Yvette, France.

Correspondence to: Christophe Boissard (christophe.boissard@lsce.ipsl.fr)

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Abstract

We aimed at quantifying Biogenic Volatile Organic Compounds (BVOC) emissions in June from three Mediterranean species located at the O_3HP site (Southern France): *Quercus pubescens*, *Acer monspessulanum* and *C. coggygria* (for isoprene only). As *Q. pubescens* was shown to be the main BVOC emitter with isoprene representing ≈ 99% of the carbon emitted as BVOC, we mainly focused on this species. *C. coggygria* was found to be a non-isoprene emitter (no other BVOC were investigated).

To fully understand both, the canopy effect on *Q. pubescens* isoprene emission and the inter-individual variability (tree to tree and within canopy), diurnal variations of isoprene were investigated from nine branches (seven branches located to the top of canopy at ≈ 4 m Above Ground Level (AGL), and two inside the canopy at ≈ 2 m AGL).

Q. pubescens daily mean isoprene emission rates (ERd) fluctuated between 23 and 98 µgC g_{DM}^{-1} h^{-1}. *Q. pubescens* daily mean net assimilation (*Pn*) ranged between 5.4 and 13.8, and 2.8 and 6.4 µmolCO_2 m^{-2} s^{-1} for sunlit and shaded branches respectively. Both ERd and isoprene emission factors (Is) assessed according to Guenther et al., (1993) algorithm, varied by a factor of 4.3 among the sunlit branches. While sunlit branches ERd was clearly higher than for shaded branches, there was a non-significant variability on Is (59 to 77 µgC g_{DM}^{-1} h^{-1}). Diurnal variations of isoprene emission rates (*ER*) for sunlit branches were also investigated. *ER* were detected at dawn 2h after *Pn* became positive and, for most of them, exponentially dependent on *Pn*. Diurnal variations of *ER* were not equally well described along the day by temperature (C_T) and light (C_L) parameters according to G93 algorithm. Temperature had more impact than PAR in the morning emission increase, and *ER* was no more correlated to C_L x C_T between solar noon (maximum *ER*) and mid-afternoon, possibly due to thermal stress of the plant. A comparison between measured and calculated emissions using two isoprene algorithms (G93 and MEGAN) highlighted the importance of isoprene emission factor Is value used, and some weakness in assessing isoprene emissions under Mediterranean environmental conditions (drought) with current isoprene models.

1 Introduction

Isoprene (2-methylbuta-1,3-diene) is the most abundant Biogenic Volatile Organic Compound (BVOC) released into the atmosphere with a global annual flux estimation of 400-660 $TgC.yr^{-1}$ (Guenther et al., 2006). Once in the atmosphere and due to the high quantity emitted, isoprene strongly impacts the atmospheric chemistry. Indeed, this molecule is going to react quickly with the main oxidant compound (OH), leading to the formation of oxidative highly reactive products in the atmosphere (Atkinson, 2000; Ciccioli et al., 1999; Claeys et al., 2004; Steiner and Goldstein, 2007).

At a smaller scale, isoprene plays a key role in the tropospheric chemistry since, alike other VOC, it is an ozone precursor in presence of NOx and light (Atkinson, 2000). NOx being mainly emitted by anthropogenic sources, isoprene emissions occurring close to mega-cities surrounded by large ecosystem areas (such as Mediterranean) can significantly contribute to high O_3 levels in summer (Curci et al., 2009).

Isoprene emissions are well recognized to be strongly driven by temperature and light conditions. Indeed, without any other environmental constraints, these two parameters drive the diurnal cycle of isoprene emission (Guenther et al., 1991). More precisely, light affects the photosynthetic processes which, in turn, impact the quantity of isoprene precursor (especially Glyceraldehyde 3-Phosphate) for isoprene synthesis, and temperature increases isoprene synthase activity (Niinemets et al., 2010b). As a result, it was shown that the branch location inside a canopy is an important source of isoprene emission variability, with significant lower isoprene emissions from shaded branches inside the canopy compared to sunlit branches at the top of the canopy (Harley et al., 1994; Monson and Fall, 1989).

However, other factors can explain isoprene emission variability. In particular, the capacity to emit isoprene (or emission factor Is) is intrinsically bound to the plant species. Guenther et al. (1994) proposed therefore to divide isoprene emitter species into four groups with negligible (<0.1 $\mu gC\ g_{DM}^{-1}\ h^{-1}$), low (14 ± 7 $\mu gC\ g_{DM}^{-1}\ h^{-1}$), moderate (35 ± 17 $\mu gC\ g_{DM}^{-1}\ h^{-1}$) and high (> 70 ± 35 $\mu gC\ g_{DM}^{-1}\ h^{-1}$) emitter species.

In Europe, *Quercus pubescens* Willd. is one of the most important isoprene emitter species, and represents thus one of the most significant biogenic isoprene sources in the Mediterranean region (Keenan et al., 2009). Previously reported Is values were observed to vary for this species in the Mediterranean area over a large range. Kesselmeier et al. (1998)

and Owen et al. (1998) assessed a fairly similar Is of 50 and 66 µgC g_{DM}^{-1} h^{-1} respectively at a site near Montpellier (France), which was 50% lower than what Simon et al. (2005) found 250 km from this site. On the other hand, Steinbrecher et al. (2013) observed a remarkable Is stability from seedlings of various oak species (including *Q. pubescens*) originating from different environmental climates (precipitation, temperature) and coming from different European sites. Simpson et al. (1999) proposed in his European BVOC inventory review an Is value of 53 µgC g_{DM}^{-1} h^{-1} for *Q. pubescens*.

This emission factor variability represents one of the main uncertainties of BVOC emission models. Parameters such as edaphic conditions, natural hybridization between plant species, or environmental tree history have been suggested to impact the overall capacity of a plant to emit isoprene.

This study was part of the CANOPÉE project which aimed at analysing and quantifying intra-canopy processes in the reactive organic compound exchange between the biosphere and the atmosphere, with a focus on isoprene (further details can be found at https://wiki.lsce.ipsl.fr/CANOPÉE). An intensive field campaign took place at the Oak Observatory at OHP (O_3HP), a Mediterranean site located in Southern France.

Our objectives during this campaign were, *(i)* to extensively screen, at the branch scale and using dynamic enclosures, BVOC emissions from the O_3HP forest, with a focus on *Q. pubescens* and, to a lesser extent, *Acer monspessulanum* L. whose emission data has never been reported so far; *Cotinus coggygria* was also investigated in terms of isoprene alone; (ii) to survey the canopy variability (tree to tree and within the canopy) and (iii) the diurnal variability of *Q. pubescens* isoprene emissions, and (iv) to test the ability of two commonly used algorithms to assess, under Mediterranean environment constraints, the observed diurnal variations of isoprene emission.

2 Methods

2.1 Experimental site

BVOC measurements took place at the O_3HP experimental site located in the research center 'Observatoire de Haute Provence', 60 km north of Marseille (5°42'44" E, 43°55'54" N), at an elevation of 650 m above mean sea level. The O_3HP (955 m²), free from human disturbance

for 70 years, consists of a flat homogeneous forest mainly composed of *Q. pubescens* (≈ 90% of the biomass and ≈75% of the trees). The remaining 10 % of the biomass is mainly represented by *A. monspessulanum* trees. The mean *Q. pubescens* diameter at 1.3 m is 8.8 cm (*n*=272) and the stage of the whole canopy closure was assessed by a mean leaf area index of 2.2. Dry leaf production was assessed for *Q. pubescens* to range between 1.4 and 1.6 t y^{-1}. The O_3HP site was created in 2009 in order to study the downy oak (*Q. pubescens*) forest ecosystem at soil and tree scale, under both natural and accentuated water stress conditions (a control and a rain exclusion plot respectively) induced by a rainfall exclusion device (an automated monitored roof deployed during rain events) set up over a part of the O_3HP canopy. A dense network of sensors in the soil, under and over the canopy, continuously recorded the climatic and edaphic parameters (air and soil temperatures and relative humidity, photosynthetically active radiation or PAR). A two level metallic scaffold allows the canopy access at two heights (under the canopy at 0.8 m and at the top of the canopy at 4 m). For further details see https://o3hp.obs-hp.fr.

2.2 Sampling strategy

The experiment took place from 29 May till 19 June 2012. A total of nine different *Q. pubescens* and one *A. monspessulanum* were studied for isoprene emissions during the campaign. *C. coggygria* was found to be a non-isoprene emitter (no other BVOC were investigated).

At the beginning of the campaign, in order to screen the composition of BVOC emissions and monitor diurnal variations over a 24 h period, a PTR-MS was connected to an enclosure system (described below) set up on one *A. monspessulanum* and one *Q. pubescens* sunlit branch (*Am*, 2 June and *Qp*4, 1 June respectively). *Am* and *Qp*4 were located in a clearing 40 m north of the O_3HP scaffold (Fig. 1) close to where the PTR-MS system was set up during the CANOPÉE campaign (see Kalogridis et al., (2014)).

To further investigate the variability of isoprene emission at the canopy scale two strategies were undertaken.

On the one hand, tree-to-tree variability was evaluated by studying three healthy and sunlit *Q. pubescens* branches within the control (*Qp*1, *Qp*2, *Qp*3) and the rain exclusion (*Qp*5, *Qp*6, *Qp*7) plot. On the other hand, variability of isoprene emissions between shaded and sunlit

branches was assessed on *Qp*1 and *Qp*2. In addition to a sunlit branch, a shaded branch was also studied for those two trees, approximately 2 m above ground ($Qp1_{shade}$ and $Qp2_{shade}$). Isoprene samples were collected on adsorbent cartridges.

When cartridges were used, isoprene emissions were sampled approximately hourly from sunrise to sunset. One of the enclosures was maintained on the *Qp*1 branch during the whole campaign (15 days) in order to follow continuous diurnal variations of isoprene emission rates during the concomitant isoprene canopy flux measurements carried out by Kalogridis et al. (2014). The second enclosure was used to alternatively investigate, over one to two days, isoprene emissions from the other eight branches selected (sunlit and shaded). Concomitant microclimate (PAR, temperature, relative humidity) and physiological parameters (net photosynthesis *Pn*, and stomatal conductance to water *Gw*) were continuously monitored during the BVOC sampling.

No other *A. monspessulanum* branches were studied since the on-line PTR-MS screening revealed very low BVOC emissions.

2.3 Branch scale sampling methods

Dynamic branch enclosures were used for sampling BVOC. Branches (mature leaves ≈ 3 month old) were enclosed in a ≈ 60 L PTFE (PolyTetraFluoroEthylene) frame closed by a sealed 50 µm thick PTFE film to which ambient air was introduced at 11–14 L min^{-1} using a PTFE pump (KNF N840.1.2FT.18®, Germany). A PTFE propeller ensured a rapid mixing of the chamber air and a slight positive pressure within the enclosure enabled it to be held away from the leaves to minimise damage to the biomass. Microclimate (PAR, temperature, relative humidity) inside the chamber was continuously (every minute) monitored by a data logger (Licor 1400®; Lincoln, NE, USA) coupled to a RHT probe (relative humidity and temperature, Licor 1400-04®, Lincoln, NE, USA) and a quantum sensor (Licor, PAR-SA 190®, Lincoln, NE, USA); the later sensor was set up and maintained horizontally in the enclosure and located close to the leaves. CO_2/H_2O exchanges from the enclosed branches were also continuously measured using infrared gas analysers (IRGA 840A®, Licor).

Pn (μmol_{CO2} m^{-2} s^{-1}) was calculated using equations described by Von Caemmerer and Farquhar, (1981) as follows:

$$Pn = \frac{F \times (Cr - Cs)}{S} - Cs \times E \quad \text{Eq. (1)}$$

where *F* is the incoming air flow rate (mol_{H2O} s^{-1}), *Cs* and *Cr* are the sample and reference CO_2 molar fractions respectively (μmol_{CO2} mol^{-1} or ppm), *S* is the leaf area (m^2), $Cs \times E$ is the fraction of CO_2 diluted in the water evapotranspirated (μmol_{CO2} m^{-2} s^{-1}), and *E* is the transpiration rate (mol_{H2O} m^{-2} s^{-1}) calculated as follows:

$$E = \frac{F \times (Ws - Wr)}{S \times (1 - Ws)} \quad \text{Eq. (2)}$$

where *Ws* and *Wr* are the sample and reference H_2O molar fractions respectively (mol_{H2O} mol^{-1}).

Gw (mol_{H2O} m^{-2} s^{-1}) was calculated using the following equation:

$$Gw = \frac{E \times \left(1 - \frac{Wl + Ws}{2}\right)}{Wl - Ws} \quad \text{Eq. (3)}$$

where *E* and *Ws* are described in equation (2), *Wl* is the molar concentration of water vapour within the leaf (mol_{H2O} mol^{-1}) calculated using the equation :

$$Wl = \frac{VP_{sat}}{P} \quad \text{Eq. (4)}$$

where *VPsat* is the saturated vapour pressure (kPa), and *P* is the atmospheric pressure (kPa).

Air flow rates were controlled by mass flow controllers (Bronkhorst) and all tubing lines were PTFE-made.

Total dry biomass matter (DM) was assessed during this study for each sampled branch by manually scanning every leaf enclosed in the chamber and applying an area factor (AF) conversion extrapolated from concomitant measurements made on the same site. For top and shaded canopy branches, mean (range) DM measured during this study was 0.16 (0.01 - 0.45) and 0.10 (0.01 - 0.38) g_{DM} respectively, and mean (range) AF was 13.17 (0.82 - 36.67) and 11.98 (2.10 - 41.85) cm^{-2} respectively. A mean leaf to mass area ratio (LMA) of 123.2 ± 1.0 (*n*=5 trees) and 87.1 ± 1.8 g_{DM} m^{-2} (*n*=15 trees) was then assessed for sunlit and shaded branches respectively. Since the sampled *A. monspessulanum* was not located into the protected O_3HP site, DM was assessed directly by cutting off the branch, drying and weighting foliar biomass; LMA was 75.4 g_{DM} m^{-2}.

Branch enclosures were mostly installed on the previous day before the first emission rate measurement took place, and, at least, 2 h before.

For BVOC screening, the PTR-MS was connected to the enclosure system with a 25 m length ¼" PTFE tubing (not heated) in order to follow, on-line, the rapid diurnal variations of BVOC

emission rates from a *Q. pubescens* and an *A. monspessulanum* branch; flow rate entering the chamber was fixed at 14.7 L min^{-1} (for details on PTR-MS system see Kalogridis et al., 2014).

Due to the number of samples collected during this study, BVOC sampled on cartridges were analysed by the two partnered laboratories (IMBE, LSCE) using very similar analytical techniques. BVOC concentrations were measured in both the inflowing and the outflowing air by passing at 0.1 L min^{-1} for 1-3 min through adsorbent cartridges: Chrompack glass tubes 6.1 od, 150 mm length packed with 0.06 g Tenax TA and 0.14 g Carbotrap B, and Perkin Elmer stainless-steel (SS) tubes 6.1 mm od, 90 mm length packed with 0.3 g Tenax TA for IMBE and LSCE respectively. Sampling rates were controlled by mass flow controllers. Before measurement, tubes were preconditioned at 300 °C for 2-3 h under continuous helium purge. During sampling, glass tubes were protected from direct sunlight with an aluminium foil. Tubes were removed from a cold box located close to the enclosures just before the measurements. Subsequent to sampling, tubes were sealed with Swagelock end caps and PTFE ferrules and stored at 4 °C before laboratory analyse within the following three weeks. Ozone was removed from sampled air by placing PTFE filters impregnated with sodium thiosulfate ($Na_2S_2O_3$) onto the sampling lines accordingly to Pollmann et al. (2005).

BVOC emission rates (*ER*) using PTR-MS and cartridges were calculated by considering the BVOC concentrations in the inflowing and outflowing air as:

$$ER = Q_0 \times (C_{out} - C_{in}) \times B^{-1} \quad \text{Eq. (5)}$$

where *ER* is expressed in µgC g_{DM}^{-1} h^{-1}, Q_0 is the flow rate of the air introduced into the chamber (L h^{-1}), C_{out} and C_{in} are the concentrations in the inflowing and outflowing air (µgC L^{-1}) and *B* is the total dry biomass matter (g_{DM}).

Intercomparison exercises between isoprene determination using both, IMBE and LSCE cartridges, and the on-line PTR-MS, showed a mean difference (bias) between 4.0 and 8.6 %.

In addition to these parameters recorded inside the enclosures, daily mean PAR, temperature and relative humidity were recorded above the canopy (6 m) during the campaign and are presented in Figure 2a together with the mean daily soil water content (Sw, Fig. 2b) obtained in the control and the rain exclusion plots (mean of 6 and 5 different probes respectively).

2.4 Analytical methods

BVOCs collected into glass and SS cartridges were analysed using similar GC-MS techniques. Glass tubes were analysed with a gas chromatograph (GC, HP 6890N ®) coupled to a thermal desorption injector (Gerstel TDS3/CIS4 ®) and a quadrupole mass selective detector (MSD, HP 5973®). Sampling tubes were thermally desorbed at 250 °C with carrier gas (He) flowing at 50 mL min^{-1} for 10 min. Isoprene was re-concentrated onto a Carbotrap B cold trap maintained at -50 °C. Secondary desorption was set up at 250 °C for 3 min. An "Al/KCl" capillary type column (30 m × 0.250 mm i.d., 5 μm thickness film) was used for the analysis using helium (5.6, Linde gas) as carrier gas at 1 mL min^{-1} and the following temperature program: 40 °C (1 min) to 200 °C (1 min) at 20 °C min^{-1}. The MS detector was set up at 250 °C in scan mode with m/z ranging from 40 to 150 amu. The isoprene detection limit was 0.015 ng on column, corresponding to 3 pptv in air for a 1 L sample, with a level of analytical precision better than 5 %. Under sampling conditions (similar flow rate, volume, biomass) 3 pptv corresponds to a minimum emission rate of 0.003 $\mu gC.g_{DM}^{-1}\ h^{-1}$. Isoprene quantification was achieved using a 5.00 ± 0.25 ppm diluted in N_2 certified gas standard (Air Liquide). Desorption and quantitative analysis of BVOC from SS sampling tubes was carried out using a Perkin Elmer ATD-300 automatic thermal desorption unit connected via a transfer line heated at 220 °C to a Varian CP 3800 GC connected to a MSD, Varian Saturn 2200 MSD. Compound desorption started at 225 °C for 10 min at 30 mL min^{-1} onto a mixed Carbotrap B and Carbosieve SII cold trap maintained at 0 °C. Secondary desorption was at 300 °C for 1 min. Compound separation was achieved using a fused silica capillary (25 m × 0.25 mm i.d. coated with PoraBOND Q) porous layer open tubular column (PLOT). Initial oven column was 50 °C maintained for 3 min and then increased at 5 °C min^{-1} up to 250 °C maintained for 10 min. The carrier gas was helium N6 at 1.2 mL min^{-1}. Samples were analysed in total ion current mode, with m/z ranging from 20 to 250. The detection limit was 0.006 ng and 0.10 ng on column for isoprene and monoterpene respectively, corresponding to 1.2 pptv and 40 pptv respectively in air for a 1 L sample, with a level of analytical precision better than 7.5 %. Under sampling conditions (similar flow rate, volume, biomass) this correspond to a minimum isoprene (monoterpene) emission rates of 0.0025 $\mu gC\ g_{DM}^{-1}\ h^{1}$. Isoprene quantification was made using a 3.97 ± 0.08 ppb in N_2 certified gas standard (NPL, Teddington Middlesex, UK) for lower concentrations and a 3.90 ± 0.29 ppm in N_2 certified

gas standard (Air Liquide) for higher concentrations. Monoterpene quantification was made by comparison with liquid standard (Fluka) appropriately diluted in MeOH. GC-MS quantification was made for the ion m/z 67 and 93 for isoprene and monoterpene respectively. Daily whole range calibrations were carried out.

Laboratory intercomparison between IMBE and LSCE analytical GC-MS system was carried out by loading IMBE and LSCE isoprene standards in both types of tubes (glass and SS) over a 12–1400 ngC range. A coefficient of determination R^2 of 0.953 (n=14) and 1.000 (n=7) for the GC-MSD HP 5973 and the GC-MSD Saturn 2200 respectively was found, with an estimation bias ranging from 3 to 10 %, close to the analytical precisions. Likewise, no significant differences were found between isoprene *in-situ* samples (0 - 150 ngC) simultaneously collected into glass and SS cartridges on either the inflowing or outflowing air of the enclosures (n = 20; slope = 1.05: R^2 = 0.90). No breakthroughs were observed for isoprene, neither on laboratory tests (up to 1400 ngC) nor on *in-situ* samples (up to 660 ngC) for both cartridges. No intercomparison was carried out for monoterpene analysis.

The overall uncertainty associated with emission rate measurements (including sampling and analytical uncertainties) for both sets of cartridges was between 15 and 20 %.

Details on VOC determination using the PTR-MS can be found in Kalogridis et al. (2014). Twelve masses were followed for both the *Acer* and the *Quercus* branch. Measurements of the inflowing and outflowing air were made alternatively every 15 min, allowing an *ER* assessment every 30 min.

2.5 Statistics

All statistics were performed on STATGRAPHICS® centurion XV by Statpoint, Inc. To compare the relationship between BVOC emitted by *A. monspessulanum* and *Q. pubescens* branches studied with PTR-MS and the $C_L \times C_T$ factor, we performed a linear regression analyses. In order to check the absence of water stress impact on isoprene emission, slopes of the regression lines between *ER* and $C_L \times C_T$ in the control and rain excluded plots were compared using an ANOVA. The same test was used to compare differences between sunlit and shaded branch emissions by comparing slopes of the regression lines between *ER* and $C_L \times C_T$ for this modality. Moreover differences in *Pn*, *Gw*, and Sw between control and rain excluded trees were analysed using Mann & Whitney tests (W).

3 Results and discussion

3.1 Experimental site conditions

During the first half of the campaign, the weather was fairly unstable, with few showers or longer rains, in particular on 12 June which was rainy most of the day, and an ambient temperature decreasing down to a mean daily value of about 13 °C. From 13 June and until the end of the measurements, the weather became more stable, sunnier, warmer and dryer; the daily mean air temperature increased constantly up to nearly 24 °C at the end of the campaign, the ambient relative humidity decreased down to 40 %, and Sw in both plots decreased down to 0.11 and 0.15 L_{H2O} L_{soil}^{-1} for the rain exclusion and control plot respectively. From 6 June, Sw in the rain exclusion plot was systematically lower than in the control plot (Fig. 2b). Indeed, the annual cumulated precipitation in 2012 in the rain exclusion plot (data not shown) became significantly different since the beginning of May and was around 30 % lower compared to the control plot (comparison of means, Mann & Whitney test, $W=508.0$, $P<0.05$).

3.2 BVOC emission screening in the O_3HP forest

3.2.1 *Q. pubescens* BVOC emissions

BVOC emissions from *Q. pubescens* (obtained by PTR-MS; *Qp*4, Table 1) were consistent with previous literature results (Owen et al., 1998; Simon et al., 2005). Indeed, *Q. pubescens* was found to be a strong isoprene emitter, with a daily mean value of isoprene emission rate (ER_{iso}) of 98 µgC g_{DM}^{-1} h^{-1} representing, on average, 98.8 % of the carbon emitted by the *Qp*4 branch. The remaining 1.2 % was found to represent a negligible quantity of the carbon assimilated as CO_2 and was, in decreasing order, composed by methanol, total monoterpenes, acetone (altogether ≈ 84 % of the non-isoprene BVOC), and methyl-vinyl-ketone (MVK) + methacrolein (MACR), and acetaldehyde whose emissions were of the order of 0.1 µgC g_{DM}^{-1} h^{-1}. Since isoprene, and total monoterpene emissions have been observed to be light and temperature dependent in this study, *Q. pubescens* emission factors (EF) could

be assessed using the G93 algorithm (Guenther et al., 1993) and are presented in Table 1 for *Qp4*.

Methanol is thought to be produced by destruction of wall cells during growth or during leaf senescence (Galbally and Kirstine, 2002). It could be, both, a non-stored or stored compound in the water compartments of the cell, such as vacuoles. However, since *Qp*4 methanol emissions were mainly exponentially dependent on temperature (R^2 = 0.9, P < 0,001) as previously observed for *Picea* species (Hayward et al., 2004) and lemon trees (Fares et al., 2011), it is likely that *Q. pubescens* methanol emission comes from an internal pool as suggested by Seco et al. (2007). In the afternoon, methanol emissions became the main non-isoprene compound emitted by *Q. pubescens*. Methanol release, as other alcohols, being strongly stomatal dependent, its maximum relative contribution to the emitted carbon was observed at dawn: up to 6.9 % of the carbon emitted as BVOC (data not shown) compared to 3.1 % and 0.8 % later in the morning and in the afternoon respectively. Although no methanol emissions were previously reported for *Q. pubescens*, the mean emission rate measured of 0.49 µgC g_{DM}^{-1} h^{-1} (or 130 ng g_{DM}^{-1} h^{-1}, or 1.13 nmol m^{-2} s^{-1}) is in the medium range of the foliar emissions reviewed by Seco et al. (2007) for methanol emission from emitters other than *Q. Pubescens*.

Total monoterpene emissions were more than 300 times lower than isoprene emissions, in agreement with a factor of 250 found by Simon et al. (2005) for *Q. pubescens* studied under Mediterranean conditions. Monoterpenes were found to be mainly under α-pinene and limonene (67 % and 33 % respectively – data from cartridge samplings, not shown) and their emission rates were more light and temperature dependent ('*de novo* emission') than only temperature dependent ('pool emission') (R^2 = 0.87 and 0.64 respectively and P < 0.001).

As for methanol, no acetone emissions have been previously reported for *Q. pubescens*. The mean emission rate of 0.20 µgC g_{DM}^{-1} h^{-1} (or 320 ng g_{DM}^{-1} h^{-1}, or 0.15 nmol m^{-2} s^{-1}) is also in the medium range of the foliar emissions reviewed by Seco et al. (2007). The relative contribution of acetone to the total BVOC emissions remained fairly stable along the whole day of measurement (around 12.5 % of the non-isoprene BVOC), and was found to be influenced by ambient light and temperature variations (R^2 = 0.88 and P < 0.001).

MVK+MACR are mainly secondary products of isoprene oxidation (Jardine et al., 2012). Our study showed that MVK+MACR emission rates were highly (R^2 = 0.97, P < 0.001, *n* = 28) correlated with ER_{iso} all along the diurnal cycle. A direct primary emission of these

compounds by the *Q. pubescens* branch could thus not be proved and values presented in the Table 1 should be then considered as the upper limit for primary emissions from this emitter.

Similarly, if acetaldehyde detected in our enclosure was mostly from primary biogenic source (cell catabolism, see Fall et al., 1999 and Loreto et al., 2006), the emission rates thus assessed (0.09 µgC g_{DM}^{-1} h^{-1} or 165 ng g_{DM}^{-1} h^{-1} or 0.10 nmol m^{-2} s^{-1}) would be in the lower range of the foliar emission rates reported in the literature for other plants (Seco et al., 2007). As for methanol emissions, the relative contribution of acetaldehyde emissions to total assimilated carbon was observed to peak in the morning (1.5 % in the morning compare to 0.06 % in the afternoon).

3.2.2 *A. monspessulanum* BVOC emissions

A. monspessulanum total BVOC emissions (< 1 µgC g_{DM}^{-1} h^{-1}) were two orders of magnitude smaller than the total *Q. pubescens* BVOC emissions (> 100 µgC g_{DM}^{-1} h^{-1}; Table 1). Isoprene and methanol were the two dominant BVOC measured, with a daily mean emission rate of 0.33 and 0.23 µgC g_{DM}^{-1} h^{-1} respectively. Acetone, acetaldehyde, and total monoterpenes were measured at lower rates, the latter being close to our detection limit. No foliar BVOC emission values have been reported in the literature for *A. monspessulanum.* Nevertheless, our findings confirm that, alike other *Acer* species (such as *Acer platanoides* L., *A. rubrum* L., or *A. saccharinum* L., Kesselmeier and Staudt, 1999), *A. monspessulanum* is a weak isoprene or other BVOC emitter.

BVOC other than isoprene represented a lower fraction of the total carbon emitted in the morning (≈ 33 %) than in the afternoon (≈ 66 %), methanol emission rates being, in the morning, even higher than isoprene emission rates. Total BVOC emissions represented less than 0.2 % of the assimilated carbon.

Ambient light and temperature variations influenced the diurnal emission variations of all the measured BVOC except methanol which, as observed for *Q. pubescens*, was found to be exponentially dependent.

To conclude, *Q. pubescens* appeared to be the main BVOC emitter in the O_3HP forest compared to *A. monspessulanum*. Isoprene represented ≈ 99 % of the BVOC emitted by *Q.*

pubescens, with daily mean values as high as ≈ 100 µgC g_{DM}^{-1} h^{-1}. Therefore, sections hereafter focus on *Q. pubescens* isoprene emissions.

3.3 *Q. pubescens* isoprene emission and associated gas exchange at the canopy scale (tree-to-tree and within canopy)

The additional drought imposed about one month before the beginning of the measurements in the rain exclusion plot was not intense enough to significantly alter either the capacity of *Q. pubescens* to assimilate CO_2 or to emit isoprene (comparison of regression lines; $R^2 = 0.63$; $P > 0.05$). Although significant differences were observed on *Gw* with a value for stressed trees half the one for control trees (Mann & Whitney; $P < 0.001$, Table 2), isoprene emission has been suggested to not be constrained by stomatal conductivity as pointed out by Niinemets and Reichstein, (2003). Thus water stress was not considered in this study. As a result, trees growing in, both, the rain exclusion and the control plot were pooled and analysed together without regard to their control/drought status.

3.3.1 Plant physiology

Daily *Pn* and *Gw* measured for top canopy branches varied between 5.4 and 13.8 µmolCO_2 m^{-2} s^{-1} and 62.5 and 268.1 mmolH_2O m^{-2} s^{-1} respectively (Table 2). These values are in agreement with observations previously reported by Damesin and Rambal, (1995) for *Q. pubescens* in June (*Pn* of 10 µmol m^{-2} s^{-1} and *Gw* ranging from 50 to 150 mmolH_2O m^{-2} s^{-1}). *Gw* up to 450 mmol H_2O m^{-2} s^{-1} was reported for *Quercus ilex* L. in the Mediterranean environment (Acherar and Rambal, 1992). Thus, despite the inherent modifications occurring in the microclimate surrounding an enclosed branch (higher relative humidity - especially during the night-time respiration - and warmer air temperature), no significant impact on the physiology of the studied branches was observed. Similarly, the rain event of 12 June had no impact on *Pn* of *Qp*1 or *Qp*6 branches studied on this day. Shaded branches $Qp1_{shade}$ and $Qp2_{shade}$ showed *Pn* values between 2.8 and 6.4 µmolCO_2 m^{-2} s^{-1}, more than half the values on sunlit branches.

3.3.2 Canopy variability of the branch isoprene emission rate

As shown in Table 2, daily mean isoprene emission rates (ERd) from top of the canopy branches were highly variable, fluctuating over one order of magnitude, between below 10 (*Qp*1 and *Qp*6, 12 June) and up to 98 µgC g_{DM}^{-1} h^{-1} (*Qp*4, 1 June). The lower ERd coincided with reduced incident PAR and ambient temperature due to some rain events on 12 June. Since *Qp*4 *Pn* was similar to *Pn* measured for the other trees (8.3 and between 5.4 and 13.8 µmolCO_2 m^{-2} s^{-1} respectively), the observed ERd range illustrates the importance of environmental conditions on the amount of carbon *Q. pubescens* allocates to isoprene emissions.

Daily mean ERd presented a high variability between sunlit branches (23 and 98 µgC g_{DM}^{-1} h^{-1}) and shaded branches (4.0 and 13 µgC g_{DM}^{-1} h^{-1}). Daily mean $Qp1_{shade}$ and $Qp2_{shade}$ PAR were reduced by a factor of six and ten respectively compared to PAR values recorded on *Qp1* and *Qp2* sunlit branches. Consequently, shaded ERd (between 4.0 and 13 µgC g_{DM}^{-1} h^{-1}) were, on average, between two and ten times lower than the values measured on the sunlit *Qp*1 and *Qp*2 branches respectively; these values were the lowest ERd observed during the study. In shaded branches, only 0.3 $\pm$ 0.2 to 0.5 $\pm$ 0.2 % of the assimilated carbon was emitted as isoprene (C_{iso}), while C_{iso} for sunlit branches ranged between 0.4 $\pm$ 0.1 and 2.9 $\pm$ 1.0 %. Daily mean C_{iso} was exceptionally high for *Qp*4 (2.7 $\pm$ 2.2 %) and reached up to 6.5 % at solar noon. Whatever their horizontal or vertical location in the canopy, for 2/3 of the sampled trees, measured isoprene emission rates exponentially increased with *Pn*, except for *Qp*3, *Qp*6 and $Qp2_{shade}$ (Fig. 3). As explained in the next section, *Qp*3 was found to be dead in August, although there were no visible sign when our study was conducted. *Qp*6 was studied during the only rainy day of our study (12 June, Table 2), and although its *Pn* was not affected, its isoprene emissions were much lower than during sunny days. The range of ER_{iso} variation observed for $Qp2_{shade}$ being much lower than for other sunlit branches, it was difficult to distinguish an exponential dependency to *Pn* as strong as for the other branches. Aside from these particular cases, such an exponential relation between ER_{iso} and *Pn* implies that, even when *Pn* reached the maxima values, the contribution of carbon fixed by each branch to produce isoprene went on increasing.

3.4 Capturing *Q. pubescens* isoprene emission variability and providing estimates

3.4.1 Canopy variability of the isoprene emission factor Is

Isoprene emissions being known to strongly depend on temperature and PAR variations, the slope of measured isoprene emission rates *vs* the $C_L \times C_T$ product was calculated in order to assess for each branch an emission factor Is (Table 2) where C_L and C_T are light and temperature dimensionless coefficients given by Guenther et al., (1993) from experimental measurements (see supplementary section). For sunlit branches, Is varied between 31 $\pm$ 8 and 138 $\pm$ 10 µgC g_{DM}^{-1} h^{-1} for *Qp*3 and *Qp*4 respectively, which is in the range of values given in the literature (50, 66 and 118 µgC g_{DM}^{-1} h^{-1}, Kesselmeier et al. (1998), Owen et al. (1998) and Simon et al. (2005) respectively). A factor of more than two was found between, on the one hand, *Qp*4 emission factor and all the other branches in the control plot, and, on the other hand, between Is from *Qp*1 and *Qp*2 (72 $\pm$ 3 and 74 $\pm$ 4 µgC g_{DM}^{-1} h^{-1} respectively) and *Qp*3 (31 $\pm$ 8 µgC g_{DM}^{-1} h^{-1}). The overall factor of variability of 4.3 observed on Is illustrate how *in-situ* condition variations, even on a fairly homogenous site, can impact BVOC emissions. Moreover, even under similar prevailing environmental conditions, the physiological status variability that may exist between branches can lead to strong differences in the branch capacity to emit isoprene. The smaller (by a factor of two) Is observed for *Qp*3 compared to other O_3HP tree branches was *a posteriori* explained by the fact that this branch died in August despite no injuries were visible during our study in June. By contrast Steinbrecher et al. (2013) observed a remarkable stability on Is values from seedlings of various oak species originating from different environmental climates (precipitation, temperature) with a factor of only 1.6 for *Q. pubescens* Is.

Regarding the canopy shading effect, the studied shaded branches showed no significant difference (R^2 = 72.8 and 89.2 for *Qp1* and *Qp2* branches respectively; $P > 0.05$) in their capacity to emit isoprene (Is of 77$\pm$ 3 and 59 $\pm$ 12 µgC g_{DM}^{-1} h^{-1} for $Qp1_{shade}$ and $Qp2_{shade}$ respectively) compared to the sunlit branch of the corresponding tree, (Is of 72 $\pm$ 3 and 74 $\pm$ 4 µgC g_{DM}^{-1} h^{-1} for *Qp*1 and *Qp*2 respectively). This similarity occurred despite an observed LMA vertical gradient: 87 ± 2 and 123 ± 1 g m^{-2} for shaded and sunlit branches respectively. Such a gradient is similar to what Harley et al. (1994) reported for a *Quercus alba* forest: 75.4

491 ± 7.0 and 111.5 ± 5.9 g m^{-2} for shaded and sunlit branch respectively; when these authors
492 expressed Is on a leaf area basis they observed significantly lower Is values for a shaded
493 branch. Note that if the sunlit branch LMA value was used for assessing Is from all our
494 branches (shaded and sunlit branches) - as it may be done in global upscaling inventory
495 when no appropriate LMA information is available - shaded Is value would then become
496 significantly lower than Is sunlit branches. As any other factors used when BVOC canopy
497 fluxes are extrapolated from branch to canopy scale, determination of appropriate LMA
498 should thus be as accurate as possible since it represents one of the biases of such an
499 exercise.
500 Based on our assessed Is range (31 to 138 µgC g_{DM}^{-1} h^{-1}) and using an average branch scale Is
501 value of 60 µgC g_{DM}^{-1} h^{-1}, Kalogridis et al. (2014) extrapolated a canopy isoprene emission
502 flux of 15 mg m^{-2} h^{-1}, twice the mean canopy flux measured in June during this study by the
503 disjunct eddy covariance technique (6.6 mg m^{-2} h^{-1}). The authors pointed out that such a
504 factor of discrepancy is reasonable since it is in the range of uncertainties typically obtained
505 for upscaling exercises (see for example Guenther et al., 1995), and is within the range of the
506 tree to tree variability observed for *Q. pubescens* Is on this site (a factor of 4.3). This
507 illustrates the limit of precision in BVOC canopy flux assessments, how much the Is canopy
508 variability is extensively and intensively is studied.
509
510 **3.4.2 Diurnal variability: how well $C_L \times C_T$ captured the observed features?**
511
512 The diurnal range of isoprene *ER* variations observed over the seven sunlit different
513 branches studied (Fig. 4a) was found to fluctuate from day to day and with environmental
514 conditions (Fig. 4b). The maximum value observed on June 12 (rainy day) for the sun
515 exposed *Qp*1 branch (17 µgC g_{DM}^{-1} h^{-1}) was about five times lower than the maximum
516 observed at the end of the campaign (especially on 16 June, 78 µgC g_{DM}^{-1} h^{-1}) when weather
517 was much warmer and sunnier (Table 2 and Fig. 4b); it was about the same than the
518 maximum *ER* measured for the shaded branch *Qp*1 at the beginning of the campaign (June
519 6-7, ≈ 20 µgC g_{DM}^{-1} h^{-1}). *Qp*1 C_{iso} was the highest (up to 1.8 %, Table 2) at the end of the
520 campaign, compared to values < 1 % at the beginning of our measurements, which is
521 consistent with previous findings for *Q. pubescens* in June (0.62 to 1.8 %, Kesselmeier et al.,
522 1998).

523 Diurnal variations were studied in more detail during the *Qp*4 high frequency measurements
524 carried out with the PTR-MS system. Positive *Pn* values were measured at 06:30, as soon as
525 PAR became detectible and increased at dawn in parallel of a C_L increase (Fig. 5). Detectable
526 isoprene emissions were observed only 2 h later (08:30), when ambient temperature
527 significantly increased (Fig. 5). Consequently, isoprene *ER* increased then as C_T. This finding
528 contrasts with previous studies (Owen et al., 1998) where *Q. pubescens ER* were more PAR
529 than temperature dependent. The morning delay observed between *Pn* and the isoprene
530 emission onset was found to correspond to a temperature increase d*T* of nearly 3 °C;
531 interestingly, a similar d*T* was observed for the *Qp*1 branch when early morning
532 measurements were made. Temperature continued to significantly (compared to PAR)
533 impact isoprene until the maximum *ER* (229 µgC g_{DM}^{-1} h^{-1} at 13:30). Between 13:30 and
534 17:30 isoprene emission remained constantly more temperature than light dependent. As
535 soon as PAR decreased (17:30), *ER* started to decrease to non-detectable values, while the
536 branch continued to assimilate CO_2 and *Pn* decreased only 1 h later. If the diurnal variations
537 of *Qp*4 *ER* were mostly well described by $C_L \times C_T$ (in particular from dawn to midday
538 maximum and during the evening, the relative influence of light and temperature varied
539 along the day as presented in Figure 6: from 13:30 to 16:00 *ER* decreased from 220 to less
540 than 150 µgC g_{DM}^{-1} h^{-1} at nearly constant $C_L \times C_T$; on the contrary, after 16:00, *ER* remained
541 close to 75 µgC g_{DM}^{-1} h^{-1} although $C_L \times C_T$ fluctuated over nearly a factor of 3 (from 1.1 to 0.4).
542 Thus, after the solar noon, *ER* presented an overall reverse sigmoid shape diurnal
543 dependency with $C_L \times C_T$. The sudden decrease of *ER* at 13:30 while $C_L \times C_T$ remained
544 constant may illustrate a possible temperature midday stress of the branch, with an
545 emission falling down to a minimum value of ≈ 75 µgC g_{DM}^{-1} h^{-1}. The thermal stress lasted
546 until 16:00 when isoprene emission regulation became again well correlated to $C_L \times C_T$.
547 Indeed, as reported by Niinemets et al. (2010a) heat stress could modify isoprene emission
548 by decreasing foliar metabolism. For instance, Funk et al. (2004) observed that during a heat
549 stress, an alternative source of carbon (carbon pool stored as carbohydrates) is used for
550 isoprene synthesis. As showed by Fortunati et al. (2008) for *Populus nigra* L., this alternative
551 carbon source being unaffected by temperature, our observations could illustrate a similar
552 uncoupling between isoprene emissions and $C_L \times C_T$ for *Q. pubescens*. Note that such a
553 response was also observed during water stress on *Quercus* species by Tani et al. (2011) who

suggested that, when photosynthesis was completely suppressed in the afternoon due to severe water stress, the DMAPP content (or dimethylallyl pyrophosphate, the substrate for isoprene synthase), was not high enough to maintain isoprene emission level as before stress.

3.4.3 Assessment of the diurnal profiles of *Q. pubescens* isoprene emission rates using different algorithms

Most of the different isoprene emission algorithms available for emission inventory are based on the empirical leaf-level isoprene emission dependency on light and temperature (Guenther et al., 1993). Among them, two were tested to evaluate their ability in assessing the diurnal profiles of *Q. pubescens* isoprene emission observed in this Mediterranean climate: *(i)* the simple and well known G93 algorithm (Guenther et al., 1993) which only takes into account the instantaneous variations of incident light and ambient temperature – hereafter referred to as G93, and (ii) the MEGAN parameterisation (Guenther et al., 2006), a modified version of the former algorithm developed in an attempt to better capture the emission seasonality through the consideration of the dimensionless γ_{age} factor dependent on leaf age (here set at 0.6), the lower frequency variations (up to ten days) of environmental conditions, and the impact of soil humidity through the γ_{SM} factor. The algorithms were tested for *Qp*4 branch using, both, an Is value of 53 µgC g_{DM}^{-1} h^{-1} as recommended by Simpson et al. (1999) for European *Q. pubescens* and our values obtained in this study (72 and 138 µgC g_{DM}^{-1} h^{-1} for *Qp*1 and *Qp*4 respectively).

As a whole, both algorithms underestimated the *Qp*4 measured *ER* (65 and 55 % for G93 and MEGAN respectively, Fig. 7, Table 3) when Simpson et al. (1999) Is value was used. This discrepancy reached a factor of three for midday maximum emission (74 and 93 µgC g_{DM}^{-1} h^{-1} for G93 and MEGAN respectively compared to 229 µgC g_{DM}^{-1} h^{-1}). When Is values observed during this study were employed, a much better agreement was found (a slight over- and under- estimation of 16 and 8 %, and a root mean square error (RMSE) value ≈ two and three times lower for G93 and MEGAN respectively, Fig. 7, Table 3). The main bias was thus found to be linked with Is, since the general diurnal trend was roughly captured by both algorithms ($R^2 > 0.91$ for all comparisons). However, note that the maximum *Qp*4 emissions calculated with both algorithms, were reached at 14:00 (MEGAN) and 15:30 (G93), later than

what was observed (13:30) and whatever the Is value used. Besides, predicted *ER* remained mostly constant until 16:00, while the observed emissions decreased to *ER* values 50% smaller than the midday maximum as previously described and commented (section 3. 4.2). Both algorithms being strongly dependant on temperature variations, such an observed uncoupling between *ER* and elevated temperature (here higher than 33 °C) could not be captured. *ER* evening decrease was predicted to occur more rapidly and earlier (18:00) compared to *in-situ* observations, resulting in assessed *ER* of ≈ 10 µgC g_{DM}^{-1} h^{-1} compared to the observed value of 75 µgC g_{DM}^{-1} h^{-1}. On the contrary *ER* was assessed to occur much earlier at dawn (6:30 compared to 8:00), thus as soon as *Pn* became positive, and was overestimated by a factor of three by G93 over this period. Note that, for *Qp*4, the simpler G93 algorithm performed almost as well as the more complex MEGAN parameterisation (similar slope, R^2 and RMSE, Table 3).

Some similar findings were observed when G93 and MEGAN algorithms were tested over the longer time series (13 days) of *Qp*1 diurnal measurements: when the measured Is was employed instead of the literature value, the underestimation of G93 and MEGAN was reduced from 46 and 77 % respectively down to 27 and 68 % respectively, although RMSE remained in the same range (Table 3). However, MEGAN performance became much weaker (R^2 = 0.15) for *Qp*1, especially for the assessment of *ER* measured at the end of the 13 day period (detailed data not shown), when much warmer and drier conditions settled down at the O_3HP site. Indeed, the soil water content becoming lower than the wilting point used for our soil type (0.138 m^3 m^{-3} for clay soil type, Chen and Dudhia, 2001), the MEGAN γ_{SM} factor was no longer 1 but significantly lowered most of the assessed isoprene emissions. Unfortunately, the consideration of superficial (-0.1 m depth) soil moisture does not take into account the tree ability to access to deeper water sources. Weather being cooler and rainy at the beginning of the campaign, such a γ_{SM} modulation did not operate neither on *Qp*4 measurements nor on the first day of the *Qp*1 measurements (γ_{SM} was 1). When γ_{SM} was not considered anymore and set to 1 for all the *Qp*1 measurements, MEGAN performed much better and assessed nearly 60 % of the observed variability compared to 15 %. However, in this case, MEGAN only slightly reduced the overall *Qp*1 underestimation (≈ 60 %) compared to the simpler G93 algorithm (≈ 40 %), as for *Qp*4 tree.

4 Conclusions

The extensive study, at branch scale, of BVOC emissions from a Mediterranean forest ecosystem dominated by *Q. pubescens* revealed that, unlike *Q. pubescens*, *C. coggygria* was a non-isoprene emitter (no other BVOC were investigated) and *A. monspessulanum* was a weak BVOC emitter (daily mean total <1 μgC g_{DM}^{-1} h^{-1}) with isoprene (36.3 %) and methanol (25.3 %) being the two dominant emitted compounds (ERd, of 0.33 and 0.23 μgC g_{DM}^{-1} h^{-1} respectively); acetone, acetaldehyde and total monoterpenes were also measured at lower rates.

Q. pubescens was found to be a strong isoprene emitter (≈ 99 % of the BVOC carbon mass) with mean *ER* fluctuating between 23 and 98 μgC g_{DM}^{-1} h^{-1} for sunlit branches and 6.1 and 11.5 μgC g_{DM}^{-1} h^{-1} for canopy shaded branches; methanol (ERd = 0.49 μgC g_{DM}^{-1} h^{-1}; 0.5 % of total BVOC) and total monoterpenes (ERd = 0.30 μgC g_{DM}^{-1} h^{-1}; 0.3 % of total BVOC) dominated the other emitted BVOC, but traces of acetaldehyde and acetone were also measured.

For both shaded and sunlit *Q. pubescens* branches, most of the isoprene emission rates exponentially increased with *Pn*, although *Pn* was half smaller for shaded than sunlit branches. In shaded branches, a very small fraction of the recently assimilated CO_2 (C_{iso}) was emitted as isoprene (0.25 - 0.5 %) whereas C_{iso} ranged between 0.5 - 1.8 % for sunlit branches with a maximum of 6.7 % under elevated temperature and sunlight stress.

Tree to tree isoprene emission variability was high considering the sunlit branches (n = 7) and, to a lesser extent, the shaded (n = 2) branches. ERd sunlit branches varied over a factor of ten and emission factor Is over a factor of 4.3 (between 31 $\pm$ 8 and 138 $\pm$ 10 μgC g_{DM}^{-1} h^{-1}). Shaded branch variability was lower, a factor of three for ERd (between 4.0 and 13 μgC g_{DM}^{-1} h^{-1}) and not significant for Is (between 59 $\pm$ 12 and 77 $\pm$ 3.0 μgC g_{DM}^{-1} h^{-1}).

Within the canopy (shaded *vs* sunlit branches), ERd varied by a factor of 25. However, this difference between shaded and sunlit branches disappeared when Is were calculated.

Such variability represents an assessment of the tree-to-tree and branch-to-branch variability originating from *in-situ* conditions that should always be taken into account when canopy BVOC fluxes are extrapolated from branch scale measurements. Thus, if experiments conducted from saplings grown under near-natural, but controlled, conditions give a fairly

straightforward estimation of BVOC emissions by a plant, it cannot give the full picture obtained by *in-situ* long term measurements.

The morning onset of isoprene emission rates was mainly driven by temperature and not *Pn* which was, as expected, light triggered. By contrast, emission evening decline was mainly correlated with PAR. In between, an uncoupling of isoprene emission with light and temperature was noticed, with emissions starting to decline during the early afternoon temperature stress whereas light and temperature remained stable.

If MEGAN and G93 algorithms succeed in capturing the overall diurnal pattern of isoprene emission at the O_3HP, they significantly underestimated emissions by an average factor of up to 3, and especially the midday maximum values when an Is other than those assessed for this site was employed. Both algorithms were found to be very sensitive to Is, and showed difficulties in properly assessing detailed isoprene diurnal variations, in particular at dawn and when midday thermal stress occurred. Under water shortage, MEGAN performances were even worse due to its inadequate local description of the soil moisture impact on *Q. pubescens* isoprene emissions. When soil moisture was no more considered, MEGAN performed similarly to the much simpler G93 algorithm for our June study; however, the G93 performance may be significantly reduced compared to MEGAN, when seasonal variations are considered.

This comparison illustrates how uncertain global isoprene emission algorithms or models, such as G93 and MEGAN, can be when employed for high temporal resolution air quality predictions in Mediterranean areas.

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681 (https://o3hp.obs-hp.fr/index.php/fr/), Europe (FED*ER*) and ADEME/PACA for Ph-D funding.

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684 Fig. 1: Location of the studied *i Q. pubescens* (*Qp*i) and *Acer monspessulanum* (*Am*) trees.
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686 were measured using an online PTR-MS. All other *Qp*i branches were sampled from the
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689

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695

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699

700 Fig. 4: (a) Diurnal variations of isoprene emission rate ER_{iso} (µgC g_{DM}^{-1} h^{-1}) measured from all *i*
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703

704 Fig. 5: Diurnal variations of *Qp*4 isoprene emission rates ER_{iso} (µgC g_{DM}^{-1} h^{-1}) ± SD *vs* the
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707

708 Fig. 6: Diurnal variation of *Qp*4 isoprene emission rate ER_{iso} (µgC g_{DM}^{-1} h^{-1}) *vs* $C_L \times C_T$ as in
709 Guenther et al., 1993 (1 June).
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713

714 Fig. 7: Comparison between *Qp*4 isoprene emission rates ER_{iso} (µgC g_{DM}^{-1} h^{-1} ± SD) measured
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718 *pubescens* emission factor Is value of ([a]) 53 µgC g_{DM}^{-1} h^{-1} (as in Simpson et al., 1999, open
719 diamonds), and ([b]) of 138 µgC g_{DM}^{-1} h^{-1} (this study, plain diamonds). PAR (µmol m^{-2} s^{-1}) and
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Table 1: BVOC emitted by *Q. pubescens* (*Qp*4) and *A. monspessulanum* (*Am*) branches, 1st and 2nd of June respectively, measured with a PTR-MS.

Daily mean (*n*=30) and maximum (parenthesis) BVOC branch emission rates *ER* are in µgC g_{DM}^{-1} h^{-1}. Values are expressed ± their SD.

[a] Measurement information measured inside the enclosure chamber are daily averaged; PAR is in µmol m^{-2} s^{-1}, temperature T in °C, relative humidity RH in %, photosynthetic net assimilation *Pn* in µmolCO_2 m^{-2} s^{-1} and stomatal conductance *Gw* in mmolH_2O m^{-2} s^{-1}.

[b] Percentage of speciated BVOC relative to total BVOC and to non-isoprene BVOC (brackets)

[c] Emission factors EF (µgC g_{DM}^{-1} h^{-1}) were the best fit slope of *ER vs* $C_L \times C_T$ as in Guenther et al. (1993).

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Table 2: Environmental and physiological parameters recorded during isoprene measurements on seven sunlit (*Qp*i) and two shaded (Qpi_{shade}) *Q. pubescens* branches.

PAR (µmol m^{-2} s^{-1}), temperature T (°C), relative humidity RH (%), photosynthetic net assimilation *Pn* (µmolCO_2 m^{-2} s^{-1}) and stomatal conductance *Gw* (mmolH_2O m^{-2} s^{-1}) were recorded inside the enclosure and averaged over 2:00-22:00. Daily emission rates ERd (µgC g_{DM}^{-1} h^{-1}) were averaged over the *n* isoprene measurements of the sampled branch; values in brackets are minimum-maximum.

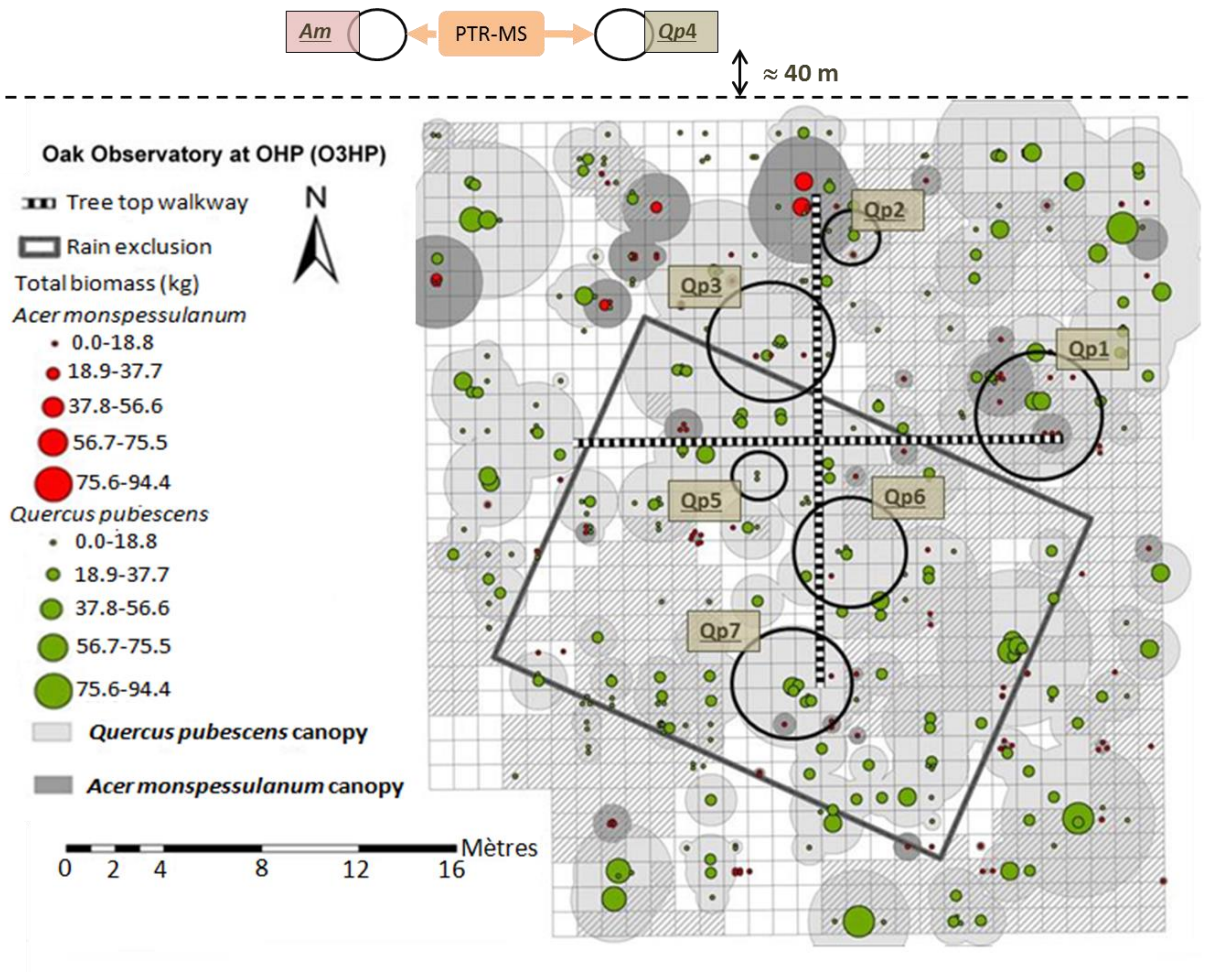
Assimilated carbon emitted as isoprene C_{iso} (%) is given ± their SD.

For every branch, isoprene emission rates ER_{br} and emission factor Is (as in Guenther et al. 1993) ± their SD are given in µgC g_{DM}^{-1} h^{-1} and ngC m^{-2} h^{-1} (parenthesis)

Table 3: Results of the comparison between calculated *vs* measured *Q. pubescens* isoprene emission rates using, both, the G93 and MEGAN algorithm and an emission factor Is of ([a]) 53 µgC g_{DM}^{-1} h^{-1} (as in Simpson et al., 1999), and ([b]) of 72 and 138 µgC g_{DM}^{-1} h^{-1} (*Qp*1 and *Qp*4 respectively, this study). The *a*x+*b* best fit equations are given, together with the determination coefficient (R^2) and the root mean square error (RMSE).

753 **Fig. 1**

754



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756

757 **Fig. 2**

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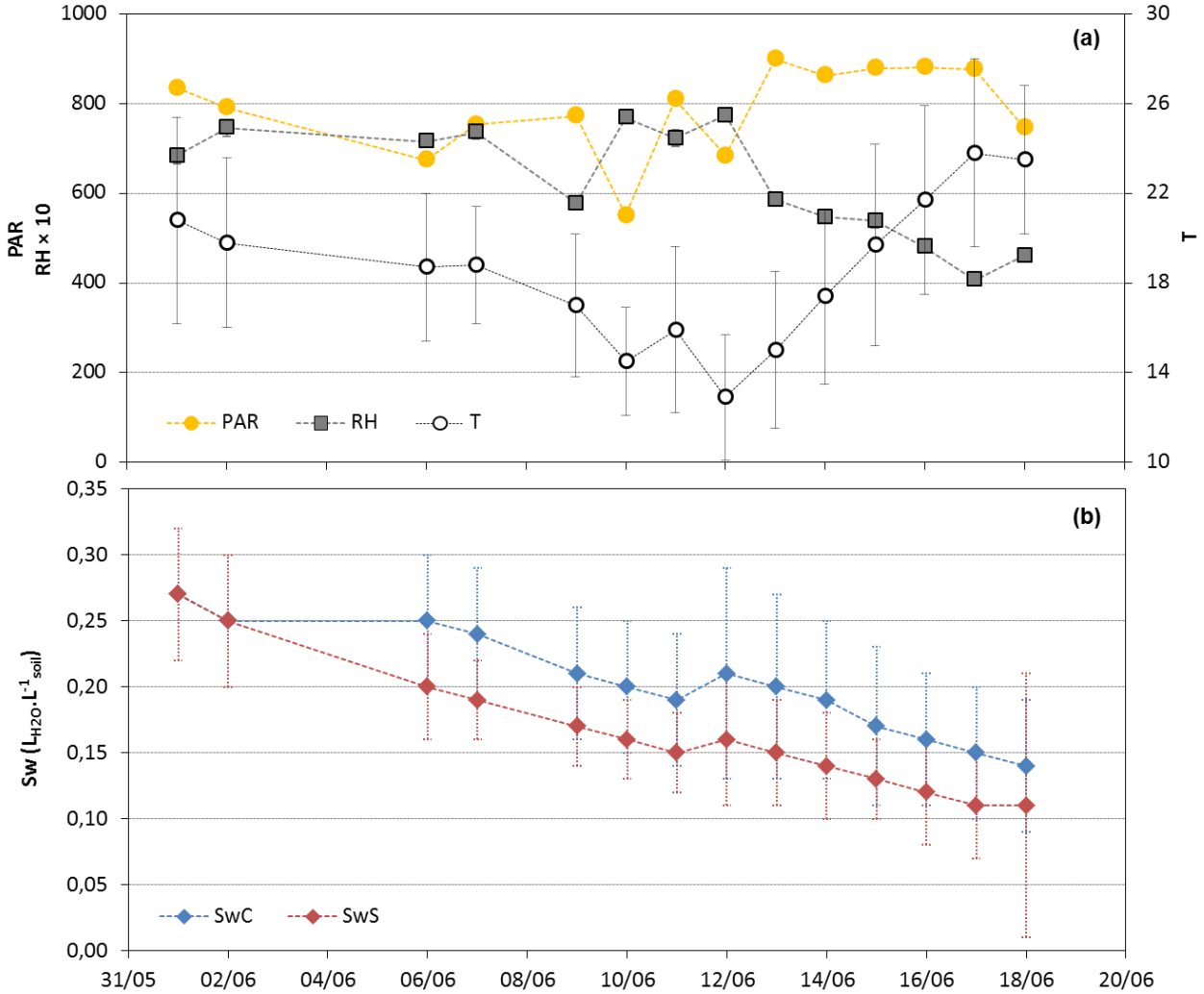

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760

761 **Fig. 3**

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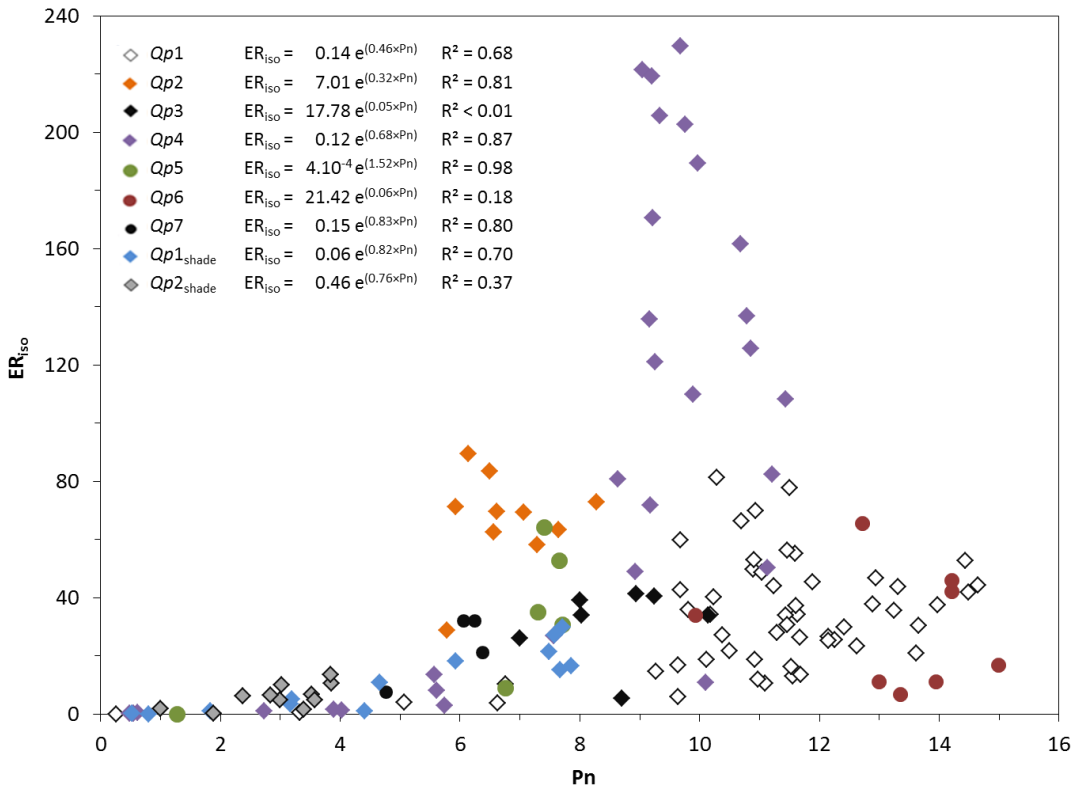

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764 **Fig. 4a and 4b**

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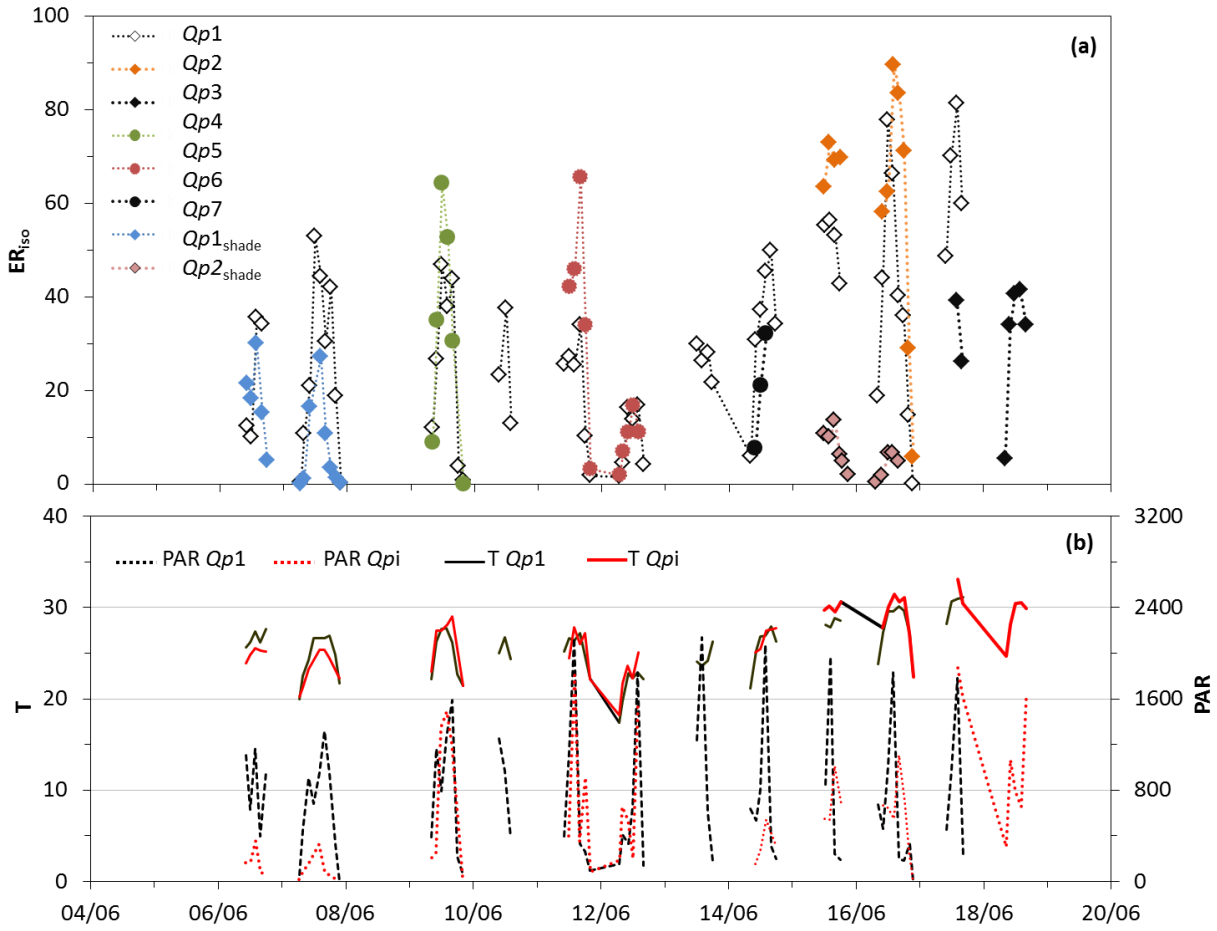

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769 **Fig. 5**

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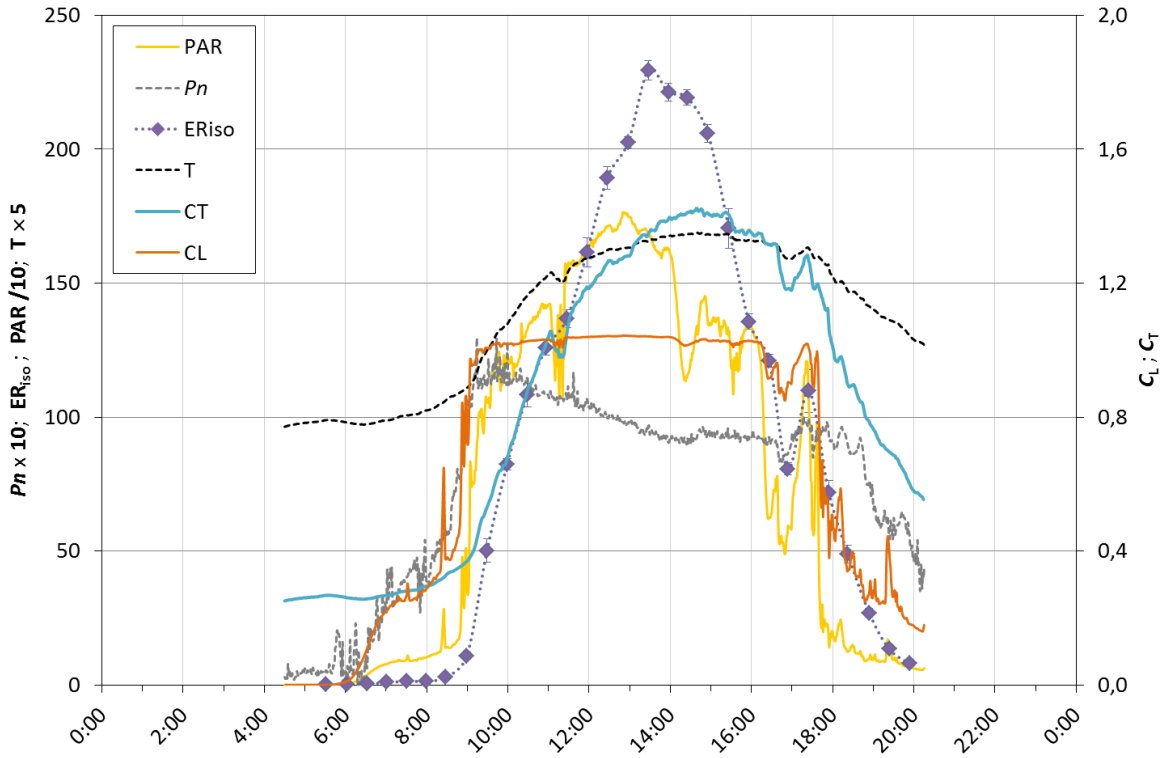

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774 **Fig. 6**

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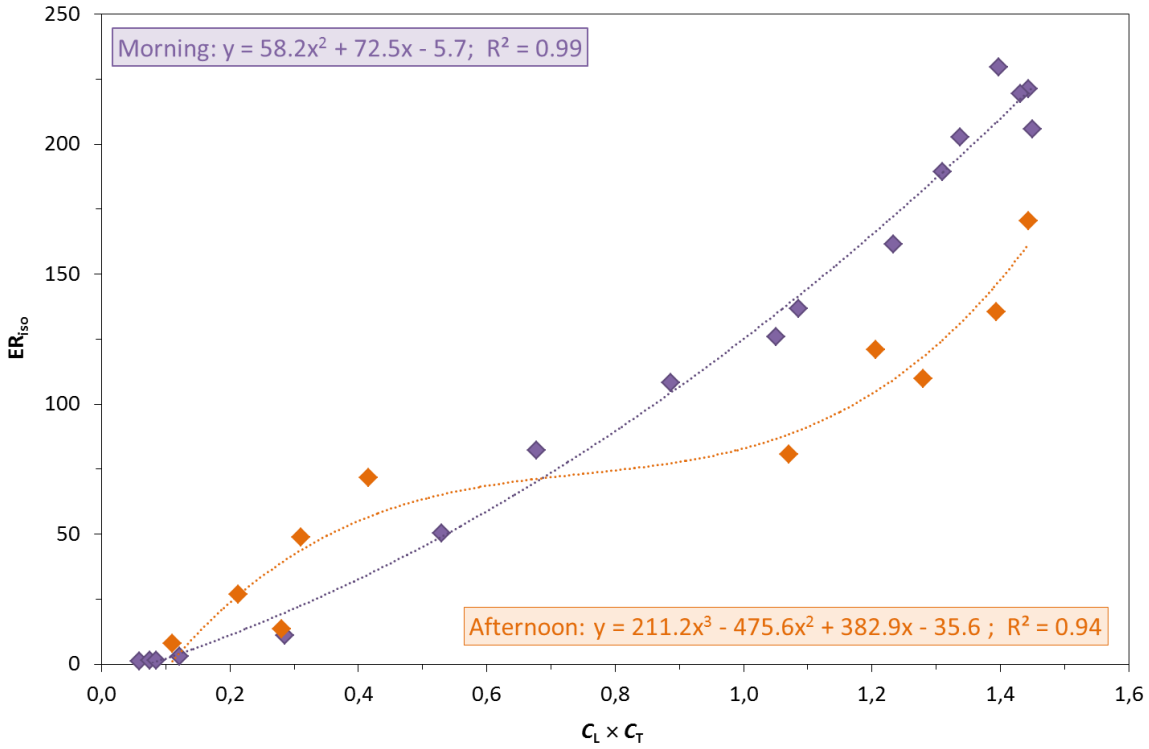

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778 **Fig. 7**

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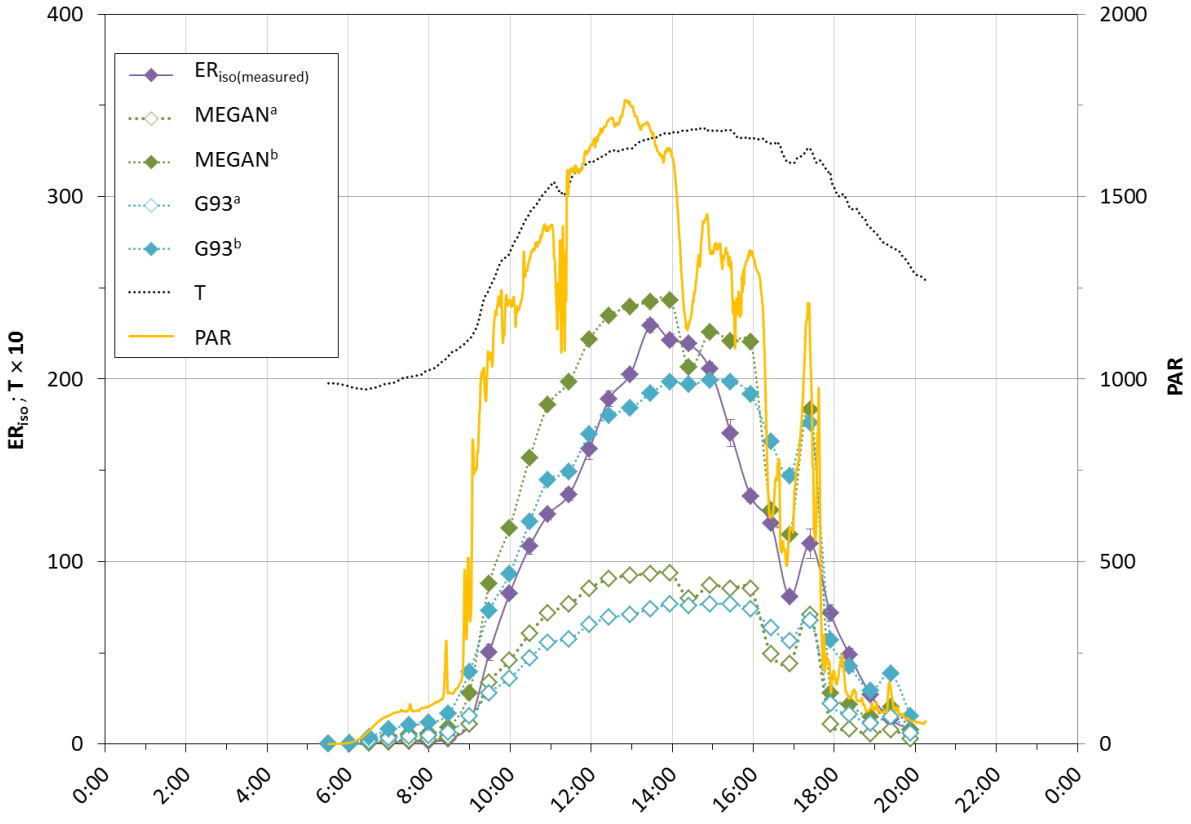

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Table 1

Compound	*Qp*4 (PAR=851.7; T=28.7±4.9; RH=68.7±10.3; *Pn*=8.3±2.8; *Gw*=189.6±157.6)[a]					*Am* (PAR=460.9; T=26.6±4.4; RH=75.2±18.7; *Pn*=2.3±1,3; *Gw*=85.3±45.9)[a]				
	ER		Relative composition[b]		EF[c]	*ER*		Relative composition[b]		EF[c]
Methanol	0.49±0.10	(0.98)	0.5	{41.5}	0.50±0.04	0.23±0.08	(0.57)	26.7	{43.4}	0.39±0.04
Acetaldehyde	0.09±0.03	(0.30)	0.1	{7.6 }	0.12±0.01	0.13±0.06	(0.38)	15.1	{24.5}	0.28±0.03
Acetone	0.20±0.06	(0.46)	0.2	{16.9}	0.27±0.02	0.14±0.04	(0.32)	16.3	{26.4}	0.24±0.02
Isoprene	98±31	(229)	98.8	-	138±10	0.33±0.09	(0.73)	38.4	-	0.47±0.04
MVK+MACR	0.10±0.03	(0.26)	0.1	{8.5}	0.15±0.01	0.01±0.005	(0.04)	1.2	{1.9}	0.030±0.002
Monoterpenes[d]	0.30±0.10	(0.77)	0.3	{25.4}	0.44±0.03	0.02±0.01	(0.07)	2.3	{3.8}	0.050±0.003

788 **Table 2**

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	Quercus pubescens tree	*n*	Measurement information						ER_d	C_{iso}	ER_{br}		I_S	
			Date	PAR	T	RH	*Pn*	*Gw*						
Control plot	Qp4	28	1-Jun	851.7	28.7±4.9	68.7±10.3	8.3±2.8	189.6±157.6	98 {0.4-229}	2.7±2.2	98±31	(11.1±3.5)	138±10	(15.6±1.1)
	Qp1	4	6-Jun	851.7	26.6±0.9	66.2±4.5	12.4±1.1	263.7±31.0	23 {9.8-35}	0.8±0.1	30±5	(3.7±0.6)	72±3	(8.8±0.3)
		9	7-Jun	625.9	24.5±2.5	70.8±5.3	11.6±5.0	228.9±137.4	24 {0.16-52}	0.6±0.3				
		7	9-Jun	780.5	24.9±2.7	64.4±6.7	10.3±3.8	191±99.9	24 {0.5-47}	0.6±0.4				
		3	10-Jun	868.3	25.4±1.2	61.1±6.0	12.7±1.2	155±27.4	24 {13-37}	0.5±0.2				
		6	11-Jun	725	25.4±1.8	58.6±3.2	10.6±2.3	154.5±47.2	21 {1.7-34}	0.6±0.2				
		6	12-Jun	585.1	21.2±2.2	70.4±6.3	9.5±3.1	114.8±24.6	9.4 {1.4-17}	0.4±0.1				
		4	13-Jun	1040.8	24.5±1.2	-	11.4±0.8	-	26 {22-30}	0.6±0.1				
		6	14-Jun	758	25.7±2.4	58.0±4.6	10.9±0.9	157.5±62.4	34 {5.8 -50}	0.9±0.4				
		4	15-Jun	810.9	28.4±0.4	56.0±4.4	10.9±0.9	268.1±75.1	52 {43-56}	1.3±0.1				
		8	16-Jun	584.7	27.4±2.9	55.1±6.0	9.1±3.6	177.7±86.2	37 {<d.l.-78}	1.0±0.6				
		4	17-Jun	858.1	30.3±1.4	50.9±4.3	10.4±0.6	243.2±48.4	65 {49-81}	1.8±0.4				
	$Qp1_{shade}$	5	6-Jun	166.7	24.9±0.6	84.3±5.1	6.4±1.9	102.7±16.6	13 {3.5-21}	0.5±0.2	12±6	(1.0±0.6)	77±2	(6.7±0.2)
		8	7-Jun	92.1	23.1±1.9	80.1±10.1	3.8±2.8	54.0±62.6	5.3 {<d.l.-19}	0.3±0.2				
	Qp2	4	15-Jun	693.8	30.0±0.5	57.5±6.6	7.4±0.7	92.8±25.8	69 {63 -72}	2.7±0.3	61±16	(7.5±1.2)	74±4	(9.1±0.5)
		7	16-Jun	559.9	28.7±3.2	65.0±7.0	5.4±2.5	106.7±44.4	57 {5.6 -90}	2.9±1.0				
	$Qp2_{shade}$	*6*	15-Jun	60,9	24.3±1.6	54.3±4.2	2.8±1.1	11.5±9.6	7.8 {1.9-14}	0.3±0.2	6.1±4.1	(0.5±0.4)	59±12	(5.1±0.1)
		5	16-Jun	29,5	24.1±3.3	55.5±15.9	3.0±0.7	11.9±10.4	4.0 {0.3-6.6}	0.5±0.2				
	Qp3	2	17-Jun	1742.5	31.8±1.8	49.3±8.8	7.5±0.7	133.7±8.3	33 {26-39}	1.2±0.2	32±12	(3.9±1.1)	31±8	(3.8±1.0)
		5	18-Jun	885.6	28.7±2.4	61.4±10.9	9.0±0.8	140.2±26.3	31 {5.2 -41}	1.0±0.5				

Rain exclusion plot	Qp5	6	9-Jun	757.6	26.1±3.1	65.5±8.1	6.3±2.5	68.8±26.4	31.9 {<d.l.-64}	1.2±0.9	31.9±25.8	(3.9±3.2)	58±17	(7.2±2.1)
	Qp6	5	11-Jun	708.6	25.5±2.3	60.7±9.2	12.8±2.0	130.1±46.8	38.1 {3.2-66}	1.2±0.9	23.8±15.5	(2.9±1.9)	54±13	(6.7±1.6)
		5	12-Jun	633.1	22.2± 2.6	63.6±10.4	13.8±0.9	75.8±46.9	9.5 {1.8-17}	0.3±0.1				
	Qp7	4	14-Jun	318.2	26.4±1.3	65.8±5.1	5.9±0.7	62.5±26.7	23.1 {7.4-32}	1.1±0.5	23.2±18.5	(2.9±2.3)	62±8	(7.6±0.9)

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Table 3

Tree		Is[a]			Is[b]		
		*a*x + *b*	R^2	RMSE	*a*x + *b*	R^2	RMSE
*Qp*4	G93	0.35x + 6.96	0.91	73.67	0.92x + 18.05	0.91	26.59
	MEGAN	0.45x + 2.66	0.92	65.89	1.16x + 6.90	0.92	36.69
*Qp*1	G93	0.54x + 10.08	0.74	11.88	0.73x + 13.61	0.74	11.61
	MEGAN	0.23x + 9.00	0.15	23.53	0.32x + 12.14	0.15	21.88

Appendix

Supplementary materials: emission factor Is **calculation**

The empirical relationship used to describe changes in isoprene emission rates I (μgC g_{DM}^{-1} h^{-1}) *vs* light and temperature was as in Guenther et al. (1993):

$$I = Is \times C_T \times C_L \quad \text{(A1)}$$

where

Is is the isoprene emission factor standardised at T = 30 °C and PAR = 1000 μmol m^{-2} s^{-1} (μgC g_{DM}^{-1} h^{-1}), and C_L and C_T are, respectively, light and temperature coefficient defined by

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1+\alpha^2 L^2}} \quad \text{(A2)}$$

and

$$C_T = \frac{e^{\frac{C_{T1}(T-T)_s}{RTTs}}}{1+e^{\frac{C_{T2}(T-T_M)}{RTTs}}} \quad \text{(A3)}$$

where α=0.0027 m^2 s μmol^{-1}, C_{L1}=1.066 units, C_{T1}=95000 J mol^{-1}, C_{T2}=230000 J mol^{-1}, T_M = 314 K are empirically derived constants, L is the Photosynthetically Active Radiation (PAR) flux (μmol(photon) m^{-2} s^{-1}), T is the predicted temperature (K), and T_S is the leaf temperature at standard condition (303 K); at standard conditions of 1000 μmol(photon) m^{-2} s^{-1} PAR and 303 K, $C_T \times C_L$=1.

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