

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

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Abstract

We aimed at quantifying Biogenic Volatiles Organic Compounds (BVOC) emissions in June from three Mediterranean species located at the O₃HP site (Southern France): *Quercus pubescens*, *Acer monspessulanum* and *C. coggygia* (for isoprene only). As *Q. pubescens* was shown to be the main BVOC emitter with isoprene representing $\approx 99\%$ of the carbon emitted as BVOC, we mainly focused on this species. *C. coggygia* 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 23.1 and 97.7 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$. *Q. pubescens* daily mean net assimilation (Pn) ranged between 5.4 and 13.8, and 2.8 and 6.4 $\mu\text{molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ 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 4.4 among the sunlit branches. While sunlit branches ERd was clearly higher than for shaded branches, there was a non-significant variability on Is (58.5 to 76.5 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$). 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 $C_L \times C_T$ 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 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 products also highly reactive in the atmosphere (Atkinson, 2000; Ciccioli et al., 1999; Claeys et al., 2004; Goldstein and Steiner, 2007).

At a smaller scale, isoprene plays a key role in the tropospheric chemistry, since, isoprene, alike other VOC, is an ozone precursor in presence of NO_x and light (Atkinson, 2000). NO_x being mainly emitted by anthropogenic sources, isoprene emissions in areas where megacities are surrounded by large ecosystem areas (such as Mediterranean) can significantly contribute to high levels of O₃ 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 2 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 with 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 *I_s*) 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 µgC g_{DM}⁻¹ h⁻¹), low (14 ± 7 µgC g_{DM}⁻¹ h⁻¹), moderate (35 ± 17.5 µgC g_{DM}⁻¹ h⁻¹) and high (> 70 ± 35 µgC g_{DM}⁻¹ h⁻¹) emitter species.

In Europe, *Quercus pubescens* Willd. accounts for the most important isoprene emitter species, and represents thus one of the first biogenic isoprene source in the Mediterranean region (Keenan et al., 2009). Previously reported emission factors *I_s* for this species were observed to fluctuate in the Mediterranean area over a large range. Kesselmeier et al. (1998)

and Owen et al. (1998) assessed a fairly similar Is of 50 to 66 $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ respectively at a site near Montpellier (France), which was 50% lower than what Simon et al., (2005) found at 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) using seedlings coming from different European sites. Simpson et al. (1999) proposed in his BVOC inventory review a value of 53 $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ for *Q. pubescens* for the whole Europe.

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 CANOPEE project which aimed at analysing and quantifying intra-canopy processes in the reactive organic compound exchange between biosphere and atmosphere, with a focus on isoprene (further details can be found at <https://wiki.lsce.ipsl.fr/CANOPEE>). An intensive field campaign took place at the Oak Observatory at OHP (O₃HP), 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 O₃HP 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 study 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 2 commonly used algorithms to assess, under a Mediterranean environment, the observed diurnal variations of isoprene emission.

2 Methods

2.1 Experimental site

BVOC measurements took place at the O₃HP 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 O₃HP (955 m²), free from human disturbance

for 70 years, consists of a flat homogeneous forest mainly composed of *Q. pubescens* ($\approx 90\%$ of the biomass and $\approx 75\%$ 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 LAI of 2.2. Dry leaf production was assessed for *Q. pubescens* to range between 1.4 and 1.6 t y^{-1} . The O₃HP site was created in 2009 in order to study the downy oak forest ecosystem at soil and tree scale, under both a natural and an accentuated water stress plot (control and rain exclusion plots respectively) induced by a rainfall exclusion device (an automated monitored roof deployed during rain events) set up over a part of the O₃HP 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 RH, 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 experimentation 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* (*Am*, 2 June) and one *Q. pubescens* sunlit branches (*Qp4*, 1 June). *Am* and *Qp4* were located in a clearing 40 m north of the O₃HP 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 (*Qp1*, *Qp2*, *Qp3*) and the rain exclusion plot (*Qp5*,

Qp6, *Qp7*). Isoprene was sampled from the highest level of the scaffold using the off-line cartridge collection method.

On the other hand, variability of isoprene emissions between shaded and sunlit branches was assessed in *Qp1* and *Qp2*. For these trees, besides from the sunlit branches, one shaded branch was also studied (approx. 2 m above ground, *Qp1_{shade}* and *Qp2_{shade}*). These samples were also taken using the cartridges method.

When cartridges were used, isoprene emissions were approximately hourly sampled from sunrise to sunset. One enclosure was maintained on the *Qp1* 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). A second enclosure was used to alternatively investigate, during 1 to 2 days, isoprene emissions from the other 8 branches selected (sunlit and shaded). Concomitant microclimate (PAR, temperature *T*, RH) and physiological parameters (net photosynthesis *Pn*, and stomatal conductance to water *Gw*) were monitored during 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 \approx 3 month old) were enclosed in a \approx 60 L PTFE (PolyTetraFluoroEthylene) frame closed by a sealed 50 μ m 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, *T*, RH) 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. CO₂/H₂O exchanges from the enclosed branches were also continuously measured using infrared gas analysers (IRGA 840A®, Licor).

178 Pn ($\mu\text{mol}_{\text{CO}_2} \text{ m}^{-2} \text{ s}^{-1}$) was calculated using equations described by Von Caemmerer and
 179 Farquhar, (1981) as follows:

$$180 \quad P_n = \frac{F \times (C_r - C_s)}{S} - C_s \times E \quad \text{Eq. (1)}$$

181 where F is the incoming air flow rate ($\text{mol}_{\text{H}_2\text{O}} \text{ s}^{-1}$), C_s and C_r are the sample and reference
 182 CO_2 molar fractions respectively ($\mu\text{mol}_{\text{CO}_2} \text{ mol}^{-1}$ or ppm), S is the leaf area (m^2), $C_s \times E$ is the
 183 fraction of CO_2 diluted in the water evapotranspired ($\mu\text{mol}_{\text{CO}_2} \text{ m}^{-2} \text{ s}^{-1}$), and E is the
 184 transpiration rate ($\text{mol}_{\text{H}_2\text{O}} \text{ m}^{-2} \text{ s}^{-1}$) calculated as follows:

$$185 \quad E = \frac{F \times (W_s - W_r)}{S \times (1 - W_s)} \quad \text{Eq. (2)}$$

186 where W_s and W_r are the sample and reference H_2O molar fractions respectively ($\text{mol}_{\text{H}_2\text{O}}$
 187 mol^{-1}).

188 G_w ($\text{mol}_{\text{H}_2\text{O}} \text{ m}^{-2} \text{ s}^{-1}$) was calculated using the following equation:

$$189 \quad G_w = \frac{E \times \left(1 - \frac{W_l + W_s}{2}\right)}{W_l - W_s} \quad \text{Eq. (3)}$$

190 where E and W_s are described in equation (2), W_l is the molar concentration of water
 191 vapour within the leaf ($\text{mol}_{\text{H}_2\text{O}} \text{ mol}^{-1}$) calculated using the equation :

$$192 \quad W_l = \frac{VP_{\text{sat}}}{P} \quad \text{Eq. (4)}$$

193 where VP_{sat} is the saturated vapour pressure (kPa), and P is the atmospheric pressure (kPa).
 194 Air flow rates were controlled by mass flow controllers (Bronkhorst) and all tubing lines were
 195 PTFE-made.

196 Total dry biomass matter (DM) was assessed during this study for each sampled branch by
 197 manually scanning every leaf enclosed in the chamber and applying an area factor (AF)
 198 conversion extrapolated from concomitant measurements made on the same site. For top
 199 and down canopy branches, mean (range) DM measured during this study was 0.16 (0.01 -
 200 0.45) and 0.10 (0.01 - 0.38) g_{DM} respectively, and mean (range) AF was 13.17 (0.82 - 36.67)
 201 and 11.98 (2.10 - 41.85) cm^{-2} respectively; DM and AF values enabled us to assess a mean
 202 leaf to mass area ratio (LMA) of 123.2 ± 1.0 ($n=5$ trees) and 87.1 ± 1.8 $\text{g}_{\text{DM}} \text{ m}^{-2}$ ($n=15$ trees)
 203 for sunlit and shaded branches respectively. Since the sampled *A. monspessulanum* was not
 204 located into the protected O_3HP site, DM was assessed directly by cutting off the branch,
 205 drying and weighting foliar biomass; LMA was $75.4 \text{ g}_{\text{DM}} \text{ m}^{-2}$.

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

For BVOC screening, the PTR-MS was connected to one 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, 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 light with an aluminium foil. Tubes were removed from a cold box located close to the enclosures just before 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 3 weeks. Ozone was removed from sampled air by placing PTFE filters impregnated with sodium thiosulfate (Na₂S₂O₃) 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 difference between 4.0 and 8.6 %.

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

2.4 Analytical methods

BVOCs collected into glass and stainless steel cartridges were analysed using a similar GC-MS technique.

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 (helium) 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 0.0031 µgC.g_{DM}⁻¹ h⁻¹. Isoprene quantification was achieved using a 5 ppm ± 0.25 ppm diluted in N₂ 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 µgC g_{DM}⁻¹.h¹ (0.26 µgC g_{DM}⁻¹.h¹, respectively). Isoprene quantification was made using a 3.97 ± 0.08 ppb in

N₂ certified gas standard (NPL, Teddington Middlesex, UK) for lower concentrations and a 3.90 ± 0.29 ppm in N₂ 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. An intercomparison between both analytical GC-MS systems used to analyse BVOC trapped within glass and SS cartridges was carried out by loading isoprene standards in both types of tubes over a 12–1400 ngC range. A coefficient of determination R² 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 metal cartridges on either the inflowing or outflowing air of the enclosures (*n* = 20; slope = 1.05; R² = 0.90). No breakthroughs were observed for isoprene, neither on laboratory tests (up to 1400 ngC) nor on *in-situ* samples (range of 0 - 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 *Quercus* branches. Measurements of the inflowing and outflowing air were made alternatively every 15 min, allowing an emission rate 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 C_L × C_T factors, 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 × 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 emission by comparing slopes of the regression lines between ER and C_L × 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 mainly rainy most of the day, and an ambient T 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 T increased constantly up to nearly 24 °C at the end of the campaign, the ambient RH decreased down to 40 %, and Sw in both plots decreased down to 0.11 and 0.15 $L_{H_2O} L_{soil}^{-1}$ for the rain exclusion and control plot respectively. From 6 June, soil humidity 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 O₃HP forest

3.2.1 *Q. pubescens* BVOC emissions

BVOC emissions from *Q. pubescens* (obtained by PTR-MS; $Qp4$, Table 1) are 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 97.7 $\mu gC g_{DM}^{-1} h^{-1}$ representing, on average, 98.8 % of the carbon emitted by the $Qp4$ branch. The remaining 1.2 % was found to represent a negligible quantity of the carbon assimilated as BVOC (< 0.03 %), and was, in decreasing order, composed by methanol, total monoterpenes, acetone (altogether \approx 84 % of the non-isoprene BVOC), and methyl-vinyl-ketone (MVK) + methacrolein (MACR), and acetaldehyde whose emissions were of the order of 0.1 $\mu gC g_{DM}^{-1} h^{-1}$. Since isoprene, and total monoterpene emissions have been observed to

be light and temperature dependent in this study and previous studies, *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 *Qp4* 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 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 (6.88 % data not shown) compared to 3.14 % and 0.76 % 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 $0.49 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (or $130 \text{ ng g}_{\text{DM}}^{-1} \text{h}^{-1}$, or $1.13 \text{ noml m}^{-2} \text{s}^{-1}$), is in the medium range of the foliar emissions reviewed by Seco et al. (2007) for methanol emission from other emitters.

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 at another Mediterranean site. Monoterpenes were found to be mainly α -pinene and limonene (67 % and 33 % respectively – data from cartridge sampling results, not shown) and their emission rates were more light and temperature dependent ('*de novo* emission') than only temperature dependent ('pool emission') (with $R^2 = 0.87$ and 0.64 respectively and $P < 0.001$).

As for MeOH, no acetone emissions have been previously reported for *Q. pubescens*. The mean emission rate of $0.20 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (or $320 \text{ ng g}_{\text{DM}}^{-1} \text{h}^{-1}$, or $0.15 \text{ noml m}^{-2} \text{s}^{-1}$) 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 oxydation (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 not be proved; values shown in the Table 1 may thus represent the highest limit of the primary emission rate range for these compounds.

If acetaldehyde detected in our enclosure was mostly from primary biogenic source (cell catabolism, (see Fall et al., 1999; Loreto et al., 2006), the emission rates thus assessed ($0.09 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ or $165 \text{ ng g}_{\text{DM}}^{-1} \text{h}^{-1}$ or $0.10 \text{ nmol m}^{-2} \text{s}^{-1}$) would be in the lower range of the foliar emission rates reported in the literature for other plants (Seco et al., 2007). As for MeOH emissions, the relative contribution of acetaldehyde emissions to total assimilated carbon was observed to peak in the morning (1.47 % in the morning compare to 0.06 % in the afternoon).

3.2.2 A. *monspessulanum* BVOC emissions

A. monspessulanum total BVOC emissions ($< 1 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) were two orders of magnitude smaller than the total *Q. pubescens* BVOC emissions ($> 100 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$; Table 1). Isoprene and methanol were the two dominant BVOC measured with a daily mean emission rate of 0.33 and $0.23 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ 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 T variations influenced the diurnal emission variations of all the measured BVOC except methanol which, as observed for *Q. pubescens*, was found to be exponentially T dependent.

To conclude, *Q. pubescens* appeared to be the main BVOC emitter in the O₃HP forest compared to *A. monspessulanum*. Isoprene represented more than 98 % of the BVOC emitted by *Q. pubescens*, with daily mean values as high as $\approx 100 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$. Therefore, the 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 CO₂ 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 plots 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 $\mu\text{molCO}_2 \text{m}^{-2} \text{s}^{-1}$ and 62.5 and 268.1 $\text{mmolH}_2\text{O m}^{-2} \text{s}^{-1}$ 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 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and Gw ranging from 50 to 150 $\text{mmolH}_2\text{O m}^{-2} \text{s}^{-1}$). Gw up to 450 $\text{mmol H}_2\text{O m}^{-2} \text{s}^{-1}$ 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 RH - especially during the night-time respiration - and warmer air T), 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

Qp1 or *Qp6* branches studied on this day. Shaded branches *Qp1_{shade}* and *Qp2_{shade}* showed Pn values between 2.8 and 6.4 $\mu\text{molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$, 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 canopy branches were highly variable, fluctuating over one order of magnitude, between below 10 (*Qp1* and *Qp6*, 12 June) and 97.7 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$ (*Qp4*, 1 June). The lower ERd coincided with reduced incident PAR and ambient *T* due to some rain events on 12 June. Since *Qp4* Pn was similar to Pn measured for the other trees (8.3 and between 5.4 and 13.8 $\mu\text{molCO}_2 \text{ m}^{-2} \text{ s}^{-1}$ 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 (23.1 and 97.7 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$) and shaded branches (4.0 and 12.6 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$). Daily mean *Qp1_{shade}* and *Qp2_{shade}* PAR were reduced by a factor of 6 and 10 respectively compared to PAR values recorded on *Qp1* and *Qp2* sunlit branches. Consequently, shaded ERd (between 4.0 and 12.6 $\mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$) were, on average, between 2 and 10 times lower than the values measured on the sunlit *Qp1* and *Qp2* branches respectively; these values were the lowest ERd observed during the study. In shaded branches, only 0.25 ± 0.15 to 0.53 ± 0.18 % of the assimilated carbon was emitted as isoprene (C_{iso}), while C_{iso} for sunlit branches ranged between 0.36 ± 0.1 and 2.9 ± 1.0 %. Daily mean C_{iso} was exceptionally high for *Qp4* (2.7 ± 2.2 %) and reached up to 6.5 % at solar noon.

Whatever their horizontal or vertical location in the canopy, 2/3 of the isoprene emission rates measured from the studied branches exponentially increased with Pn, except for *Qp3*, *Qp6* and *Qp2_{shade}* (Fig. 3). As explained in the next section, *Qp3* was found to be dead in August, although there were no visible signs when our study was conducted. *Qp6* 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 T 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, respectively, light and temperature dimensionless coefficients given by Guenther et al., (1993) from experimental measurements see supplementary section). For sunlit branches, Is varied between 30.7 ± 8.2 and $137.5 \pm 10.1 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ for *Qp3* and *Qp4* respectively, which is in the range of values given in the literature (50 , 66 and $118 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$, Kesselmeier et al. (1998), Owen et al. (1998) and Simon et al. (2005) respectively). A factor of more than 2 was found between, on the one hand, *Qp4* emission factor and all the other branches in the control plot, and, on the other hand, between Is from *Qp1* and *Qp2* (71.6 ± 2.6 and $73.9 \pm 4.4 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ respectively) compared to *Qp3* ($30.7 \pm 8.2 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$). The overall factor of 4.4 observed on Is showed the extent to which *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 *Qp3* Is smaller by a factor of 2 than the other *O₃HP* tree branches was *a posteriori* linked with the fact that the *Qp3* branch died in August despite no visible injuries were visible when it was selected for 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 1.6 for *Q. pubescens* Is.

Regarding the canopy shading effect, the studied shaded branches showed no significant difference in their capacity to emit isoprene (76.5 ± 2.6 and $58.5 \pm 11.5 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ for *Qp1_{shade}* and *Qp2_{shade}* respectively) compared to the sunlit branch of the corresponding tree, 71.6 ± 2.6 and $73.9 \pm 4.4 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ for *Qp1* and *Qp2* respectively (comparison of

regression lines; $R^2 = 72.8$ and $R^2 = 89.2$ for *Qp1* and *Qp2* branches respectively; $P > 0.05$). This similarity occurred despite the existence of a LMA vertical gradient in our study: 87.1 ± 1.8 and $123.2 \pm 1.0 \text{ g m}^{-2}$ for shaded and sunlit branches respectively. This gradient is similar to what was previously reported by Harley et al. (1994) for a *Quercus alba* forest: LMA was 111.5 ± 5.9 and $75.4 \pm 7.0 \text{ g m}^{-2}$ for sunlit and shaded branch respectively; when these authors expressed I_s on a leaf area basis they observed significantly lower I_s values for a shaded branch. Note that if the sunlit branch LMA value was used for assessing I_s from all branches (shaded and sunlit branches) - as it may be done in global up scaling inventory when no appropriate LMA value is available - shaded I_s value would then become significantly lower than I_s sunlit branches. As any other factors used when BVOC canopy fluxes are extrapolated from branch scale measurements to canopy scale, determination of appropriate LMA should be as accurate as possible since it can represent one of the biases in such an exercise.

Based on our assessed I_s range (30.7 to $137.5 \text{ } \mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$) and using an average branch scale I_s value of $60 \text{ } \mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$, Kalogridis et al. (2014) extrapolated a canopy isoprene emission flux of $15 \text{ mg m}^{-2} \text{ h}^{-1}$ twice the mean canopy flux measured by the disjunct eddy covariance technique ($6.6 \text{ mg m}^{-2} \text{ h}^{-1}$). These authors point out that this factor of 2 of discrepancy is reasonable since it is in the range of uncertainties typically obtained for such up-scaling exercises (see for example Guenther et al., 1995). It is anyway within the range of the tree to tree variability observed for *Q. pubescens* I_s on this site (a factor of 4.4). However, this exercise illustrates the limit of precision in BVOC canopy flux assessments, how much I_s canopy variability is extensively and intensively is studied.

3.4.2 Diurnal variability: how well $C_L \times C_T$ captured the observed features?

The diurnal range of isoprene emission rate (ER) variations observed over the 7 sunlit different branches studied (Fig. 4a) was found to fluctuate from day to day and with environmental conditions (Fig. 4b). The maximum value observed on June 12 (rainy day) for the sun exposed *Qp1* branch ($16.6 \text{ } \mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$) was about 5 times lower than the maximum observed at the end of the campaign (especially on 16 June, $77.6 \text{ } \mu\text{gC g}_{\text{DM}}^{-1} \text{ h}^{-1}$) when weather was much warmer and sunnier (Table 2 and Fig. 4b); it was about the same than the maximum ER measured for the shaded branch *Qp1* at the beginning of the campaign (June

524 6-7, $\approx 20 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$). *Qp1* C_{iso} was the highest (up to 1.8 %, Table 2) at the end of the
525 campaign, compared to values under 1 % at the beginning of our measurements, which is
526 consistent with previous findings for *Q. pubescens* in June (0.62 to 1.8 %, Kesselmeier et al.,
527 1998).

528 Diurnal variations were studied in more detail during the *Qp4* high frequency measurements
529 carried out with the PTR-MS system. At dawn, *Qp4* ER became significant about 2 h after
530 sunrise when the CO_2 assimilation started (Fig. 5). More precisely, positive Pn values were
531 obtained at 06:30 a.m., as soon as PAR became detectible and increased in the early
532 morning in parallel of a C_L increase (Fig. 5). Detectable isoprene emissions were observed 2 h
533 later (08:30), only when ambient temperature significantly increased. Consequently,
534 isoprene emissions were then observed to increase as C_T . This finding contrasts with
535 previous studies (Owen et al., 1998) where *Q. pubescens* ER were more PAR than
536 temperature dependant. The delay observed between Pn and the isoprene emission onset in
537 the morning was found to correspond to a temperature increase dT of nearly 3°C ;
538 interestingly, a similar dT was observed for the *Qp1* branch when early morning
539 measurements were made. T continued to be the leading parameter compared to PAR until
540 ER reached its maximum ($229 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ at 13:30). Between 13:30 and 17:30 isoprene
541 emission remained constantly more temperature than light dependent. As soon as PAR
542 decreased (17:30), ER started to decrease to non-detectable values, although the branch
543 continued to assimilate CO_2 ; Pn decreased only 1 h later. If the diurnal variations of *Qp4* ER
544 were mostly well described by $C_L \times C_T$ (in particular from dawn to midday maximum and
545 during the evening, the relative influence of light and T respectively varied along the day as
546 presented in Figure 6: from 13:30 to 16:00 ER decreased from 220 to less than $150 \mu\text{gC g}_{\text{DM}}^{-1}$
547 h^{-1} at nearly constant $C_L \times C_T$; on the contrary, after 16:00, ER remained close to $75 \mu\text{gC g}_{\text{DM}}^{-1}$
548 h^{-1} although $C_L \times C_T$ fluctuated over nearly a factor of 3 (from 1.1 to 0.4). Thus, after the solar
549 noon, ER presented an overall reverse sigmoid shape diurnal dependency with $C_L \times C_T$. The
550 sudden decrease of ER at 13:30 while $C_L \times C_T$ remained constant may illustrate a possible
551 temperature midday stress of the branch, with an emission falling down to a minimum value
552 of $\approx 75 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$. The thermal stress lasted until 16:00 when isoprene emission
553 regulation became again well correlated to $C_L \times C_T$. Indeed, as reported by Niinemets et al.
554 (2010a) heat stress could modify isoprene emission by decreasing foliar metabolism. For

instance, Funk et al. (2004) observed that during a heat stress an alternative source of carbon (carbon pool stored as carbohydrates) is used for isoprene synthesis. As showed by Fortunati et al. (2008) for *Populus nigra* L., this alternative carbon source being unaffected by temperature, our observations could illustrate a similar uncoupling between isoprene emissions and $C_L \times C_T$ for *Q. pubescens*. Note that such 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 (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 we 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, (ii) the MEGAN parameterisation (Guenther et al., 2006), a modified version of the former algorithm in an attempt to better capture the emission seasonality through the consideration of a dimensionless factor dependent on leaf age γ_{age} (here set at 0.6), the lower frequency variations (up to 10 days) of environmental conditions, and the impact of soil humidity through a factor γ_{SM} . Both algorithms were tested for *Qp4* branch using, both, an I_s of $53 \mu\text{gC g}_{DM}^{-1} \text{h}^{-1}$ as recommended by Simpson et al. (1999) for European *Q. pubescens* and our values obtained in this study (71.6 and $137.5 \mu\text{gC g}_{DM}^{-1} \text{h}^{-1}$ for *Qp1* and *Qp4* respectively, Fig. 7).

As a whole, both algorithms underestimated the *Qp4* measured ER (65 and 55 % for G93 and MEGAN respectively, Fig. 7, Table 3) when Simpson et al. (1999) I_s value was used. This discrepancy reached a factor of 3 for midday maximum emission (74 and $93 \mu\text{gC g}_{DM}^{-1} \text{h}^{-1}$ for G93 and MEGAN respectively compared to $229 \mu\text{gC g}_{DM}^{-1} \text{h}^{-1}$). When I_s values obtained in 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 \approx 2 and 3 times lower for G93 and MEGAN respectively, Fig. 7, Table 3). The main bias was thus found to be linked with I_s , since the general diurnal trend was roughly captured by both algorithms ($R^2 > 0.91$ for all comparisons). However, the maximum Q_{p4} emissions calculated with algorithms, were reached at 14:00 (MEGAN) and 15:30 (G93), later than what was observed (13:30) and whatever the I_s value used. Besides, predicted ER remained mostly constant until 16:00, while the observed emissions decreased to values 50% smaller than the midday maximum as previously described and commented (section 3. 4.2). Both algorithms being strongly dependant on T variations, such an observed uncoupling between ER and elevated T (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 $\approx 10 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ compared to the observed value of $75 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$. On the contrary ER was assessed to occur much earlier at dawn (6:30 compared to 8:00) and was overestimated by a factor of 3 by G93 over this period. Note that, for Q_{p4} , 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 Q_{p1} diurnal measurements: when measured I_s 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 Q_{p1} , 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 O₃HP site. Indeed, the soil water content becoming lower than the wilting point used for our soil type ($0.138 \text{ m}^3 \text{ m}^{-3}$ 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 (around -0.1m deeper) soil moisture does not take into account the tree ability to have 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 Q_{p4} measurements nor on the first day of Q_{p1} measurements (γ_{SM} was 1). When γ_{SM} was not considered anymore and set to 1 for all Q_{p1} 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 *Qp1* underestimation ($\approx 60\%$) compared to the simpler G93 algorithm ($\approx 40\%$), as for *Qp4* 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 $<1\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$) with isoprene (36.3 %) and methanol (25.3 %) being the two dominant emitted compounds (daily mean emission rate, ERd, of 0.33 and $0.23\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$ respectively); acetone, acetaldehyde and total monoterpenes were also measured at lower rates.

Q. pubescens was found to be a strong isoprene emitter (99 % in carbon mass) with mean emission rates fluctuating between 23.2 and $97.7\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$ for sunlit branches and 6.1 and $11.5\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$ for canopy shaded branches; methanol (ERd = $0.49\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$; 0.5 % of total BVOC) and total monoterpenes (ERd = $0.30\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$; 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 P_n , although P_n 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 (0.25-0.53 %) whereas C_{iso} ranged between 0.53-1.77 % for sunlit branches with a maximum of 6.7 % under elevated T and sunlight stress.

Tree to tree isoprene emission variability was high considering both, sunlit branches ($n = 7$) and, to a lesser extent, shaded ($n = 2$) branches. In sunlit branches, ERd varied over a factor of 10 and emission factor (Is) over a factor of 4.4 (between 30.7 ± 8.2 and $137.5 \pm 10.1\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$). Shaded branch variability was lower, a factor of 3 for ERd (between 4.0 and $12.6\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$) and not significant for Is (between 58.9 ± 11.5 and $76.5 \pm 2.6\ \mu\text{gC g}_{\text{DM}}^{-1}\text{ h}^{-1}$). 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 that is originating from *in-situ* conditions that should always be considered 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 emission by a plant species, it cannot give the full picture obtained by *in-situ* long term measurements.

The morning onset of isoprene emission rates was mainly driven by T while P_n was, as expected, light dependent. By contrast, emission evening decline was mainly described by PAR. In between, an uncoupling of isoprene emission with light and T effect was noticed, with emissions starting to decline whereas light and T remained stable.

If MEGAN and G93 algorithms succeed in capturing the overall diurnal pattern of isoprene emission at the O₃HP, they significantly underestimated emissions by an average factor of up to 3, and especially the midday maximum values when isoprene emission factor I_s other than those assessed for this site was employed. Both algorithms were found to be very sensitive to I_s . Moreover, the two algorithms showed difficulties in properly assessing detailed isoprene diurnal variations, in particular 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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List of Figures

Fig. 1: Location of the *i Q. pubescens* (*Qpi*) and the *Acer monspessulanum* (*Am*) trees studied. Branches *Qp4* and *Am* were located about 40 m north of the O₃HP footbridge and their BVOC sampled using online PTR-MS. All other *Qpi* branches were sampled from the O₃HP footbridge for measurements.

Black circles in the O₃HP area represent the assessed crown area for every sampled tree.

Fig. 2: Environmental conditions prevailing at the O₃HP site.

(a) Daily mean photosynthetically active radiation PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), temperature T ($^{\circ}\text{C}$) and ambient relative humidity RH (%) measured above canopy (6.5 m above ground), and, (b) soil water content Sw ($L_{\text{H}_2\text{O}} L_{\text{soil}}^{-1}$) recorded in the control (6 different probes) and rain exclusion plots (5 different probes) at -0.1 m.

Fig. 3: Isoprene emission rate ER_{iso} ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) vs net photosynthetic assimilation Pn ($\mu\text{mol}_{\text{CO}_2} \text{m}^{-2} \text{s}^{-1}$). Exponential dependency equation and determination coefficient R^2 are given for each *Qpi* branch sampled.

Fig. 4: (a) Diurnal variations of isoprene emission rate ER_{iso} ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) measured from all *i Qpi* branches sampled on the O₃HP footbridge, with (b) corresponding PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$) and T ($^{\circ}\text{C}$) conditions.

Fig. 5: Diurnal variations of *Qp4* isoprene emission rates ER_{iso} ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) \pm SD vs the corresponding net photosynthetic assimilation Pn ($\mu\text{mol}_{\text{CO}_2} \text{m}^{-2} \text{s}^{-1}$), PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), temperature T ($^{\circ}\text{C}$), and C_L and C_T parameters (as in Guenther et al., 1993).

Fig. 6: Diurnal variation of *Qp4* isoprene emission rate ER_{iso} ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) vs $C_L \times C_T$ as in Guenther et al., 1993 (data from 1 June).

Plain purple diamonds are measurements between 08:00 a m to 14:00 p m; plain orange diamonds are measurements between 14:30 to 20:00 p m. Polynomial best fit equation and determination coefficient R^2 are given for morning and afternoon.

718 Fig. 7: Comparison between *Qp4* isoprene emission rates ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1} \pm \text{SD}$) measured *in-*
719 *situ* (1 June, purple diamonds) and assessed using isoprene emission algorithm as in (i)
720 Guenther et al. (1993) (G93, green diamonds) and as in (ii) MEGAN model (Guenther et al.,
721 2006, blue diamonds) using a leaf age γ_{age} of 0.6, a soil water γ_{SM} of 1 and a *Q. pubescens*
722 emission factor I_s value of ^(a) $53 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (as in Simpson et al., 1999, open diamonds),
723 and ^(b) of $137.5 \mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (this study, plain diamonds). PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$) and
724 temperature $T \times 10$ ($^{\circ}\text{C}$) were recorded inside the enclosure.

List of tables

Table 1: BVOC branch emission rates from *Q. pubescens* (Qp4) and *A. monspessulanum* (Am) branches, 1st and 2nd of June, respectively, measured with a PTR-MS.

Daily mean ($n=30$) and maximum (parenthesis) BVOC emission rates ER are in $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$. Values are expressed \pm their SD.

^a Measurement information measured inside the enclosure chamber are daily averaged; PAR is in $\mu\text{mol m}^{-2} \text{s}^{-1}$, temperature T in $^{\circ}\text{C}$, relative humidity RH in %, photosynthetic net assimilation Pn in $\mu\text{molCO}_2 \text{m}^{-2} \text{s}^{-1}$ and stomatal conductance Gw in $\text{mmolH}_2\text{O m}^{-2} \text{s}^{-1}$.

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

^c Emission factors EF ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) were the best fit slope of ER vs $C_L \times C_T$ as in Guenther et al. (1993).

^d Total monoterpenes emissions measured from the PTR-MS were derived from absolute concentrations at m/z 137.

Table 2: Environmental and physiological parameters recorded during isoprene measurements on seven *Qpi* sunlit and two *Qpi*_{shade} *Q. pubescens* branches.

PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), temperature T ($^{\circ}\text{C}$), relative humidity RH (%), photosynthetic net assimilation Pn ($\mu\text{molCO}_2 \text{m}^{-2} \text{s}^{-1}$) and stomatal conductance Gw ($\text{mmolH}_2\text{O m}^{-2} \text{s}^{-1}$) were recorded inside the enclosure and averaged over 2:00-22:00. Daily emission rates ERd were averaged over the n isoprene measurements for each sampled branch; ERd are in $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ and values in brackets are minimum-maximum values recorded.

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

For every branch, isoprene emission rates ER_{br} and emission factor Is (as in Guenther et al. 1993) \pm their SD are given in $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ and $\text{ngC m}^{-2} \text{h}^{-1}$ (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 $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (as in Simpson et al., 1999), and (^b) of 71.6 and 137.5 $\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$ (Qp1 and Qp4 respectively, this study). The $ax+b$ best fit equations are given, together with the determination coefficient (R^2) and the root mean square error (RMSE).

Fig. 1

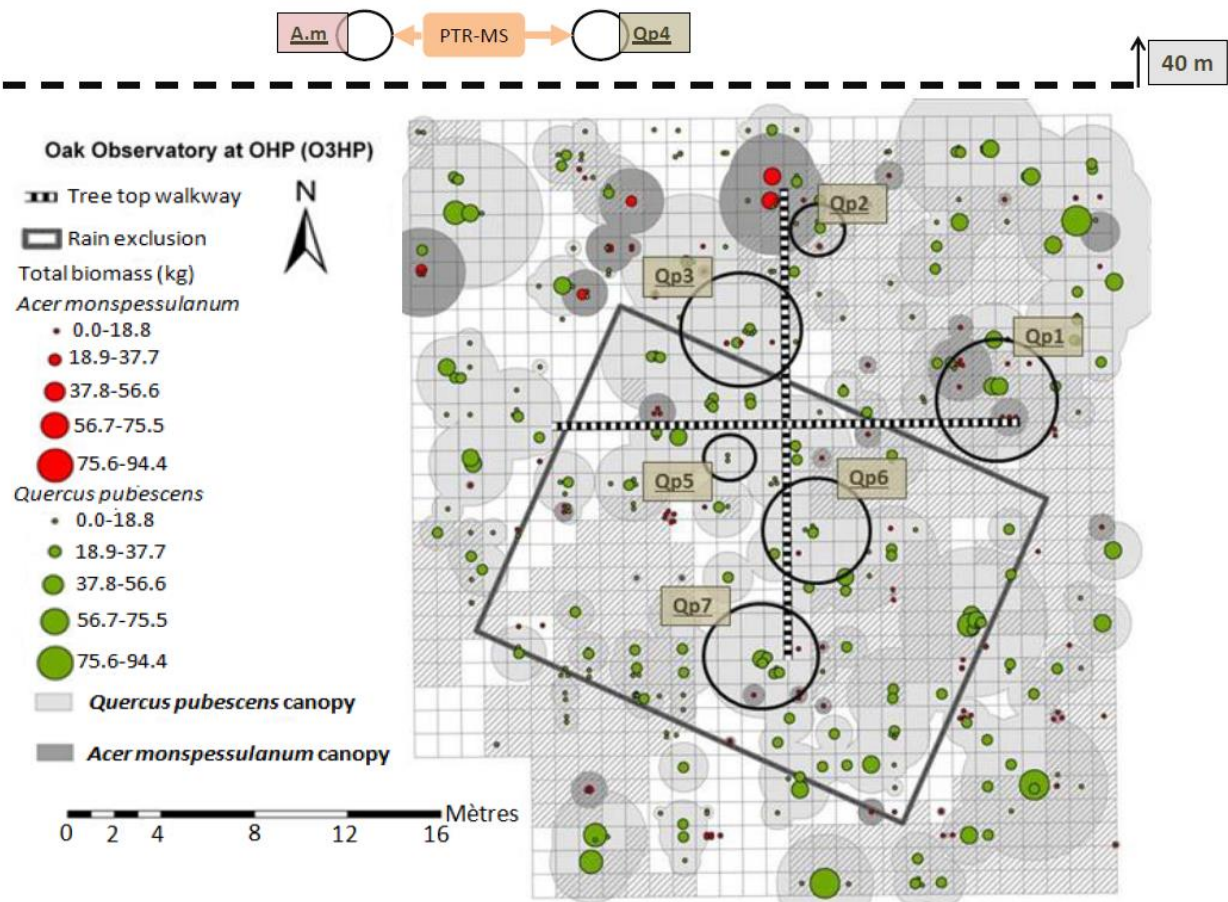
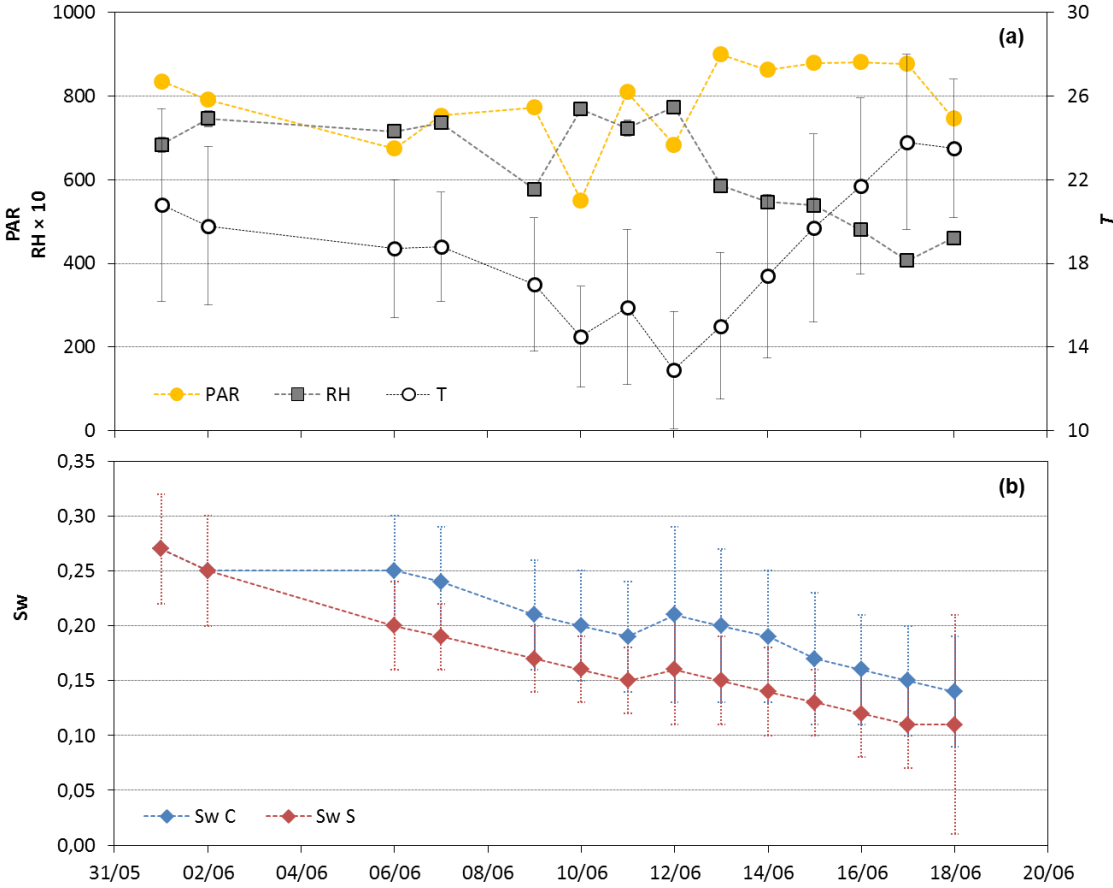
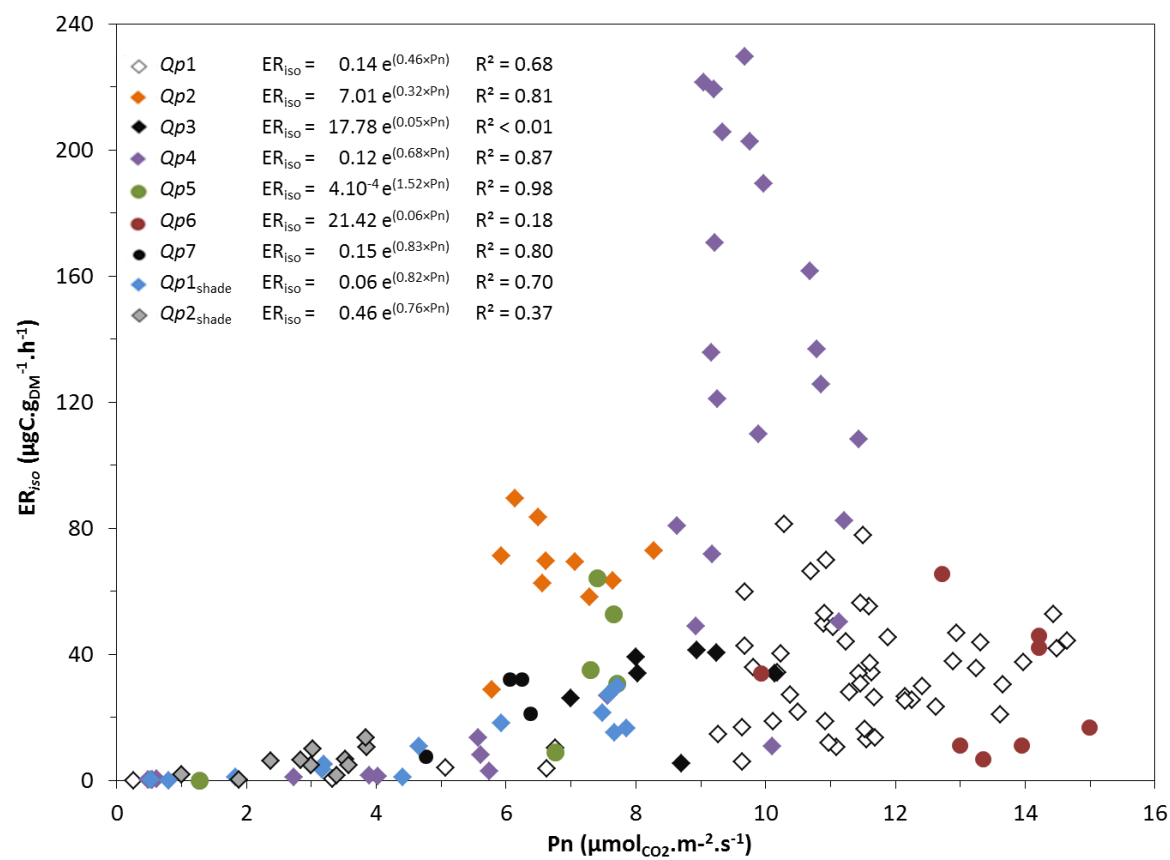


Fig. 2



765 **Fig. 3**



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Fig. 4a and 4b

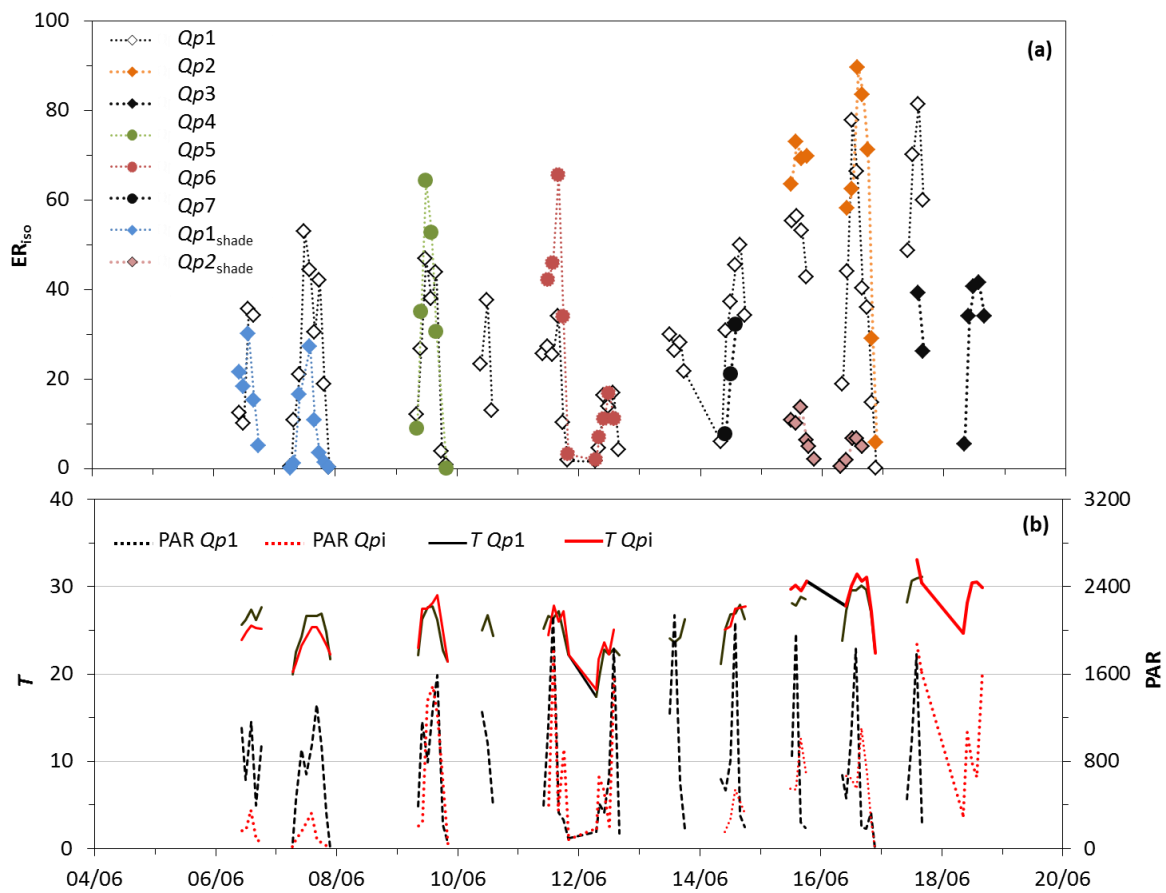


Fig. 5

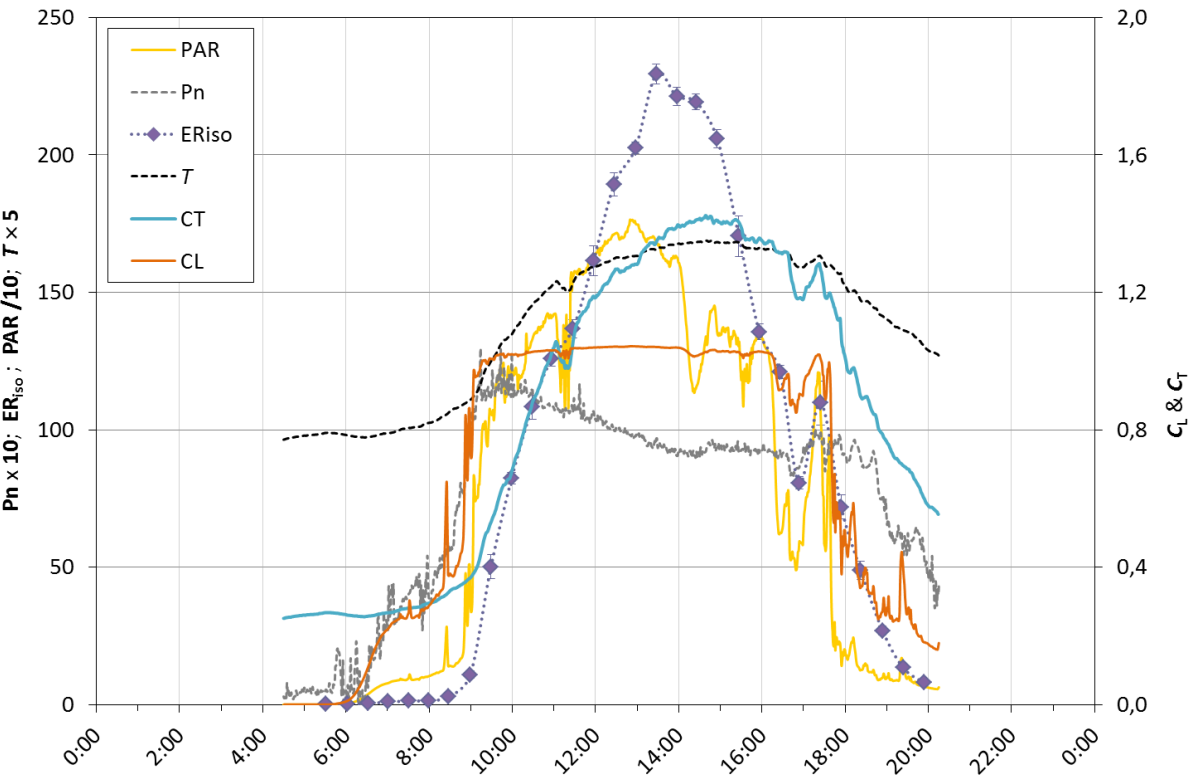
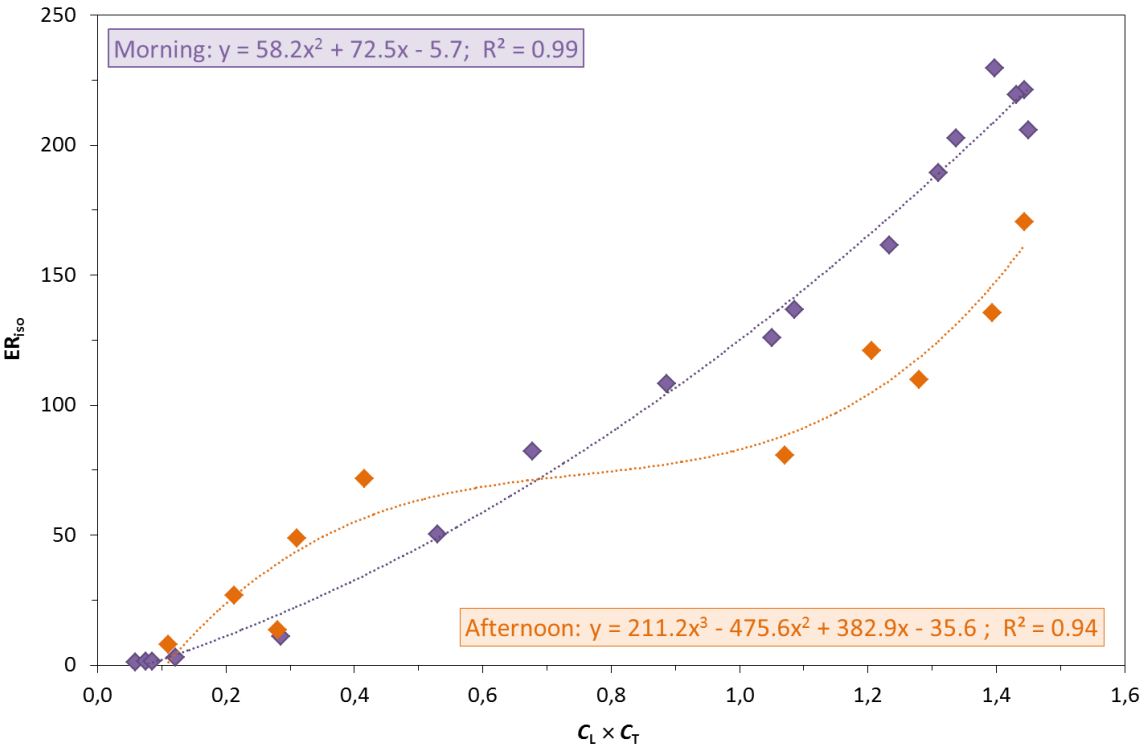
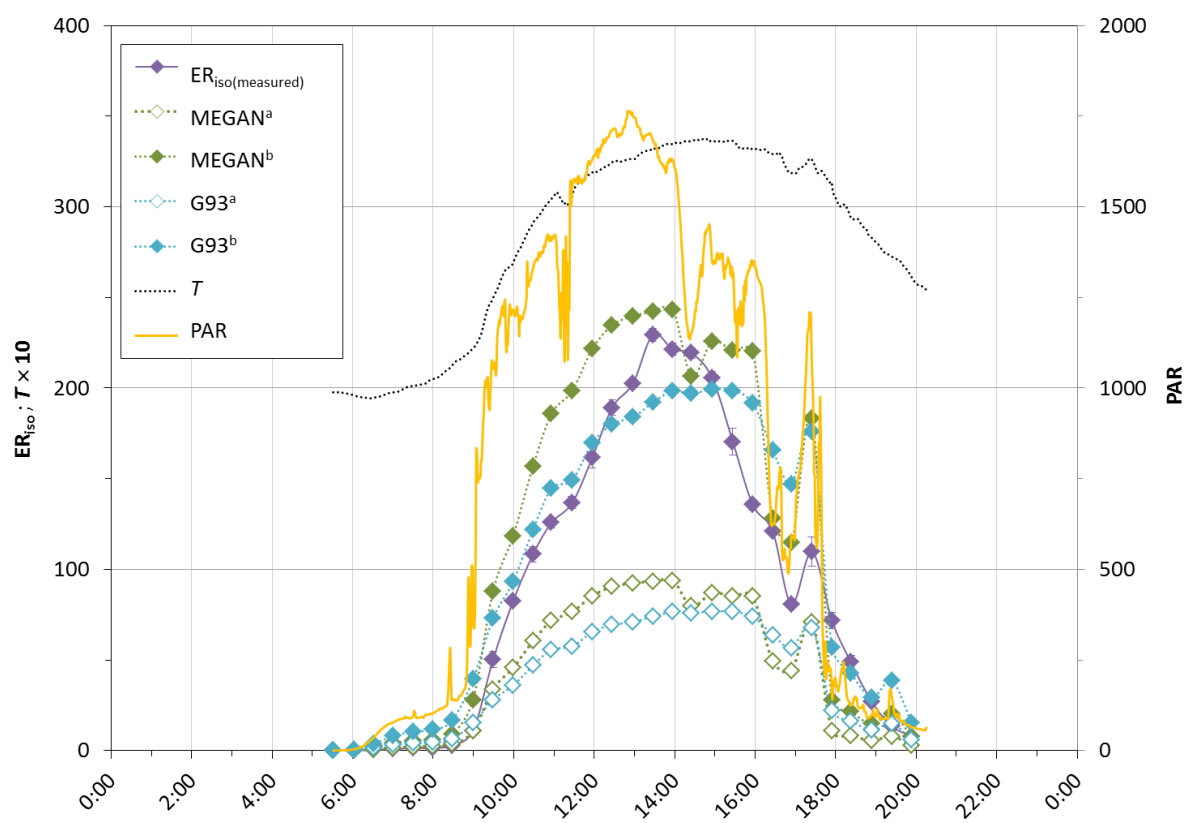


Fig. 6



782 **Fig. 7**

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785 **Table 1**
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| Compound | <i>Qp4</i> | | | | | <i>Am</i> | | | | |
|---------------------------|---|----------|-----------------------------------|---------|-----------------|---|--------|-----------------------------------|---------|-----------------|
| | (PAR: 851.7; T: 28.7±4.9; RH: 68.7±10.3; Pn: 8.3±2.8; Gw: 189.6±157.6) ^a | | | | | (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) | 0.50 | {41.52} | 0.50±0.04 | 0.23±0.08 | (0.57) | 26.74 | {43.40} | 0.39±0.040 |
| Acetaldehyde | 0.09±0.03 | (0.30) | 0.09 | {7.62 } | 0.12±0.01 | 0.13±0.06 | (0.38) | 15.11 | {24.53} | 0.28±0.030 |
| Acetone | 0.2±0.06 | (0.46) | 0.20 | {16.94} | 0.27±0.02 | 0.14±0.04 | (0.32) | 16.28 | {26.41} | 0.24±0.020 |
| Isoprene | 97.7±31.00 | (229.43) | 98.8 | - | 137.5±9.63 | 0.33±0.09 | (0.73) | 38.37 | - | 0.47±0.040 |
| MVK+MACR | 0.1±0.03 | (0.26) | 0.1 | {8.47} | 0.15±0.01 | 0.01±0.005 | (0.04) | 1.16 | {1.89} | 0.03±0.002 |
| Monoterpenes ^d | 0.30±0.10 | (0.77) | 0.30 | {25.42} | 0.44±0.03 | 0.02±0.01 | (0.07) | 2.33 | {3.77} | 0.05±0.003 |

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791 **Table 2**

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| <i>Quercus pubescens</i> tree | <i>n</i> | Measurement information | | | | | | ER _d | C _{iso} | ER _{br} | | <i>I_S</i> | |
|-------------------------------|----------------------|-------------------------|--------|--------|----------|-----------|----------|-----------------|------------------------------|------------------|----------------------|-----------------------|--|
| | | 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 | 97.7 {0.4-229} | 2.7±2.2 | 97.7±31.0 (11.1±3.5) | 137.5±10.1 (15.6±1.1) | |
| | | 4 | 6-Jun | 851.7 | 26.6±0.9 | 66.2±4.5 | 12.4±1.1 | 263.7±31.0 | 22.9 {9.8-35.3} | 0.8±0.05 | | | |
| | | 9 | 7-Jun | 625.9 | 24.5±2.5 | 70.8±5.3 | 11.6±5.0 | 228.9±137.4 | 24.4 {0.16-52.5} | 0.6±0.3 | | | |
| | | 7 | 9-Jun | 780.5 | 24.9±2.7 | 64.4±6.7 | 10.3±3.8 | 191±99.9 | 24.4 {0.5-46.5} | 0.56±0.4 | | | |
| | | 3 | 10-Jun | 868.3 | 25.4±1.2 | 61.1±6.0 | 12.7±1.2 | 155±27.4 | 24.4 {13-37.2} | 0.53±0.2 | | | |
| | | 6 | 11-Jun | 725 | 25.4±1.8 | 58.6±3.2 | 10.6±2.3 | 154.5±47.2 | 20.6 {1.7-34} | 0.64±0.2 | | | |
| | Qp1 | 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 ⁻¹ -6.6} | 0.36±0.1 | 29.6±5.2 (3.7±0.6) | 71.6±2.6 (8.8±0.3) | |
| | | 4 | 13-Jun | 1040.8 | 24.5±1.2 | - | 11.4±0.8 | - | 26.3 {21.5-30.0} | 0.6±0.05 | | | |
| | | 6 | 14-Jun | 758 | 25.7±2.4 | 58.0±4.6 | 10.9±0.9 | 157.5±62.4 | 33.8 {5.8 -50.0} | 0.86±0.4 | | | |
| | | 4 | 15-Jun | 810.9 | 28.4±0.4 | 56.0±4.4 | 10.9±0.9 | 268.1±75.1 | 51.7 {42.5-56.3} | 1.32±0.1 | | | |
| | | 8 | 16-Jun | 584.7 | 27.4±2.9 | 55.1±6.0 | 9.1±3.6 | 177.7±86.2 | 37.1 {<d.l.-77.6} | 0.99±0.6 | | | |
| | | 4 | 17-Jun | 858.1 | 30.3±1.4 | 50.9±4.3 | 10.4±0.6 | 243.2±48.4 | 64.9 {48.6-81.2} | 1.77±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 | 12.6 {3.5-21.1} | 0.5±0.2 | 11.5±6.4 (1.0±0.6) | 76.5±2.2 (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.-19.2} | 0.25±0.2 | | | |
| | Qp2 | 4 | 15-Jun | 693.8 | 30.0±0.5 | 57.5±6.6 | 7.4±0.7 | 92.8±25.8 | 68.7 {63.3 -72.0} | 2.66±0.3 | 61.3±16.2 (7.5±1.2) | 73.9±4.4 (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 | 57.0 {5.6 -89.5} | 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 ⁻¹ -3.5} | 0.25±0.15 | 6.1±4.1 (0.5±0.4) | 58.5±11.5 (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} | 0.53±0.18 | | | |
| | Qp3 | 2 | 17-Jun | 1742.5 | 31.8±1.8 | 49.3±8.8 | 7.5±0.7 | 133.7±8.3 | 32.6 {26.0-39.0} | 1.2±0.2 | 31.5±11.7 (3.9±1.1) | 30.7±8.2 (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 | 31.0 {5.2 -41.3} | 0.98±0.5 | | | |

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| | | | | | | | | | | | | | | |
|---------------------|-----|---|--------|-------|-----------|-----------|----------|------------|-----------------------------|-----------|-----------|-----------|-----------|-----------|
| 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.-64.2} | 1.21±0.9 | 31.9±25.8 | (3.9±3.2) | 58.1±16.6 | (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 {3.2-65.5} | 1.2±0.9 | 23.8±15.5 | (2.9±1.9) | 54.1±13.4 | (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 ⁻¹ 6.7} | 0.26±0.05 | | | | |
| | 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} | 1.09±0.5 | 23.2±18.5 | (2.9±2.3) | 61.8±7.6 | (7.6±0.9) |

Table 3

| Tree | | Is ^a | | | Is ^b | | |
|------|-------|-----------------|----------------|-------|-----------------|----------------|-------|
| | | $ax + b$ | R ² | RMSE | $ax + b$ | R ² | RMSE |
| Qp4 | 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 |
| Qp1 | 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 I_s calculation

The empirical relationship used to describe changes in isoprene emission rates I ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$) vs light and temperature was as in Guenther et al. (1993):

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

where

I_s is the isoprene emission factor standardised at $T = 30^\circ\text{C}$ and $\text{PAR} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ($\mu\text{gC g}_{\text{DM}}^{-1} \text{h}^{-1}$), 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

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

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

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