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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 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, and two inside the canopy at ≈ 2 m a.g.l.).

Q. pubescens daily mean isoprene emission rates (ER_d) fluctuated between 23.1 and 97.7 $\mu g\, C\, g_{DM}^{-1}\, h^{-1}$ and were exponentially correlated with net assimilation (Pn). *Q. pubescens* daily mean Pn ranged between 5.4 and 13.8, and 2.8 and 6.4 $\mu mol\, CO_2\, m^{-2}\, s^{-1}$ for sunlit and shaded branches respectively. Both ER_d and isoprene emission factors (Is) assessed according to Guenther et al. (1993) algorithm, varied by a factor of 4 among the sunlit branches. While sunlit branches ER_d was clearly higher than for shaded branches, there was an non-significant variability on Is (58.5 to 76.5 $\mu g\, C\, g_{DM}^{-1}\, h^{-1}$). Diurnal variations of isoprene emission rates (ER) for sunlit branches were also investigated. ER were detected at dawn 2 h after Pn became positive and, 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. 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 difficulty in assessing isoprene emissions under Mediterranean environmental conditions with current isoprene models.

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1 Introduction

Isoprene (2-methylbuta-1,3-diene) is the most abundant Biogenic Volatile Organic Compound (BVOC) released in the atmosphere with a global annual flux estimation of 400–660 Tg C 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; Steiner and Goldstein, 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 mega-cities are surrounded by large ecosystem areas (such as Mediterranean) can significantly contribute to high levels of O_3 in summer (Curci et al., 2009).

Isoprene emissions are well recognized to be strongly triggered by temperature and light conditions. Indeed, without any other environmental constraints, these 2 parameters drive the circadian cycle of isoprene emission (Guenther et al., 1991). More precisely, light affects the photosynthetic processes which, in turn, impacts 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 emission 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 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 µg C g_{DM}^{-1} h^{-1}), low ($14 \pm 7 -$ µg C g_{DM}^{-1} h^{-1}), moderate (35 ± 17.5 µg C g_{DM}^{-1} h^{-1}) and high (70 ± 35 µg C g_{DM}^{-1} h^{-1}) emitter species.

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In Europe, *Quercus pubescens* Willd. was shown to belong to 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 Is 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 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ respectively at a site near Montpellier (France), which was twice 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 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ 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 CANOPÉE 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/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, including *Q. pubescens* but also *Acer monspessulanum* L. which emission data has never been reported so far (ii) to study the canopy variability (tree to tree and within canopy) and (iii) diurnal variability of *Q. pubescens* isoprene emissions (iv), to assess the ability of 2 commonly used algorithms to estimate, under a Mediterranean environment, the observed diurnal variations of isoprene emission.

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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 m^2), free from human disturbance for 70 years, consists of a flat homogeneous forest mainly composed of *Q. pubescens* (≈ 90 % of the biomass and ≈ 80 % of the trees). The remaining 20 % of the biomass is mainly represented by *A. monspessulanum* trees. The O_3HP 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 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 humidity, Photosynthetically active radiations 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 at 4 m). For further details see https://o3hp.obs-hp.fr.

2.2 Sampling strategy

The experimentation took place from 29 May until 19 June 2012. A total of 9 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 (*Qp*4, 1 June). *Am* and *Qp*4 were located in

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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 one hand, tree-to-tree variability was evaluated by studying 3 healthy and sunlit *Q. pubescens* branches within the control (*Qp*1, *Qp*2, *Qp*3) and rain exclusion plot (*Qp*5, *Qp*6, *Qp*7). Isoprene was sampled from the highest level of the scaffold using the off-line cartridge collection.

On the other hand, variability of isoprene emissions from, shaded vs. sunlit branches, was assessed in *Qp*1 and *Qp*2. For these trees, asides from the sunlit branches, one shaded branch was also studied (approx. 2 m above ground, $Qp1_{shade}$ and $Qp2_{shade}$).

Isoprene emissions were approximately hourly sampled from sunrise to sunset. One enclosure 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). 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, T, RH) and physiological parameters (Pn, and 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 were enclosed in a ≈ 60 L Teflon frame closed by a sealed 50 µm thick Teflon-PTFE film to which ambient air was introduced at 11–14 L min^{-1} using a Teflon-PTFE pump (KNF N840.1.2FT.18®, Germany). A Teflon 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)

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inside the chamber was continuously (every minute) monitored by a data logger (Licor 1400®; Lincoln, NE, USA) coupled to an RHT probe (relative humidity and temperature, Licor 1400–104®, 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).

Net photosynthetic assimilation Pn ($\mu mol_{CO_2}\, m^{-2}\, s^{-1}$) was calculated using equations described by von Caemmerer and Farquhar (1981) as follows:

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

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

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

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

Stomatal conductivity for water vapour Gw ($mol_{H_2O}\, m^{-2}\, s^{-1}$) was calculated using the following equation:

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

where E and Ws are described in Eq. (2), Wl is the molar concentration of water vapour within the leaf ($mol_{H_2O}\, mol^{-1}$) calculated using the equation:

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

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where VP_{sat} 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 PFTE-made.

Total dry biomass matter (DM) was assessed for each sampled branch by manually scanning every leaf enclosed in the chamber and applying an area factor conversion. For top and down canopy, the leaf mass area (LMA) was 123.2 ± 1.0 ($n = 5$ trees) and $87.1 \pm 1.8\,g_{DM}\,m^{-2}$ ($n = 15$ trees) respectively. Since the sampled *A. monspessulanum* was not located into the protected O_3HP site, dry biomass was assessed directly by cutting off the branch, drying and weighting foliar biomass LMA was found to be $75.4\,g_{DM}\,m^{-2}$.

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 one enclosure system (with a 25 m length PTFE tubing) 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).

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 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 closed to the enclosures just before measurements. Subsequent to sampling, tubes were sealed with Swagelock end caps and Teflon ferrules and stored at 4 °C before laboratory analyse within the following 3 weeks. Ozone was removed from sampled air by placing glass

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fibre 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:

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

where ER is expressed in $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$, 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 ($\mu g\,C\,L^{-1}$) 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 Table 1 together with the mean daily soil water content (Sw) obtained in the control (6 different probes) and the rain exclusion plots (5 different probes).

2.4 Analytical methods

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

Glass tubes were analysed with a gas chromatography (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 rang-

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ing 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 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ (0.32 $\mu g\,C\,m^{-2}\,h^{-1}$ for sunlit branches). Isoprene quantification was achieved using a 5 ppm ±0.25 ppm diluted in N_2 certified gas standard (Air Liquide). Desorption and quantitative analysis of BVOC from metal 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 gas chromatography 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 (PLOT) column. 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 (TIC) 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 $\mu g\,C\,g_{DM}^{-1}\,h^{1}$ (0.26 $\mu g\,C\,g_{DM}^{-1}\,h^{1}$, respectively). 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.

An intercomparison between both analytical GC-MS systems used to analyse BVOC trapped within glass and metal cartridges – was carried out by loading isoprene stan-

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dards in both types of tubes. The intercomparison showed, for the GC-MSD HP 5973 and the GC-MSD Saturn 2200 a coefficient of determination R^2 of 0.953 (n = 14) and 1.000 (n = 7) respectively over a 12–1400 ng C range, 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 ng C) simultaneously collected into glass and metal 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 ng C) nor on in situ samples (range of 0–660 ng C) for both cartridges. No intercomparison was carried out for monoterpene analysis.

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

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* branch. 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 relationship between BVOC emitted by *A. monspessulanum* and *Q. pubescens* branches studied with PTR-MS, and $C_L \times C_T$ 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 $C_L \times C_T$ 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 emission by comparing slopes of the regression lines between ER and $C_L \times C_T$ for this modality. Moreover differences in photosynthesis (Pn), stomatal conductivity (Gw), and soil water content (Sw) between control and rain excluded trees were analysed using Mann and Whitney tests (W).

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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 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 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. 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 and Whitney test, $W = 508.0$, $P < 0.05$).

3.2 BVOC emission screening from *Q. pubescens* and *A. monspessulanum*

BVOC emissions from *Q. pubescens* (obtained by PTR-MS; *Qp*4, Table 2) are consistent with previous literature results (Owen et al., 1998; Simon et al., 2005). *Q. pubescens* was found to be a strong isoprene emitter, with a daily mean value of isoprene emission rate (ER_{iso}) of 97.7 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ 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 BVOC (< 0.03 %), 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 which emissions were of the order of 0.1 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$. MVK + MACR are mainly secondary products of isoprene degradation (Jardine et al., 2012). Therefore, our study showed that MVK + MACR emission rates were highly

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($R^2 = 0.97$, $P < 0.001$, $n = 28$) correlated with ER_{iso} all along the diurnal cycle as acetaldehyde and methanol ($R^2 = 0.80$, $P < 0.001$, $n = 28$). A direct primary emission of these compounds by the *Q. pubescens* branch could not be proved. Values shown in the Table 2 may thus represent the highest limit of the primary emission rate range for these compounds. However, if acetaldehyde detected in our enclosure was mostly from biogenic source (cell catabolism), the emission rates thus assessed ($0.09\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ 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). Although no acetone nor methanol emissions have been previously reported for *Q. pubescens*, we measured a mean emission rate of $0.20\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ (or $320\,ng\,g_{DM}^{-1}\,h^{-1}$, or $0.15\,nmol\,m^{-2}\,s^{-1}$) and $0.49\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ (or $130\,ng\,g_{DM}^{-1}\,h^{-1}$, or $1.13\,nmol\,m^{-2}\,s^{-1}$) for these compounds respectively. These values were in the medium range of the foliar emissions reviewed by Seco et al. (2007) for these 2 compounds from other emitters. 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 $P = 0$). Methanol 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 methanol emission comes from an internal pool as suggested by Seco et al. (2007). In the afternoon, methanol emissions became the highest 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 % in the morning and in the afternoon respectively. A similar observation was made for acetaldehyde (1.47 % in the morning and 0.06 % in the afternoon). Total monoterpene emissions were more than 300 times lower than iso-

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prene 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 $P < 0.001$). Since isoprene, and total monoterpene emissions have been observed to be light and temperature dependent in this and previous studies, *Q. pubescens* emission factors (EF) could be assessed using the G93 algorithm (Guenther et al., 1993) and are presented in Table 2 for *Qp4*.

A. monspessulanum total BVOC emissions ($< 1\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) were found to be two orders of magnitude smaller than the total *Q. pubescens* BVOC emissions ($> 100\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$; Table 2). Isoprene and methanol were the two dominant BVOC measured with a daily mean emission rate of 0.33 and $0.23\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ respectively. Acetone, acetaldehyde, and total monoterpenes were measured at lower rates, the latter being close to our detection limit. BVOC other than isoprene represented a greater 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 were found to represent less than 0.2 % of the assimilated carbon. Ambient light and temperature variations were found to influence the diurnal emission variations of all the measured BVOC except methanol which, as observed for *Q. pubescens*, was found to be exponentially temperature dependent. No foliar BVOC emission values have been reported in the literature for *A. monspessulanum.* Nevertheless, our findings confirm that *Acer* species such as *Acer platanoides* L., *A. rubrum* L., or *A. saccharinum* L. are weak isoprene or other BVOC emitters (Kesselmeier and Staudt, 1999).

To conclude, *Q. pubescens* was found to be the main BVOC emitter in the O_3HP forest compared to *A. monspessulanum*. Isoprene represented more than 98 % of the BVOC emitted by *Q. pubescens*, with daily mean values as high as $\approx 100\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$. Therefore, the sections hereafter focuses on *Q. pubescens* isoprene emissions.

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3.3 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; $R^2 = 0.63$; $P > 0.05$). The only significant difference was observed on stomata conductivity with a value for stressed plot twice weaker than for control plots (Mann and Whitney; $P < 0.001$). Water stress will thus be not considered in this article.

3.3.1 Plant physiology

Daily photosynthesis (Pn) and stomata conductivity (Gw) measured for top canopy branches varied between 5.4 and 13.8 µmol CO_2 m^{-2} s^{-1} and 62.5 and 268.1 mmol H_2O m^{-2} s^{-1} respectively (Table 3). 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 mmol H_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). 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 µmol CO_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 3, daily mean isoprene emission rates ER_d from top canopy branches were highly variable, fluctuating over one order of magnitude, between below

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10 (*Qp*1 and *Qp*6, 12 June) and 97.7 µg C g_{DM}^{-1} h^{-1} (*Qp*4, 1 June). The lower ER_d 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 µmol CO_2 m^{-2} s^{-1} respectively), the observed ER_d range illustrates the importance of environmental conditions on the amount of carbon *Q. pubescens* allocates to isoprene emissions.

Mean daily ER_d presented a high variability between sunlit branches (23.1 and 97.7 µg C g_{DM}^{-1} h^{-1}) and shaded branches (4.0 and 12.6 µg C g_{DM}^{-1} h^{-1}). Mean daily $Qp1_{shade}$ 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. 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 to 2.9 ± 1.0 %. Mean daily C_{iso} was exceptionally high for *Qp*4 (2.7 ± 2.2 %) and reached up to 6.5 % at solar noon. Consequently, ER_d (between 4.0 and 12.6 µg C g_{DM}^{-1} h^{-1}) were, on average, between 2 and 10 times lower than the values measured on *Qp*1 and *Qp*2 branches respectively; that was the lowest ER_d measured during the study.

Whatever their horizontal or vertical location in the canopy, most of the isoprene emission rates measured from the studied branches – except for *Qp*3, *Qp*6 and $Qp2_{shade}$, see next section for further details – exponentially increased with Pn (Fig. 2). Such relation implies that, even when Pn reached the maxima values, the contribution of carbon fixed by each branch to produce isoprene went on increasing. However, it is important to note that during a rainy day (12 June, *Qp*1 and *Qp*6) Pn was not affected, whereas isoprene emissions were much lower than during sunny days (Table 3).

3.3.3 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 3) (C_L and C_T

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are, respectively, light and temperature dimensionless coefficients derived by Guenther et al. (1993) from experimental measurements, see Appendix A). For sunlit branches, Is varied between 30.7 ± 8.2 and 137.5 ± 10.1 µg C 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 µg C g_{DM}^{-1} 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 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 (71.6 ± 2.6 and 73.9 ± 4.4 µg C g_{DM}^{-1} h^{-1} respectively) compared to *Qp*3 (30.7 ± 8.2 µg C g_{DM}^{-1} 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 *Qp*3 Is smaller by a factor of 2 than the other O_3HP tree branches was a posteriori linked with the fact that the *Qp*3 branch died in August despite no visible injuries were visible in June when it was selected for our study. 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 canopy shading effect, the studied shaded branches showed no significant difference in their capacity to emit isoprene (76.5 ± 2.6 and 58.5 ± 11.5 µg C g_{DM}^{-1} 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 ± 4.4 µg C g_{DM}^{-1} h^{-1} for *Qp*1 and *Qp*2 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 for shaded and 123.2 ± 1.0 g m^{-2} for sunlit branches. 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 ± 7.0 g m^{-2} for sunlit and shaded branch respectively; when these authors expressed Is in leaf area basis they observed significantly lower Is value for shaded branch. Note that if the sunlit branch LMA value

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was used for assessing Is 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 Is value would then become significantly lower than Is sunlit branches. Thus, appropriate LMA should always be considered when BVOC canopy fluxes are extrapolated from branch scale measurements to canopy scale.

Based on our assessed Is range (30.7 to 137.5 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) and using a median branch scale Is value of 60 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$, (Kalogridis et al., 2014) extrapolated a canopy isoprene emission flux of 15 $mg\,m^{-2}\,h^{-1}$ twice higher than the mean canopy flux measured by the disjunct eddy covariance technique (6.6 $mg\,m^{-2}\,h^{-1}$). This reasonable factor of 2 of discrepancy being in the range of uncertainties typically obtained for such up-scaling exercises, illustrates the limit of precision in BVOC canopy flux assessments, how much extensively and intensively a canopy needs is peered into.

3.4 Diurnal variability

The diurnal range of isoprene emission rate (ER) variations observed over the 7 different branches studied was found to fluctuate from day to day (Fig. 3). The maximum value observed on June 12 (rainy day) for the sun exposed *Qp*1 branch (16.6 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) was about 5 times lower than the maximum observed at the end of the campaign (especially on 16 June; 77.6 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) when weather was much warmer and sunnier (see Table 3); it was about the same than the maximum ER measured for the shaded branch *Qp*1 at the beginning of the campaign (June 6–7, $\approx$ 20 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$). *Qp*1 C_{iso} was the highest (up to 1.8 %, Table 3) at the end of the campaign, compared to values under 1 % at the beginning of our measurements, which is consistent with previous findings for *Q. pubescens* in June (0.62 to 1.8 %, Kesselmeier et al., 1998).

Diurnal variations were studied in more details during the *Qp*4 high frequency measurements carried out with the PTR-MS system. At dawn, *Qp*4 ER became significant about 2 h after sunrise when the CO_2 assimilation started (Fig. 4). More precisely, pos-

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itive Pn values were obtained at 6.30 a.m., as soon as the relative weight of the C_L parameter compared to C_T started to increase. Detectable isoprene emissions were observed 2 h later (8.30 a.m.), only when the relative weight of the C_T parameter became predominant compared to C_L. This finding contrasts with previous studies (Owen et al., 1998) where *Q. pubescens* ER were more PAR than temperature dependant. The delay observed between the photosynthesis and the isoprene emission onset in the morning was found to correspond to a temperature increase dT of nearly 3 °C; interestingly, a similar dT was observed for the *Qp*1 branch when early morning measurements were made. The temperature kept on being the leading parameters compared to light until ER reached its maximum (229 µg C g_{DM}^{-1} h^{-1} at 13:30). Between 13:30 LT and 17:30 isoprene emission remained constantly more temperature (60 %) than light (40 %) dependent. As soon as the C_L influence lowered (17:30), ER started to decrease to non-detectable values, although the branch continued to assimilate CO_2; Pn decreased only 1 h later. Thus, although the diurnal variations of *Qp*4 ER were mostly well described by $C_L \times C_T$ (in particular from dawn to midday maximum and during the evening, Fig. 5), the relative influence of C_L and C_T varied along the day: (i) from 13:30 to 16:00 ER decreased from 220 to less than 150 µg C g_{DM}^{-1} h^{-1} at nearly constant $C_L \times C_T$; on the contrary, (ii), after 16:00, ER remained close to 75 µg C g_{DM}^{-1} 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 noon, ER presented an overall "S" shape diurnal dependency with $C_L \times C_T$ (Fig. 5). The sudden decrease of ER at 13:30 while $C_L \times C_T$ remained constant may illustrate a possible temperature midday stress of the branch, with emission falling down to a minimum value of $\approx$ 75 µg C g_{DM}^{-1} h^{-1}. The thermal stress lasted until 16:00 when isoprene emission regulation became again mainly explained by C_L and C_T. Indeed, as reported by Niinemets et al. (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

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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.

3.5 Assessment of the diurnal profiles of *Q. pubescens* isoprene emission rates according to 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 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 *Qp*4 (Fig. 6) and *Qp*1 (Fig. 7) branches, using an Is of 53 $\mu g\, C\, g_{DM}^{-1}\, h^{-1}$ as recommended by Simpson et al. (1999) for European *Q. pubescens*.

As a whole, both algorithms underestimated the *Qp*4 measured ER by 65 and 55 % (G93 and MEGAN respectively, Fig. 6). This discrepancy reached a factor of 3 for midday maximum emission (74 and 93 $\mu g\, C\, g_{DM}^{-1}\, h^{-1}$ for G93 and MEGAN respectively compared to 229 $\mu g\, C\, g_{DM}^{-1}\, h^{-1}$). Moreover, the maximum emissions calculated with algorithms, were reached at 14:00 (MEGAN) and 15:30 (G93), later than what was observed (13:30). Besides, predicted ER remained mostly constant until 16:00, while

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the observed emissions decreased to values twice smaller than the midday maximum as previously described and commented (Sect. 3.3.4). Both algorithms being strongly dependant on temperature variations, such observed uncoupling between ER and elevated temperature (here higher than 33 °C) could not be captured. The ER evening decrease was predicted to occur more rapidly and earlier (18:00) compared to in situ observations, resulting in assessed ER of $\approx 10\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ compared to the observed value of $75\,\mu g\,C\,g_{DM}^{-1}\,h^{-1}$. 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. Surprisingly, the overall algorithm correlations obtained between assessed and measured data were good (R^2 was 0.91 and 0.92 for G93 and MEGAN respectively) as if the various under- and over-estimations were counterbalanced over the diurnal cycle. Note that, for *Qp*4, the simpler G93 algorithm performed almost as well as the more complex MEGAN parameterisation.

When G93 and MEGAN algorithms were tested over the longer time series (13 days) of *Qp*1 diurnal measurements, a similar underestimation was found (46 and 77 % respectively, Fig. 7) than for *Qp*4. However, MEGAN performance became much weaker (R^2 = 0.15), especially for the assessment of ER measured at the end of the 13 day period (detailed data not shown), when much warmer and dryer 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 significantly lowered most of the assessed isoprene emissions. Weather being cooler and rainy at the beginning of the campaign, such a γ_{SM} modulation did not operate (γ_{SM} was 1) neither on *Qp*4 measurements nor on the first day of *Qp*1 measurements. When γ_{SM} was not considered anymore and set to 1 for all *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.

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4 Conclusions

The extensive study, at branch scale, of a Mediterranean forest ecosystem dominated by *Q. pubescens* revealed that *C. coggygria* was a non-isoprene emitter (no other BVOC were investigated) and that *A. monspessulanum* was a weak BVOC emitter (daily mean total < 1 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) 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 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ respectively); acetone, acetaldehyde and 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 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ for sunlit branches and 6.1 and 11.5 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$ for canopy shaded branches; methanol (ERd = 0.49 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$; 0.5 % of total BVOC) and monoterpenes (ERd = 0.30 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$; 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 isoprene emission rates exponentially increased with Pn, althought Pn was twice smaller in 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 temperature and sunlight stress.

Tree to tree isoprene emission variability studied on sunlit branches (n = 7) was high. ER_d varied over a factor of 10 and emission factor (Is) over a factor of 4.4 (between 30.7 ± 8.2 and 137.5 ± 10.1 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$). Shaded branch variability (n = 2) was lower, a factor of 3 for ERd (between 4.0 and 12.6 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) and not significant for Is (between 58.9 ± 11.5 and 76.5 ± 2.6 $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$).

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Within the canopy (shaded vs. sunlit branches), ER_d 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 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 triggered by temperature while Pn was mainly light dependent. By contract emission evening decline was mainly described by PAR. In between, an uncoupling of isoprene emission with PAR and temperature was noticed, with emissions starting to decline whereas PAR and temperature remained stable.

MEGAN and G93 algorithms significantly underestimated isoprene emission by a mean factor of 2, and especially the midday maximum values. Moreover, the two algorithms showed difficulties in properly assessing 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. Indeed, the consideration of superficial (around −0.1 m deeper) soil moisture does not take into account the tree ability to have access to deeper water sources. 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 models such as G93 and MEGAN can be, when employed, for high temporal resolution air quality predictions in Mediterranean areas.

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Appendix A: Supplementary materials: emission factor Is calculation

The empirical relationship used to describe changes in isoprene emission rates I ($\mu g\, C\, g_{DM}^{-1}\, h^{-1}$) 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 $T = 30\,^{\circ}C$ and PAR = $1000\,\mu mol\, m^{-2}\, s^{-1}$ ($\mu g\, C\, g_{DM}^{-1}\, h^{-1}$), 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

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

where $\alpha = 0.0027\, m^2\, s\, \mu mol^{-1}$, $C_{L1} = 1.066$ units, $C_{T1} = 95\,000\, J\, mol^{-1}$, $C_{T2} = 230\,000\, J\, mol^{-1}$, $T_M = 314\, K$ are empirically derived constants, L is the Photosynthetically Active Radiation (PAR) flux ($\mu mol\,(photon)\, m^{-2}\, s^{-1}$), T the predicted temperature (K), and T_s is the leaf temperature at standard condition (303 K).; at standard conditions of 1000 $\mu mol\,(photon)\, m^{-2}\, s^{-1}$ PAR and 303 K, $C_T \times C_L = 1$.

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Table 1. Environmental conditions prevailing at the O_3HP site.
Daily mean photosynthetically active radiation PAR ($\mu mol\, m^{-2}\, s^{-1}$), temperature T (° C) and ambient relative humidity RH (%) measured above canopy (6.5 m above ground), and soil water content Sw ($L_{H_2O}\, L_{soil}^{-1}$) recorded in the control (6 different probes) and rain exclusion plots (5 different probes).

Date	Ambient			Sw	
	PAR	T	RH	Control	Rain exclusion
1 Jun	835.6	20.8 ± 4.6	68.4 ± 17.5	0.27 ± 0.05	0.27 ± 0.05
2 Jun	790.9	19.8 ± 3.8	74.6 ± 17.9	0.25 ± 0.05	0.25 ± 0.05
6 Jun	674.9	18.7 ± 3.3	71.5 ± 11.4	0.25 ± 0.05	0.20 ± 0.04
7 Jun	753.1	18.8 ± 2.6	73.6 ± 14.0	0.24 ± 0.05	0.19 ± 0.03
9 Jun	773.0	17.0 ± 3.2	57.7 ± 9.4	0.21 ± 0.05	0.17 ± 0.03
10 Jun	550.8	14.5 ± 2.4	76.9 ± 13.8	0.20 ± 0.05	0.16 ± 0.03
11 Jun	809.7	15.9 ± 3.7	72.3 ± 18.0	0.19 ± 0.05	0.15 ± 0.03
12 Jun	684.3	12.9 ± 2.8	77.4 ± 14.6	0.21 ± 0.08	0.16 ± 0.05
13 Jun	899.3	15.0 ± 3.5	58.6 ± 13.5	0.20 ± 0.07	0.15 ± 0.04
14 Jun	863.2	17.4 ± 3.9	54.7 ± 10.2	0.19 ± 0.06	0.14 ± 0.04
15 Jun	879.0	19.7 ± 4.5	53.9 ± 16.7	0.17 ± 0.06	0.13 ± 0.03
16 Jun	881.1	21.7 ± 4.2	48.0 ± 10.0	0.16 ± 0.05	0.12 ± 0.04
17 Jun	876.8	23.8 ± 4.2	40.7 ± 10.2	0.15 ± 0.05	0.11 ± 0.04
18 Jun	746.0	23.5 ± 3.3	46.1 ± 10.1	0.14 ± 0.05	0.11 ± 0.1

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Table 2. BVOC branch emission rates from *Q. pubescens* (*Qp*4) and *A. monspessulanum* (*Am*) branches, 1 and 2 June, respectively.
Daily mean (n = 30) and maximum (parenthesis) BVOC emission rates ER are in $\mu g\,C\,g_{DM}^{-1}\,h^{-1}$. Values are expressed ± their SD.

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)	0.50	{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

[a] Measurement information measured inside the enclosure chamber are daily averaged; PAR is in $\mu mol\,m^{-2}\,s^{-1}$, temperature T in °C, relative humidity RH in %, photosynthetic net assimilation Pn in $\mu mol\,CO_2\,m^{-2}\,s^{-1}$ and stomatal conductance Gw in $mmol\,H_2O\,m^{-2}\,s^{-1}$.
[b] Percentage of speciated BVOC relative to total BVOC and to non-isoprene BVOC (brackets).
[c] Emission factors EF ($\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) 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.

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Table 3. Environmental and physiological parameters recorded during isoprene measurements on 7 *Qpi* sunlit and 2 Qpi_{shade} *Q. pubescens* branches.
PAR (µmol m^{-2} s^{-1}), temperature *T* (°C), relative humidity RH (%), photosynthetic net assimilation Pn (µmol CO_2 m^{-2} s^{-1}) and stomatal conductance Gw (mmol H_2O m^{-2} s^{-1}) were recorded inside the enclosure and averaged over 02:00–22:00. Daily emission rates ER_d were averaged over the *n* isoprene measurements for each sampled branch; ER_d are in µg C g_{DM}^{-1} h^{-1} and values in brackets are minimum-maximum values recorded.
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 µg C g_{DM}^{-1} h^{-1} and ng C m^{-2} h^{-1} (parenthesis).

	Quercus pubescens tree	*n*	Measurement information						ER_d	C_{iso}	ER_{br}	Is
			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)
	Qp1	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	29.6 ± 5.2 (3.7 ± 0.6)	71.6 ± 2.6 (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	24.4 {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		
		6	12 Jun	585.1	21.2 ± 2.2	70.4 ± 6.3	9.5 ± 3.1	114.8 ± 24.6	9.4 {1.4–16.6}	0.36 ± 0.1		
		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 {1.9–13.5}	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		
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 {1.8–16.7}	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)

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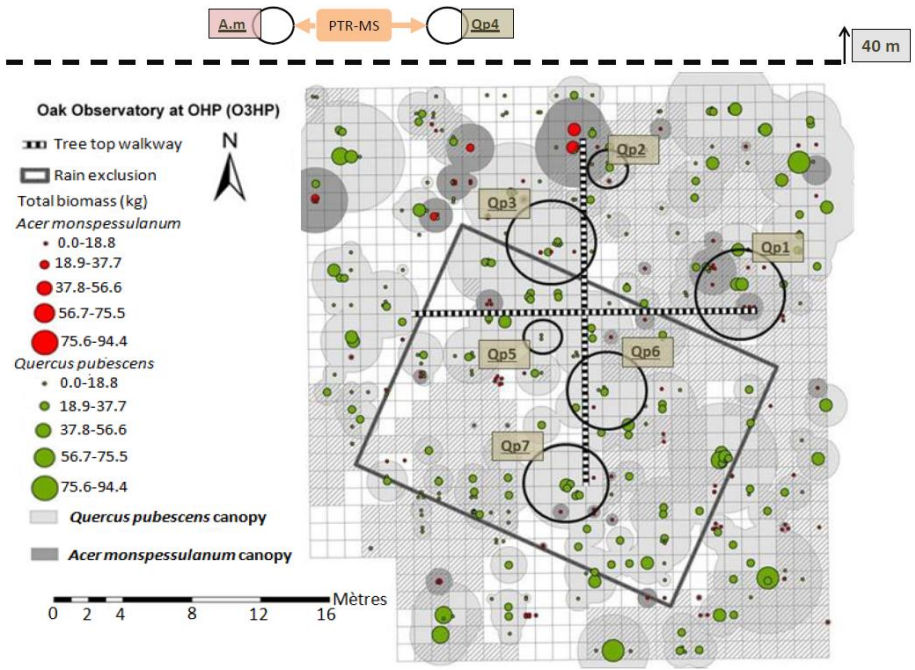

Figure 1. Location of the *i Q. pubescens* (*Qpi*) and *Acer monspessulabum* (*Am*) trees studied. Branches *Qp*4 and *Am* were located about 40 m north of the O_3HP footbrige and their BVOC sampled using online PTR-MS. All other Qpi branches were sampled from the O_3HP footbridge using cartridges.
Black circles in the O_3HP area represent the assessed crown area for every sampled tree.

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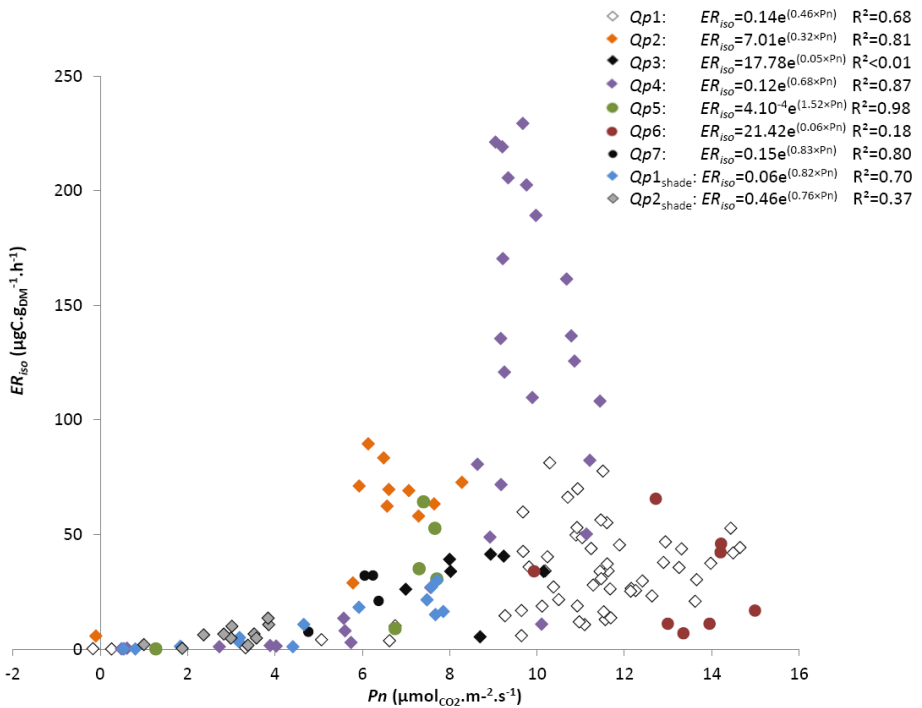

Figure 2. Isoprene emission rate ER_{iso} (µg C g_{DM}^{-1} h^{-1}) vs. net photosynthetic assimilation Pn (µmol$_{CO_2}$ m^{-2} s^{-1}). Exponential dependency equation and determination coefficient R^2 are given for each *Qpi* branch sampled.

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Variability of BVOC emissions from a Mediterranean mixed forest

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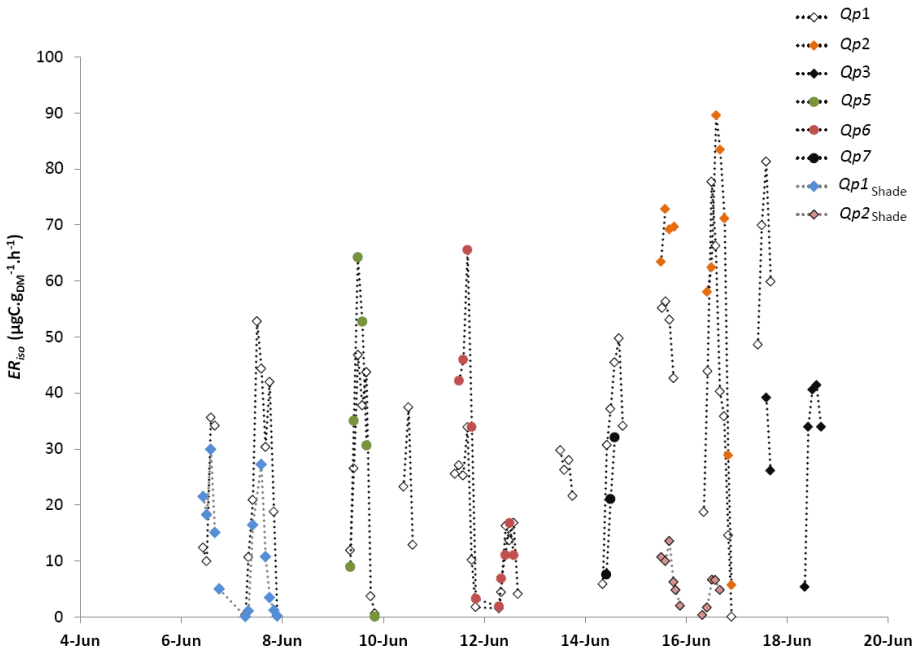

Figure 3. Diurnal variations of isoprene emission rate ER_{iso} ($\mu g\, C\, g_{DM}^{-1}\, h^{-1}$) measured from all branches sampled on the O_3HP footbridge.

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Variability of BVOC emissions from a Mediterranean mixed forest

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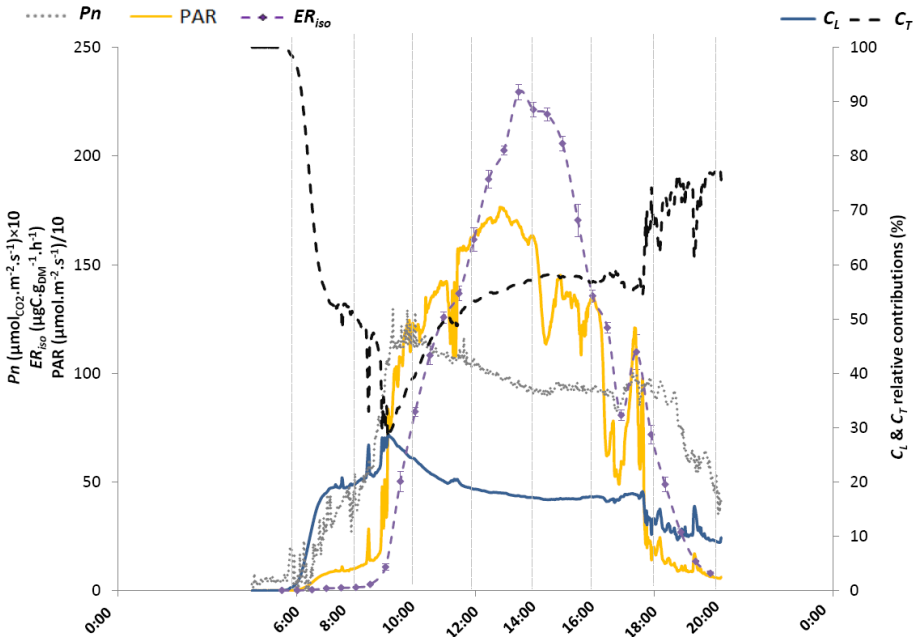

Figure 4. Diurnal variations of *Qp*4 isoprene emission rates ER_{iso} (µg C g_{DM}^{-1} h^{-1}) ± SD vs. the corresponding net photosynthetic assimilation Pn (µmol CO_2 m^{-2} s^{-1}), PAR (µmol m^{-2} s^{-1}), and relative contribution (%) of the C_L and C_T parametrs (as in Guenther et al., 1993) obtained by dividing each factors (light or temperature) by the sum of C_L and C_T.

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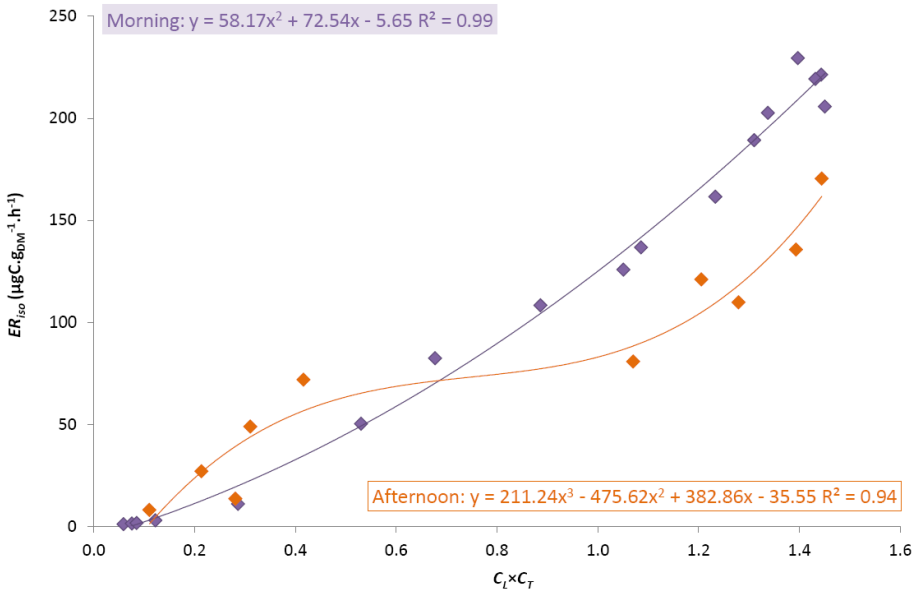

Figure 5. Diurnal variation of *Qp4* isoprene emission rate ER_{iso} ($\mu g\,C\,g_{DM}^{-1}\,h^{-1}$) vs. $C_L \times C_T$ as in Guenther et al. (1993), 1 June.
Dark purple diamonds are measurements between 08:00 LT to 14:00 LT; open purple diamonds are measurements between 14:30 to 20:00 LT. Polynomial best fit equation and determination coefficient R^2 are given for morning and afternoon period.

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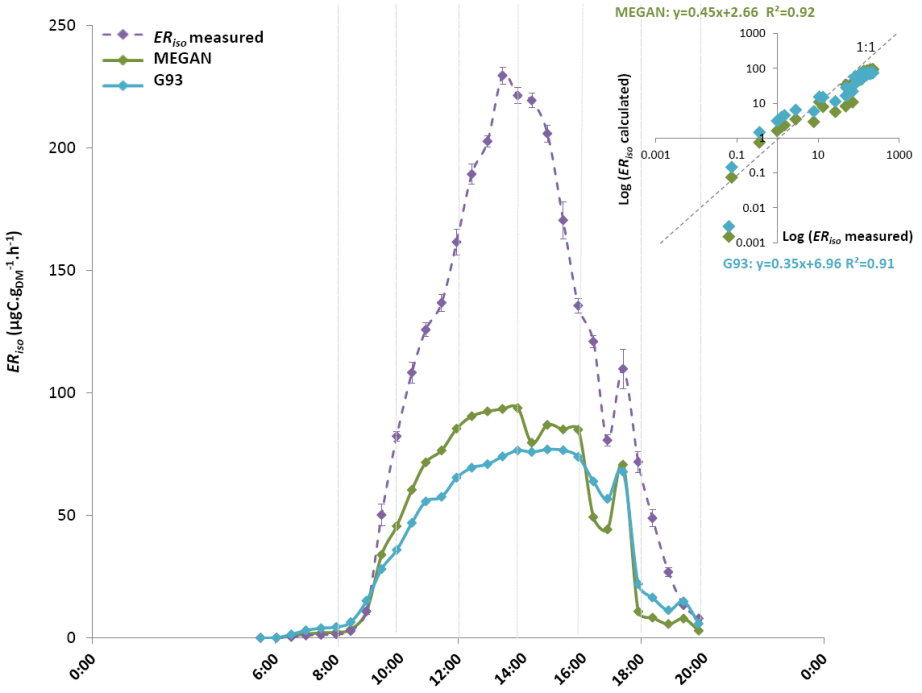

Figure 6. Comparison of Qp4 isoprene emission rates (µgC gDM^{-1} h^{-1}) ± SD measured in-situ (1 June, purple doted line) and assessed using emission algorithm as in (i) Guenther et al. (1993) and a Q. pubescens emission factor of 53 (µgC gDM^{-1} h^{-1}) as in Simpson et al. (1999) (G93, blue line), and as in (ii) MEGAN model, (Guenther et al., 2006, green line) with an isoprene emission factor of 53 (µgC gDM^{-1} h^{-1}), a leaf age Y_{age} of 0.6, and a soil water Y_{SM} of 1. Small graph is the comparison between the log of assessed emission rates using G93 (blue diamonds) and MEGAN (green diamonds) vs the log of measured emission rates.

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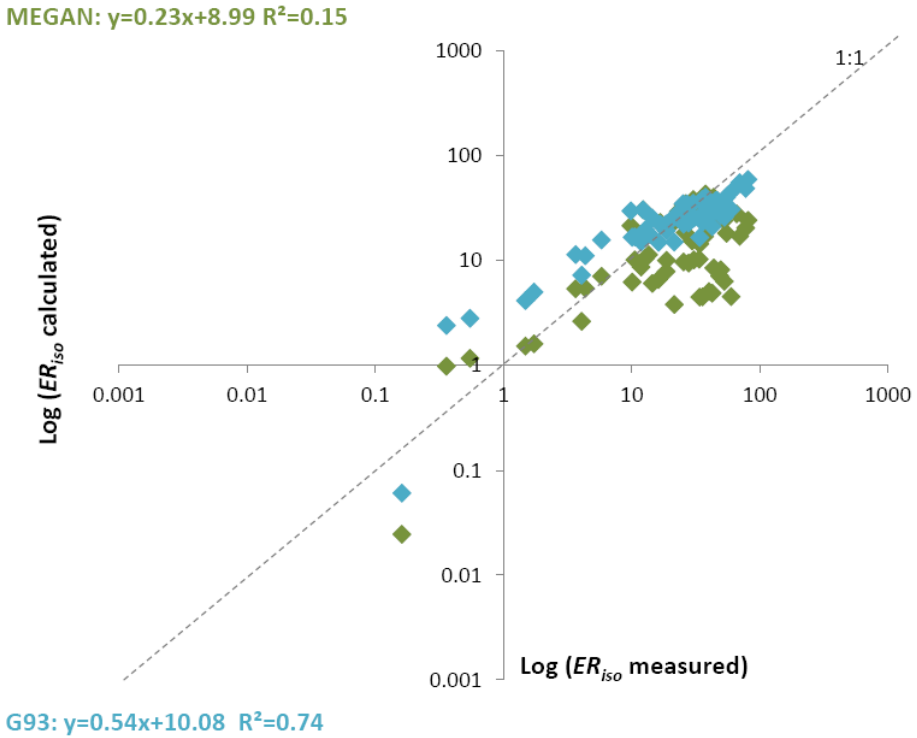

Figure 7. Comparison of the log of Qp1 isoprene emission rates measured from 6 June till 17 June and the log of emission rates assessed using an emission algorithm as in (i) Guenther et al. (1993) and a Is of 53 (μgC gDM^{-1} h^{-1}) as in Simpson et al. (1999) (G93, blue diamonds), and as in (ii) MEGAN model (Guenther et al., 2006, green diamonds) with an isoprene emission factor of 53 (μgC gDM^{-1} h^{-1}), a leaf age Y_{age} of 0.6, and a soil water Y_{SM} calculated as in Guenther et al., 2006.

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