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Concentrations and fluxes of isoprene and oxygenated VOCs at a French Mediterranean oak forest

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Abstract

The CANOPEE project aims to better understand the biosphere-atmosphere exchanges of biogenic volatile organic compounds (BVOC) in the case of Mediterranean ecosystems and the impact of in-canopy processes on the atmospheric chemical composition above the canopy. Based on an intensive field campaign, the objective of our work was to determine the chemical composition of the air inside a canopy as well as the net fluxes of reactive species between the canopy and the boundary layer. Measurements were carried out during spring 2012 at the Oak Observatory of the Observatoire de Haute Provence (O_3HP) located in the southeast of France. The field site presents one dominant tree species, *Quercus pubescens* L., a typical Mediterranean species which features large isoprene emission rates. Mixing ratios of isoprene, its degradation products methylvinylketone (MVK) and methacrolein (MACR) and several other oxygenated VOC (OxVOC) were measured above the canopy using an online proton transfer reaction mass spectrometer (PTR-MS), and fluxes were calculated by the disjunct eddy covariance approach. The O_3HP site was found to be a very significant source of isoprene emissions, with daily maximum ambient concentrations ranging between 2–16 ppbv inside and 2–5 ppbv just above the top of the forest canopy. Significant isoprene fluxes were observed only during daytime, following diurnal cycles with midday net emission fluxes from the canopy ranging between 2–8 mg m^{-2} h^{1}. Net isoprene normalised flux (at 30 °C, 1000 µmol m^{-2} s^{-1}) was estimated at 6.6 mg m^{-2} h^{-1}. The (MVK+MACR)-to-isoprene ratio was used to assess the degree of isoprene oxidation. In-canopy chemical oxidation of isoprene was found to be weak, as indicated by the low (MVK+MACR)-to-isoprene ratio (~ 0.13) and low MVK+MACR fluxes, and did not seem to have a significant impact on isoprene concentrations and fluxes above the canopy. Evidence of direct emission of methanol was also found exhibiting maximum daytime fluxes ranging between 0.2–0.4 mg m^{-2} h^{-1}, whereas flux values for monoterpenes and others OxVOC such as acetone and acetaldehyde were below the detection limit.

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BVOCs at a Mediterranean oak forest

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1 Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere from natural sources (biogenic emissions) as well as from anthropogenic sources. Biogenic VOCs (BVOCs) constitute approximately 90 % of global VOC emissions (Guenther et al., 1995). These emissions are characterized by a strong chemical diversity with more than a thousand BVOCs identified as emitted by plants. However, only a few of them contribute significantly to the global BVOC fluxes into the atmosphere (Laothawornkitkul et al., 2009). Isoprene (C_5H_8) is the most abundant BVOC in the Earth system, accounting for about half of all natural VOCs emitted at about 10^{15} g(C) yr^{-1} (Guenther et al., 2012). Monoterpenes, sesquiterpenes but also oxygenated compounds, such as methanol, acetone and acetaldehyde may also be important regarding atmospheric chemical processes (Guenther et al., 1995; Kesselmeier et al., 1998; Kesselmeier and Staudt., 1999; Fuentes et al., 2000; Park et al., 2013). Despite their relatively low atmospheric concentrations BVOCs are key components of tropospheric chemistry. Due to their high reactivity, they react rapidly with oxidants such as the OH radicals, thus significantly influencing the oxidizing capacity of the atmosphere and thereby impacting the residence time of air pollutants and the most reactive greenhouse gases such as methane (Wuebbles et al., 1989; Chiemchaisri et al., 2001). BVOCs also play a key role in the tropospheric ozone cycle. In the presence of sufficiently high NO_x concentrations and light, BVOC emissions may be important precursors of regional-scale O_3 (Trainer et al., 1987; Jacob and Wofsy; 1988; Chameides et al., 1988; Lee et al., 2006; Curci et al., 2010). As BVOC emissions increase with ambient light and temperature, the on-going climate change and its expected progression in the future may impact BVOC emissions and contribute to regional O_3 changes, but several processes still need to be better understood. BVOCs not only influence gas phase atmospheric chemistry; several studies have demonstrated that the oxidation of monoterpenes, sesquiterpenes, and, to a lesser extent, of isoprene, contributes to the formation of secondary organic aerosols (SOA) in the troposphere (Griffin et al., 1999;

Claeys et al., 2004). The contribution estimate of BVOCs to SOA formation is still rather uncertain: Andreae and Crutzen, (1997) calculated this contribution to be in the range of 30–270 Tg yr^{-1} whereas more recently Tsigaridis and Kanakidou (2003) estimated a smaller range of 2.5–44.5 Tg yr^{-1}.

In the Mediterranean region, the emissions and reactivity of BVOCs are enhanced due to high temperatures and sunny conditions and therefore are of particular interest for the production of SOA and O_3. A modelling study carried out by Curci et al. (2010) predicted that BVOC emissions may be responsible for the increase of summertime daily O_3 maxima in the Mediterranean region by 5 ppbv, whereas Richards et al. (2013) estimated that a 20 % cut in local BVOC emissions would lead to an average reduction of only 0.96 ppbv of O_3 over the Mediterranean area.

To evaluate the contribution of VOCs emitted by vegetation in the Mediterranean area to O_3 and SOA formation, a first step is to have accurate information on the amount of BVOCs released into the atmosphere. In this objective, we need to improve our knowledge regarding interactions between the terrestrial biosphere and the atmosphere which are still poorly understood and quantified. Several experimental studies demonstrated that a possible loss of BVOCs through chemical reactions and deposition inside the canopy could influence the net fluxes into the atmosphere (Ciccioli et al., 1999). The loss of isoprene for example, within the canopy, could reach up to 40 % (Makar et al., 1999). A few studies have also used Lagrangian-based stochastic model to explore the effect of chemical degradation of BVOCs inside the canopy (Strong et al., 2004; Rinne et al., 2012). Based on the Lagrangian approach along with measurements of oxidants in a Scots pine site, Rinne et al. (2012) suggested that in canopy-chemical degradation was negligible for isoprene but had a major effect on fluxes of most reactive species such as β-caryophyllene. Yet, those intra-canopy reactions are generally not considered in global vegetation or chemistry-transport models (Ciccioli et al., 1999; Makar et al., 1999; Fuentes et al., 2000; Forkel et al., 2006). Therefore, there is really a need for more experimental analysis to quantify the impact of intra-canopy processes, together with a modelling approach in order to evaluate the related error in the estimates of net BVOC fluxes to the Mediterranean atmosphere.

A few studies have determined biogenic net emissions from Mediterranean ecosystems (Seufert et al., 1997; Ciccioli et al., 1999; Darmais et al., 2000; Davison et al., 2009). During the first BEMA experiment (Biogenic Emissions in the Mediterranean Area 1994) several field campaigns were carried out at the Casteloporziano site located along the Mediterranean coast near Rome, with one of the aims being to study BVOC emission fluxes above various Mediterranean species (Valentini et al., 1997). Emissions from orange plantations have also been studied in Spain within the framework of the second BEMA project 1997, and have shown an important loss of very reactive compounds such as sesquiterpenes due to within-canopy removal (Ciccioli et al., 1999) and on the opposite, the smaller influence of chemical destruction on the less reactive monoterpenes fluxes (Darmais et al., 2000).

Among the different tree species that characterize Mediterranean ecosystems, *Q. pubescens* is of particular interest because of its large spatial coverage (most important tree species covering 20 % of the vegetated surface, i.e 260 000 ha, in the Provence-Alpes-Côte d'Azur region) and high isoprene emission potential. Keenan et al. (2009) estimated that the contribution of *Q. pubescens* to the total European isoprene emissions budget exceeded 15 % for the 1960–1990 periods. Only a very limited number of BVOC flux measurements were performed on a *Q. pubescens* ecosystem. Simon et al. (2005) measured fluxes during one day using an aerodynamic gradient method in the forest of Montmeyan, while Baghi et al. (2012) used the disjunct eddy covariance method at the Observatoire de Haute Provence, both studies focusing exclusively on isoprene.

The originality of the CANOPEE ANR-JCJC project is to combine field experiments (branch-scale to canopy-scale measurements), targeting a large variety of BVOCs over a *Q. pubescens* forest, with modelling. Experimental data and observations collected during the intensive field campaigns will eventually be used in the one-dimensional canopy-chemistry model CACHE (Forkel et al., 2006) and the regional chemistry-transport model CHIMERE (Schmidt et al., 2001; Szopa et al., 2009) in order to study both, the in-canopy processes and the role of local forested areas on the atmospheric chemical composition in the Mediterannean region.

Our work consisted in measuring ambient BVOCs inside and above the O_3HP canopy during an intensive campaign (June 2012). The objectives of this work were (1) to identify and quantify the VOC species locally produced at the Observatoire de Haute Provence, (2) describe the temporal variation of their mixing ratios, (3) assess net fluxes of BVOC from the top of the canopy to the boundary layer and (4) to discuss the isoprene fluxes and isoprene potential loss due to in-canopy oxidation.

2 Methodology

2.1 Site description and general strategy

The Observatoire de Haute Provence is an astronomical observatory located in south-eastern France (5°42′44″ E, +43°55′54″ N) on a plateau at a height of about 650 m. The Oak Observatory at the Observatoire de Haute Provence (O_3HP), a platform dedicated to the observation of the phenology and physiology of the white oak, is mostly covered by a forest of *Quercus pubescens* L. (Downy oak) (90 %). Downy oak trees at O_3HP are about 70 yr old and the highest trees of the site, with an average height of 5 m. The remaining 10 % of overstory vegetation is dominated by Montpellier maples *(Acer monspessulanum* L.). Understory vegetation is dominated by *Cotinus coggyria* Scop. also called Smoke bush and many garrigue plants. The single-sided mean leaf area index (LAI) measured at the O_3HP site is about 2.4. The climate is Mediterranean with warm-to-hot dry summers and mild-to-cool wet winters. During the field campaign the daily maximum temperatures typically ranged between 18 and 30 °C. For further details about the O_3HP site refer to https://o3hp.obs-hp.fr.

Monthly ambient isoprene samplings have been conducted at the O_3HP over an 11 month period in order to follow air concentration seasonal variations. An intensive field campaign took place in June 2012, where BVOC, NOx and ozone concentrations, as well as flux measurements of individual VOC species, were performed for about two weeks. In addition to ambient measurements, BVOCs emission rates at branch scale were followed and are described in the companion paper (Genard et al., 2014).

2.2 Monthly isoprene sampling and analysis

Prior to the intensive field campaign, air samples were collected every month inside the canopy between May 2011 and December 2011 and from April 2012 to June 2012, in order to follow air isoprene seasonal variation. Air was collected onto cartridges using an autosampler (SASS, TERA Environnement, Croles, France). Cartridges consisted of stainless-steel tubes filled with Tenax TA adsorbents. Once (or twice) a month, twelve cartridges collected air for 2 h with a volume of 700 mL. The air entering the cartridge was filtered in order to eliminate any particulate matter. Each sampling tube was kept refrigerated and analysed at the laboratory within a month. The GC-MS analysis system consisted of an automatic desorption system (ATD 300, TurboMatrix, Perkin Elmer), coupled to a GC (Varian Model 3800, Varian Inc., USA) linked to an Ion trap mass spectrometer from the same company. Blank cartridges were analysed every 3 or 5 samples and showed no significant levels of isoprene. An external multi-point calibration was performed by doping the adsorbent tubes with a VOC standard (National Physical Laboratory, Teddington, Midlesex, UK). The quantification limit was less than 140 pptv.

2.3 Ambient air sampling system during the intensive field campaign

Ambient air sampling was conducted at two different heights: 2 m a.g.l. (a.g.l.) inside the canopy – and above the top of the canopy at about 10 m. Both sampling inlets were slightly heated around 1 °C above ambient temperature with a thermocouple type K connected to a 12 V power supply in order to prevent water condensation. The lines

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were protected from radiation and attached to a pump-up mast, situated at 30 m from the van where all instruments were housed.

At 2 m a.g.l, air was pulled through a 35 m Teflon line (PFA, 1/2″ outside diameter “OD” and 3/8″ inner diameter “ID”) at about 40 $\text{L}\,\text{min}^{-1}$. Side flows were taken from a manifolds at the end of the main line through thinner Teflon lines (PFA, 1/4″ OD, 5/32″ ID) and sub-sampled by a range of gas analysers (GC-FID, NO_x and ozone analysers).

At 10 m a.g.l, air was pulled through a 45 m Teflon line (PTFE, 1/2″ OD, 3/8″ ID) at a higher flow ($\sim$ 64 $\text{L}\,\text{min}^{-1}$) in order to maintain the turbulent flow needed to minimize signal attenuation. A proton transfer reaction mass spectrometer (PTR-MS) and a CO_2/H_2O analyser (IRGA) sub-sampled continuously at a flow rate of 0.8 $\text{L}\,\text{min}^{-1}$ and 5 $\text{L}\,\text{min}^{-1}$ respectively. The displacement between the inlet and the sonic anemometer (Gill HS-50 Hz) was about 20 cm horizontally and 5 cm vertically.

2.4 BVOC measurement using proton transfer reaction mass spectrometer

2.4.1 PTR-MS operation

Concentrations and fluxes of VOCs above the canopy were investigated online with a PTR-MS (Ionicon Analytik, Innsbruck Austria), a technique which has been described in recent reviews (De Gouw and Warneke, 2007; Blake et al., 2009) and references therein. Briefly, the PTR-MS used was a high sensitivity Ionicon model. We operated the drift tube at 2.2 mbar pressure, 60 °C temperature and 600 V voltage, to achieve an E/N ratio of approximately 132 Td (E: electric field strength [V cm^{-1}], N: buffer gas number density [molecule cm^{-3}]; $1\,\text{Td} = 10^{-17}\,\text{V cm}^2$). The primary H_3O^+ ion count assessed at m/z 21 ranged between $0.9 \times 10^7 - 1.9 \times 10^7$ cps with a typically $< 5\,\%$ contribution from the monitored first water cluster at m/z 37 and $< 4\,\%$ contribution from the oxygen O_2^+ at m/z 32. The PTR-MS measurement procedure consisted of an hour-long sequence. In order to provide both flux data and information on the full VOC composition, the PTR-MS was automatically set to run continuously in 2 different modes: twice 25 min in flux mode and twice 5 min in scan mode each hour. During the flux mode, 8 protonated target masses (m/z 33, 45, 59, 61, 69, 71, 87 and 137) were measured successively with a dwell time of 500 ms per mass, while the primary ion count (m/z 21), the first water cluster ion count (m/z 37) and the photon "dark counts" (m/z 25) were all measured with a dwell time of 200 ms. This resulted in a total cycle time of 4.6 s and a total of $n \approx 326$ recorded values per 25 min flux period. In scan mode, 5 min were dedicated to measuring a wide range of VOCs (m/z 21–93) with a dwell time of 500 ms. During the remaining 5 min, the PTR-MS background was monitored by sampling zero air (Ionimed's GCU zero air generator). PTR-MS data were stored alongside those from the sonic anemometer, using a custom logging program written in LabVIEW (National Instruments, Austin, Texas, USA) as previously implemented by Langford et al. (2009).

2.4.2 Calibration and volume mixing ratios (VMR) calculations

The PTR-MS was calibrated on the first and the last days of the field campaign using a Gas Calibration Unit (GCU, Ionimed Analytik GbmH, Innsbruck, Austria) a dynamic gas dilution system that provides defined and controllable concentrations of different VOC using VOC-free air produced from ambient air with the GCU catalyst Singer et al. (2007). The VOC concentrations in the standard gas were diluted (8 dilution steps) from an initial mixing ratio of 1 ppmv to a mixing ratio of 20 ppbv. Calibration coefficients, also called normalized sensitivities (S_{norm}) were calculated for each atomic mass unit (amu, m/z) using the approach of Taipale et al. (2008). For VOC not present in our calibration gas standard, we calculated the normalized sensitive $S_{\text{norm-calculated}}$ using the procedure described by De Gouw and Warneke (2007). Further details concerning both calibration calculations are given in the Supplement (see Sect. 1.1).

The range of normalized sensitivities determined from gas calibration or calculated from the transmission coefficients is given in Table 1, together with the detection limits, calculated as two times the standard deviation of the normalized background counts when measuring from the catalytically converted "zero" air. For methanol, instrument background counts were generally high and therefore the ambient measurement signal was relatively high as well. However, all data points for methanol, and also acetone exceeded the detection limit. Approximately 9 % of m/z 45, 15 % of m/z 71, 20 % of m/z 73 and m/z 75 and 35 % of m/z 61 data points were below the detection limits, usually found at night or just before sunrise. Monoterpenes were followed at m/z 81 during the scan mode and at m/z 137 during the flux mode. Ambient mixing ratios were low at both ion channels m/z 81 and m/z 137; only 65 % and 58 % of the data points of the respective m/z exceeded the detection limits.

2.4.3 Identification of VOC and mass interferences

Standard PTR-MS instruments operate with a unit mass resolution and therefore cannot distinguish isomeric molecules. Furthermore, the formation of cluster ions and fragmentation of product ions may complicate the interpretation of PTR-MS mass spectra. For example, isoprene measurements by PTR-MS can suffer from interferences with isomers such as furans (Christian et al., 2004), 2- and 3-methyl butanal and 1-penten-3-ol (Karl et al., 2001) or by fragments of 2-methyl-3-buten-2-ol (MBO) if MBO emissions from vegetation are significant (Holzinger et al., 2005). Signal of MBO is also detected at the parent ion m/z 87. In this study, m/z 87 was about 5–10 % of the signal at m/z 69 in daytime. Despite the possibility of multiple interferences, an inter-comparison showed that the PTR-MS measurements of isoprene were slightly lower (10 %) than more specific GC-FID measurements (see Sect. 2.7). Considering the magnitude of isoprene emissions it is very unlikely that any interferences were significant.

As the GC-FID system deployed during the field campaign was designed for measuring exclusively hydrocarbons, no intercomparison with the PTR-MS was possible for the compounds attributed to C2–C6 OxVOC. For these compounds the discussion of potential interferences is therefore based on literature.

Methanol, detected at m/z 33, is expected to exhibit only little fragmentation but can suffer from interferences with the oxygen isotope $^{16}O^{17}O$ detected at the same mass (Taipale et al., 2008; De Gouw and Warneke, 2007). Minimal interferences are also expected at m/z 45, which is attributed to acetaldehyde. Acetone and propanal are both detected at m/z 59 in PTR-MS, but previous studies showed that the contribution from propanal is typically only small (0–10 %) (De Gouw and Warneke, 2007) and confined to urban and industrial areas; the measurement at m/z 59 can therefore be regarded as a measurement of acetone. The isomers methylvinylketone (MVK) and methacrolein (MACR) were detected at the same mass-to-charge ratio, $m/z = 71$, and the signal at this mass was attributed to the sum of the two compounds. Minimal interferences are also expected at this ion channel (De Gouw and Warneke, 2007). Eventually, the two compounds detected at m/z 73 and 75 are believed to correspond to methylethylketone and hydroxyacetone. However potential interferences have been previously reported from butanal at m/z 73 and butanol and propionic acid at m/z 75 (De Gouw and Warneke, 2007; Karl et al., 2009), and no further investigation was made during this work to be able to quantify these potential interferences. For monoterpenes, fragmentation occurs predominantly on the parent m/z 137 and the fragment m/z 81 ions. Two estimates of monoterpene concentrations were calculated independently from the signals at both ion channels, at m/z 81 during the scan mode and at m/z 137 during the flux mode.

2.5 Flux calculations

Flux measurements of individual VOC species were performed using the micrometeorological disjunct eddy covariance by mass-scanning (DEC-MS) method also referred to as virtual disjunct eddy covariance technique (vDEC). DEC-MS and the conventional eddy covariance (EC) method rely on the same principle, that is, when the boundary layer is fully turbulent, the net vertical transfer is due to eddies. The flux of each compound is therefore calculated using a covariance function between the vertical wind speed (w) and the VOC mixing ratio (c):

$$F = \frac{1}{n}\sum_{i=1}^{n} w'(i - t_{\mathrm{lag}}/\Delta_{\mathrm{tw}}) \cdot c'(i) \tag{1}$$

Where, $w'(=w-\bar{w})$ and $c'(=c-\bar{c})$ are the instantaneous fluctuations about the mean vertical wind and the mean VOC concentration respectively, n is the number of PTR-MS measurements during each 25 min averaging period (here, $n = 326$), t_{lag} is the variable lagtime that exists between wind and PTR-MS measurements resulting from the sample transit through the sampling line, and Δ_{tw} is the sampling interval of the vertical wind velocity measurements (20 Hz = 0.05 s).

Further details can be found in Rinne et al. (2001), Karl et al. (2002) and Langford et al. (2009). Output files from the logging program containing 30 min arrays of wind and PTR-MS data (25 min) were post-processed by an algorithm written in LabVIEW by Langford et al. (2009) in order to calculate the VOC fluxes. Each data row corresponding to a given VOC was converted to ppbv and to $\mathrm{g\,m^{-3}}$ using temperature and pressure values recorded at the site. Next, each VOC concentration data (c) was paired with the corresponding vertical wind velocity (w). The lagtime between (w) and (c) resulting from the sample residence time in the sampling line was variable due to fluctuations of temperature and pressure. For each 25 min period, lagtime (t_{lag}) was automatically determined for each compound using the maximum covariance method between the VOC concentration (c) and the vertical wind speed (w) (Taipale et al., 2010). A maximum covariance typically occurred around 15 s. The post-processing algorithm also filtered out data which did not meet specific quality criteria: (1) VOC flux data recorded during periods of low turbulence (friction velocity: $u_* < 0.15\,\mathrm{m\,s^{-1}}$). (2) VOC flux values below the detection limit. The detection limit was calculated as three times the standard deviation of the covariance for t_{lag} far away from the true lag (+150–180 s) (Spirig et al., 2005). (3) A stationary test, as suggested for the first time by Foken (1996), was applied where the 25 min flux was disaggregated into 5 min blocks and the average of these compared to the 25 min flux. When the difference (Δs) between the average of the 5 min blocks and the 25 min flux was above 60 %, data were considered as non-stationary, whereas when Δs varied between 30 and 60 % data were labelled as of low quality. Statistics about these tests are presented in Table 3.

2.6 VOC measurements by gas chromatography

An automatic gas chromatograph (airmoVOC C2-C6, Chromatotec, Saint Antoine France) equipped with a flame ionisation detector (GC-FID) suitable for the measurement of light hydrocarbons, especially for isoprene, sampled at 2 m above ground. For every half-hour analysis, 250 mL of ambient air were drawn into the system via a stainless steel inlet line with a flow rate of 18 mL min^{-1} (air sample integrated over 10 min). The air sample passed first through a Nafion dryer in order to remove the humidity and then hydrocarbons were pre-concentrated on a trap filled with Carboxen, Carbopack B and Carbotrap C. The trap was cooled to −8 °C by a cell with Peltier unit during the sampling procedure. Then, the pre-concentrated air sample was thermally desorbed at 220 °C and injected on-column into a metal capillary column (Porous Layer Open Tubular Column PLOT, Al_2O_3/KCl; 0.53 mm inner diameter and 25 m length, Varian Inc) located inside the heated oven of the GC. A time program temperature was used; the column maintained to 40 °C during one minute was then heated at a rate of 20 °C.min^{-1} up to a final temperature of 203 °C. Non-oxygenated C_2–C_6 hydrocarbons (mainly isoprene during the measurements) were finally detected and quantified by a FID. A certified standard gas mixture (National Physical Laboratory, Teddington, Midlesex, UK) containing a mixture of 17 VOC at about 4 ppbv was used as calibration standard. A complete calibration was performed twice a week. Each calibration was repeated at least three times in order to test the repeatability of the measurement. Relative standard deviations for analysis of the calibration mixtures were in the range of 1–9 %. The overall uncertainty was estimated to be better than 15 %.

2.7 GC-FID/PTR-MS isoprene field comparison

An in situ comparison was carried out during the campaign between isoprene measurements by GC-FID and PTR-MS. Both instruments sampled air from the same line at 2 m a.g.l. The GC-FID integrated air sample over 10 min every 30 min. By contrast, the PTR-MS sampled air continuously and followed isoprene at m/z 69 with a dwell time of 500 ms and a total cycle analysis of about one min. Only samples for which the GC-FID sample trapping interval and the PTR-MS sample cycle overlapped were included and the PTR-MS measurement were averaged over the 10 min sampling integration of the GC-FID. Overall a very good correlation was observed between both instruments ($R^2 = 0.92$), with 10 % higher values for the GC-FID, a difference which is within the uncertainty range. The intercomparison highlighted an average offset of +0.3 ppbv for the PTR-MS during nighttime, which was not substracted from the PTR-MS datapoints and may be due to interferences from other VOCs. This nighttime offset has to be kept in mind but remains small compared to the average daytime isoprene concentrations (2.09 ppbv).

2.8 NO_x, ozone and micrometeorological measurements

Nitrogen oxides (NO_x) and ozone concentrations were measured 2 m a.g.l. A flow of 920 mL min^{-1} was sub-sampled from the main line and directed to the NO_x analyzer. Nitrogen oxides were monitored with a T200UP instrument (Teledyne Advanced Pollution Instrumentation, San Diego, California, USA) by ozone-induced chemi-luminescence. A 30 min span calibration was performed every day using a dynamic dilution calibrator (T700 UP, API, USA) equipped with a programmable NO generator. The span calibration was automated to run 15 min of zero air (produced by the zero air generator T701H, API) followed by 15 min of NO measurements generated at 5 ppbv. A calibration at 10 ppbv of NO was performed once a week by measuring 30 min of zero air and 30 min of a certified standard gas mixture (Air Liquide, Cofrac certification).

Ozone was measured with an automatic ultraviolet absorption's analyzer API T400 (API, USA) which was calibrated prior to the field deployment with an internal ozone generator (IZS, API) and operated with a sample flow rate of approximately 740 mL min^{-1}.

Meteorological parameters such as temperature and air humidity as well as photosyntetically active radiation (PAR) profiles inside the canopy were continuously monitored. The sonic anemometer (Gill Instrument HS-50 Hz, UK) enabled the measurement of wind speed and direction and to calculate the friction velocity u_* .

3 Results

3.1 Ambient isoprene seasonal variations

Figure 1 depicts the seasonal variations of ambient, in-canopy, isoprene concentrations at the O_3HP from May 2011 until May 2012. As presented previously (see Sect. 2.2), one or two complete diurnal cycles were taken every month. Even if the values reported here are representative only of the specific sampling days, significant seasonal variations of isoprene concentration were observed and were in agreement with the well-known dependency of isoprene emission with ambient light and temperature variations (Guenther et al., 1993). As conditions have been warmer in springtime than in summertime, maximum isoprene concentrations have been observed at the end of May with a maximum value of 8 ppbv. Lower concentrations were measured on the 14 and 31 July (maximum values of 4–5 ppbv) followed by a new increase in the end of August (9.8 ppbv); concentrations then decreased during the autumn when the leaves of the downy oak were still persistent and no significant isoprene concentration above detection limit was detected after November.

3.2 Air chemical regime

During the campaign the O_3HP site was typically under the influence of the regional northerly wind regime "Mistral". As depicted on Fig. 2, air masses were usually transported from the (north) western part of France and only some sparse events of southern winds occurred (5–7 June, 14–16 June). Very low NO levels (< 0.2 ppbv) were detected and no significant influence from anthropogenic NO_x was observed ($NO_2 <$ 3 ppbv). Likewise, CO concentrations were low throughout the study (< 180 ppbv). Benzene and toluene measurements, detected and used as tracers of anthropogenic pollution, showed background levels below 0.2 ppbv with the exception of one brief episode (the 7 and 8 June) when their concentration reached 0.8 and 1.6 ppbv (Fig. 3). During this episode the benzene-to-toluene ratio was slightly lower than for the rest of the measurement period and ranged between 0.3–0.8, indicating an influence of fresh anthropogenic air masses. As benzene and toluene have different lifetimes, the higher the benzene-to-toluene ratio is the older the air mass is (Heeb, 2000). Globally, the air masses encountered were not significantly impacted by anthropogenic primary emissions.

3.2.1 Isoprene mixing ratios and above-canopy fluxes

The May–June 2012 time series of isoprene mixing ratios recorded simultaneously at 2 m (inside the canopy by GC-FID) and at 10 m height (above the canopy by PTR-MS) are shown in Fig. 4 along with air temperature. Isoprene exhibited high concentrations with an average mixing ratio of 1.2 ppbv above the canopy (Table 2). Among every observed VOCs, isoprene presented the largest amplitude between day and night time concentrations, this behaviour being typical of those biogenic compounds whose emissions are light and temperature dependent (Guenther et al., 1993; Goldstein et al., 1998). Night time isoprene concentrations were close to our detection limit and started to increase steadily early in the morning, around 6.30 a.m. in response to the temperature and PAR increase. Maximum concentrations occurred in the afternoon, peaking between 2–5 ppbv and 2–16 ppbv at 10 m and 2 m heights, respectively. In comparison, maximum atmospheric mixing ratios of about 10 ppbv were found during June above a *Q. pubescens* forest near Marseille (France) by Simon et al. (2005). A decrease in isoprene concentration was observed in the evening, as a consequence of isoprene emission dropping and the simultaneous consumption by OH radicals and diffusion. Isoprene mixing ratios continued to drop gradually during night time and reached their minimum in the early morning.

The amplitude of the isoprene air concentration diurnal cycle varied strongly from day-to-day in response to environmental condition changes. By combining all the daytime isoprene data above the canopy, a stronger correlation was found with ambient temperature than with PAR. This relationship between daytime isoprene mixing ratio and temperature was found exponential and the log linear fit of isoprene against temperature (°C) gave a relationship of $\exp(0.1334 \times T)$ with a coefficient of correlation, R^2, of 0.77 (Fig. 5).

Throughout the measurement period a clear gradient in the vertical profile of isoprene concentrations was observable, with an average of 40 % higher concentrations at 2 m than at 10 m a.g.l.

Isoprene fluxes measured during the campaign are shown in Fig. 6, along with PAR and u_* measured simultaneously at 10 m. During daytime (10:00–17:00), PAR ranged between 200 and 2015 $\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ with an average of 1500 $\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$. Of the measured compounds, isoprene showed by far the largest flux values with an average daytime emission of 2.1 $\text{mg}\,\text{m}^{-2}\,\text{h}^{-1}$. Significant positive isoprene fluxes were only observed during daytime, following diel cycles with mid-day maxima ranging from 2 to 8.0 $\text{mg}\,\text{m}^{-2}\,\text{h}^{-1}$. Isoprene fluxes reached zero after sunset or were rejected due to stratified conditions ($u_* < 0.15\,\text{m}\,\text{s}^{-1}$).

3.2.2 MVK+MACR mixing ratios and above canopy fluxes

The sum of MVK and MACR (signal at m/z 71) had an average mixing ratio of 0.2 ppbv. Most of the days, MVK+MACR displayed a diurnal variability with daytime maxima ranging between 0.1 and 0.8 ppbv and nighttime minima in the order of 20–40 pptv (Fig. 7). On the 6, 15 and 16 June, MVK+MACR did not exhibit the same diurnal trend as usually observed and its nighttime concentration remained unusually high at 0.2–0.3 ppbv. These three nights (from 5–6, 14–15 and 15–16 June) were characterized by low winds and thermally stratified conditions: indeed, the temperature profiles inside the forest canopy exhibited a clear vertical gradient (of 4 °C in 5 m) with cooler temperatures close to the forest floor. MVK+MACR high concentrations can therefore be explained by weak vertical exchanges leading to their accumulation within and just above the canopy. This suggests that night-time removal was less efficient than the high deposition rates that have recently been reported for MVK/MACR (Karl et al., 2010; Misztal et al., 2011).

The present study showed a strong correlation ($R^2 = 0.84$, slope = 0.12) between MVK+MACR and isoprene during daytime hours (07:00 a.m.–07:00 p.m.), supporting that isoprene oxidation was responsible for the formation of the first-order oxidation products MVK and MACR. A delay of about 2 h in the morning rise of concentrations was observed and likely represents the time that isoprene needed to be degraded.

Fluxes of MVK+MACR showed a general trend of emission with diurnal cycles but are subject to considerable uncertainties (Fig. 6). Indeed as MVK+MACR fluxes were small the covariance function was noisy and the true peak in the covariance function was not easily identified and consequently half of the fluxes were below the detection limit (Table 3). Considering only positive values, fluxes never exceeded 0.1 $\mathrm{mg\,m^{-2}\,h^{-1}}$ and exhibited a mean value around 0.030 $\mathrm{mg\,m^{-2}\,h^{-1}}$, which equates to 3 % of the isoprene flux averaged over the same data points. Overall, MVK+MACR fluxes were weak and no reliable evidence of deposition was found.

3.2.3 Monoterpenes mixing ratios

Due to the inability of the PTR-MS to distinguish isomer molecules, only the sum of all monoterpenes was measured. Total monoterpenes were calibrated to absolute concentrations independently at m/z 81(fragment) and m/z 137 (parent ion). The more sensitive signal at m/z 137 was used instead of their average. As ion counts at m/z 81 were derived from the 5 min hourly mass scans, temporal resolution was significantly poorer than the signal at m/z 137.

Vegetation at the O_3HP was found to be a weak monoterpene emitter. Ambient concentrations derived from m/z 137 were low, with an average value of 0.06 ppbv and a maximum at 0.25 ppbv over the whole measurement period (Fig. 4). Whereas diurnal branch-level emission rates of monoterpenes were observed for downy oaks and maple trees (Genard et al., 2014), ambient concentrations at the canopy level did not exhibit a clear diurnal variability. At nights, especially when the turbulence was low, a build-up of monoterpenes was observed. Night-time concentrations were probably affected by remaining emissions from the day, which were mixed over a small volume due to shallow nocturnal boundary layer. Concentrations of monoterpenes might also be affected by advection of emission from surrounding vegetation such as lavender or garrigue plants which are known monoterpenes emitters (Owen et al., 2001; Boeckelmann, 2008)

3.2.4 Oxygenated VOC mixing ratios and fluxes

At the O_3HP, several OxVOCs were detected. Due to their relatively long lifetimes (see Table 1) and widespread sources, OxVOCs showed elevated concentrations and less pronounced diurnal cycles than isoprene. Methanol was the most abundant VOC accounting for $\sim 40\,\%$ of the total measured VOC concentrations. Methanol mixing ratios at O_3HP ranged between 0.7 to 5.5 ppbv (Fig. 3). Methanol's relatively long atmospheric lifetime of ~ 10 days (Atkinson et al., 1999) resulted in elevated background concentrations (> 0.7 ppbv). However, it was the only OxVOC with a detectable net emission flux suggesting local biogenic emissions also influence the observed concentrations. Methanol fluxes exhibited diurnal cycles with emission fluxes starting at sunrise, increasing during daytime as temperature and PAR increased, and stopping after sunset. Daily maximum methanol fluxes ranged between 0.15 and 0.55 $\text{mg}\,\text{m}^{-2}\,\text{h}^{-1}$, i.e about 5 to 20 times lower than the isoprene fluxes. Previous studies have shown both positive and negative fluxes of methanol. In comparison, a net emission (up to 0.5 $\text{mg}\,\text{m}^{-2}\,\text{h}^{-1}$) with few transient deposition events has been reported for a tropical rainforest in Costa Rica (Karl et al., 2004), whereas a net deposition for methanol has been reported in a South-East Asian rainforest (Langford et al., 2010; Misztal et al., 2011). Our findings at the O_3HP indicated that the net exchange in methanol was always positive. As above-canopy fluxes reflect the sum of production and removal processes, this does not mean that there was no bidirectional exchange, but that the component fluxes showing emission always overwhelmed the deposition components.

Among the other OxVOCs detected were acetaldehyde (m/z 45), acetone (m/z 59), acetic acid (m/z 61) but also two compounds with a m/z ratio of 73 and 75, derived from the hourly 5 min scan and which were assumed to correspond to methylethylketone and hydroxyacetone, respectively. After methanol, acetone was the most abundant OxVOC with atmospheric mixing ratios ranging between 0.6 and 2.5 ppbv. Acetaldehyde and acetic acid followed with slightly lower concentrations around 0.2–1.2 ppbv for both of them. It is striking that all of these OxVOCs mentioned above, had a good covariance (Fig. 3) and most of them correlated well with each other. The strongest correlations were between m/z 45 and m/z 59 ($R^2 = 0.7$, slope = 0.78), m/z 75 and m/z 61 ($R^2 = 0.70$) m/z 59 and m/z 61 ($R^2 = 0.75$, slope = 1.2) but also m/z 59 and m/z 73 ($R^2 = 0.65$). Correlations with methanol were lower ($R^2 < 0.5$), likely due to its relatively strong biogenic source and also its high background. These significant correlations between every OxVOCs could be the result of the boundary layer dynamics, but still suggest that they had a common source or that their formation mechanisms responded to environmental factors in a similar manner. From 5 to 7 June, changes in the wind direction were observed with air masses coming from the south and through the region of Marseille. This southern wind shift was concurrent with the simultaneous increase of methanol, acetone, acetic acid and acetaldehyde. Respectively, from the 10 to the 14 June, when the site was under the influence of northern winds, OxVOCs were at their background levels. As OxVOCs have a relatively high lifetime of about a week, long distance transport seems to influence their ambient concentrations at the O_3HP. On the other hand, the progressive and simultaneous increase of concentrations for all these OxVOCs during the last days of the field campaign (i.e. 14–17 June) was remarkable, and was characterized by a steady rise in the ambient concentrations and solar radiation. This simultaneous increase of OxVOC concentration with temperature and PAR, likely reflects an additional biogenic source. As a matter of fact, evidence of primary emission of OxVOCs has been reported from the branch-level measurements from *Q.pubescens* individuals at the O_3HP (Genard et al., 2014). As background levels of acetone and acetaldehyde were high and emission rates at the branch-level were very low (mean: 0.21 and 0.09 µgC $g^{-1}_{\text{dry weight of biomass}}$ h^{-1} respectively), no significant fluxes were measured above the canopy by the DEC method.

4 Discussion on isoprene fluxes and in-canopy oxidation

4.1 Isoprene standardised flux and biomass emission factor

Isoprene fluxes presented in Sect. 3.2.1 confirm that emissions at O_3HP are dominated by large isoprene fluxes. During the CANOPEE intensive field campaign, isoprene daily maximums fluxes ranged between 2.0 to 8.0 mg m^{-2} h^{-1} with a mean daytime flux of 2.0 mg m^{-2} h^{-1}. This is in fairly good agreement with Baghi et al. (2012), who reported isoprene fluxes with values in the range 5.4–10 mg m^{-2} h^{-1} around midday, measured by DEC during a 2 day period in early August 2010 at the same site.

To our knowledge, above-canopy isoprene fluxes recorded at the O_3HP are the largest reported in the Mediterranean basin, since most of the measurements performed in the region were above monoterpenes emitters. In western Italy, above a low macchia ecosystem, Davison et al. (2009) reported relatively small isoprene fluxes with mean daytime values of 0.097; 0.016 and 0.032 mg m^{-2} h^{-1} measured using the DEC method with three different PTR-MS. Furthermore, no significant isoprene fluxes were found above a pine-oak forest site in Italy and above orange plantations in Spain during the BEMA's field studies (Valentini et al., 1997; Darmais et al., 2000). As the number of isoprene flux measurements at the canopy level in the Mediterranean region is limited, we extend our comparison to other ecosystems in the world. A non-exhaustive overview of isoprene flux measurements in Mediterranean, tropical, and temperate ecosystems is presented in Table 4, and confirms that isoprene emissions from Mediterranean forests can be comparable or higher than those observed in other regions of the world dominated by isoprene-emitting vegetation. For instance, maximum isoprene fluxes of 6.1, 7.1, and 10.8 mg m^{-2} h^{-1} were observed respectively above a mature lowland in the Central Amazon (Kuhn et al., 2007), a coniferous forest in eastern Belgium (Laffineur et al., 2011) or a deciduous forest in Germany (Spirig et al., 2005) and are very close to the maxima recorded at the O_3HP. Considerably higher isoprene fluxes reaching up to 30 $\mathrm{mg\,m^{-2}\,h^{-1}}$ were reported only from an oil palm plantation in Malaysia (Misztal et al., 2011)

Isoprene fluxes at the O_3HP were also normalized to standard conditions (temperature and PAR at the canopy level of 30 °C and 1000 $\mathrm{\mu mol\,m^{-2}\,s^{-1}}$ respectively) using the G93 algorithm (Guenther et al., 1993). By plotting all measured fluxes against the combined temperature and light scaling factors (C_L, C_T), a standardized flux F_standard (or basal emission rate) of 6.58 $\mathrm{mg\,m^{-2}\,h^{-1}}$ was derived from the fit line with zero intercept (Fig. 8).

For comparison, enclosure measurements for 7 different branches of *Q.pubescens* at the O_3HP during CANOPEE resulted in emission factors $\mathrm{EF_{biomass}}$ ranging between 30–140 $\mathrm{\mu g\,g^{-1}_{dry\,weight\,of\,biomass}\,h^{-1}}$ (hereafter, $\mathrm{\mu g\,g^{-1}_{dwt}\,h^{-1}}$) with an average value of 60 $\mathrm{\mu g\,g^{-1}_{dwt}\,h^{-1}}$ (Genard et al., 2014). The average $\mathrm{EF_{biomass}}$ was then upscaled to give an standardized flux F_standard using the following calculation process:

$$F_\mathrm{standard\text{-}upscaled} = \mathrm{EF_{biomass}} \times \sum_{h=0}^{h_\mathrm{c}} \mathrm{LAI}(h) \cdot \mathrm{LMA}(h) \qquad (2)$$

where h is the distance above ground (unit: m), h_c the canopy height, LAI the mean leaf area index (unit: $\mathrm{m^{-2}\,m^{-2}}$) and LMA the leaf dry mass per unit area (unit: $\mathrm{g\,m^{-2}}$). The resulting up-scaled basal emission rate $F_\mathrm{standard\text{-}upscaled}$ was about 15 $\mathrm{mg\,m^{-2}\,h^{-1}}$. Fluxes estimated by extrapolating leaf-level measurements were two fold higher than the average figure derived from DEC measurements. We consider this to be a reasonably good agreement since a factor of 2 of difference can be expected when comparing techniques over different spatial scales, due to uncertainties in the extrapolation, in addition to the uncertainties on both measurements. A reason for the difference certainly arises also from the normalization of DEC fluxes to standard conditions using the air temperature and PAR above the canopy. As a matter of fact, since a significant fraction of the canopy experiences lower light levels, the standardised emission flux from the canopy measurements is under-evaluated in a significant way. For example, a normalization using a PAR reduced by 50 % would lead to an F_{standard} increase of about 15 %. On the other hand, the normalization using actual leaf temperature, which is usually a couple of degrees higher than ambient temperature, would lead to lower F_{standard} values. A canopy structure model would be required to better quantify both effects. Additional uncertainty comes from the difference in biomass emission factors EF_{biomass}, which, as indicated by the branch-level measurements, can vary by more than a factor of 4 between tree individuals (Genard et al., 2014). Leaf level measurements are usually biased towards well exposed, sunlit, healthy and active leaves, which tend to be characterised by larger emission factors than would be representative for the biomass as a whole. Moreover, another possible reason for the overestimation of basal emission rates based on scaled up leaf level emissions could be the isoprene chemical loss within the canopy that we tentatively examine thereafter.

4.2 Isoprene oxidation within the canopy

Isoprene is oxidized mainly by OH radicals during the daytime, and by ozone and NO_3 radicals (if present) during the night (Atkinson, 1998). Therefore its chemical lifetime (τ_c) can be written as:

$$\tau_c = k_{\mathrm{ozone\text{-}ISO}} \times [\mathrm{Ozone}] + k_{\mathrm{NO3\text{-}ISO}} \times [\mathrm{NO_3}] + k_{\mathrm{OH\text{-}ISO}} \times [\mathrm{OH}] \quad (3)$$

where k is the rate constant for the reaction of isoprene (ISO) with ozone, NO_3 or OH.

Isoprene daytime lifetime was estimated at about 4 h against its oxidation by OH ($k_{\mathrm{OH\text{-}ISO}} = 1.1 \times 10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, from Atkinson et al., 1999), with typical summer daytime OH radical concentrations estimated to be $\sim 6.1 \times 10^5$ molecules $\mathrm{cm^{-3}}$ (first simulation from the CACHE model computed by Forkel et al., 2006). As isoprene oxidation by O_3 (or NO_3) is considerably slower in daytime it was considered negligible. Chemical processing of isoprene by hydroxyl radicals leads to three major first-generation oxidation products: formaldehyde, MVK and MACR (Tuazon and Atkinson, 1990; Carter and Atkinson, 1996; Zhao et al., 2004). Formaldehyde dominant sources are numerous and can include oxidation of other BVOCs, methane oxidation as well as advected anthropogenic VOCs. By contrast, in a forested area such as the OHP site, the only local and important source of MVK and MACR is the oxidation of isoprene. This is the reason why, the [MVK+MACR]-to-isoprene ratio was chosen as an indicator of the extent of isoprene oxidation. This ratio was controlled by a multitude of factors: (a) isoprene emission rates, (b) chemical reactions which remove isoprene while producing and destroying at the same time MVK and MACR, (c) atmospheric mixing as well as (d) the distance between the measurement location and the isoprene emissions (Montzka et al., 1993; Biesenthal et al., 1998; Apel, 2002). The twelve days of measurements featured a ratio varying from 0.05–0.27 during daytime (Fig. 9), which at the lower end of the range that has previously been oberved in other ecosystems of the world, which usually fall between 0.3–0.75, depending also on the height measurement (Montzka et al., 1993; Biesenthal et al., 1998; Holzinger et al., 2002). Nevertheless, a few studies have shown ratios close to our estimates: a ratio of 0.12 has been reported in a rural forest of Michigan (Apel, 2002), and a ratio of 0.1 to 0.36 was obtained in a South-East Asian tropical rainforest (Langford et al., 2010). During the 17 June, the only day when the PTR-MS measured inside the canopy (2 m a.g.l), the [MVK+MACR]-to-isoprene ratio was even lower with a mean value of about 0.06. This suggests that some of the isoprene oxidation might occur within the canopy, but to a very low extent. This low ratio inside the forest is also consistent with the weak MVK+MACR emission fluxes measured above the canopy. As presented before (see Sect. 3.2.2) MVK+MACR fluxes represented about 3 % of isoprene fluxes, which is lower than in other ecosystems of the world. Estimates of the isoprene that is converted to MVK+MACR below the flux measurement are usually in order of 5 to 15 %, also depending on the measurement height (Stroud et al., 2005). Chemical processing of isoprene inside the canopy of the O_3HP is low and no important production of MVK+MACR occurs near the ground suggesting the canopy is well ventilated and closely coupled to the boundary layer above. However, (MVK-MACR)-to-isoprene ratio measured above the canopy also clearly reflects the chemical processing above 10 m height.

A first explanation to the low rate of isoprene oxidation inside the canopy is the fact that isoprene did not have the time to react with OH radicals from the moment of its release by the vegetation and its arrival at the sampling inlet. Indeed, as the O_3HP canopy is low (5 m height on average), isoprene rapidly reaches the atmosphere. The turbulent transport time τ between ground surface and the measurement height was estimated to be around 30–60 s in daytime (See Supplement for calculation details), i.e considerably faster than the isoprene chemical degradation ($\sim$ 4 h). An additional explanation could also be the influence of the low nitrogen oxide conditions with typical values around 200 ppt. From the several field and chamber studies which examined the influence of nitrogen oxides on the OH-induced oxidation of isoprene it was found that low NO_x isoprene oxidation leads to low yields of MVK and MACR (Ruppert and Heinz Becker, 2000; Pinho, 2005; Navarro et al., 2011). We conclude that at the site of O_3HP, in-canopy isoprene chemical degradation does not influence in a significant way the net isoprene fluxes into the atmosphere.

5 Conclusions

We have presented high resolution atmospheric measurements of concentrations and fluxes of BVOCs above a Mediterranean Downy oak forest. As expected, biogenic VOCs were found to be dominated by isoprene with daytime maxima ranging between 2–15 ppbv inside the forest and 2–5 ppbv just above the top of the canopy. Isoprene concentrations showed a clear diurnal cycle with a daytime maximum and a minimum in the early morning and at night. Above the canopy, isoprene concentrations were about 40 % lower than inside the canopy; this loss was attributed to physical processes such as mixing with isoprene-depleted air masses (or, conversely, the build-up of isoprene within the canopy). Significant above-canopy isoprene fluxes were only observed in daytime, following diurnal cycles with mid-day maxima ranging between 2–

8 mg m^{-2} h^{-1}. Isoprene fluxes at the O_3HP site were among the largest fluxes reported in the Mediterranean region. Based on these measurements, an isoprene basal emission rate of 6.6 mg m^{-2} h^{-1} is recommended for downy oaks in this region for biogenic emission models. The concentration ratio of [MVK+MACR]-to-isoprene was very low in daytime with a mean value of about 0.13 just above the canopy. Low values of positive fluxes of MVK+MACR, close to the detection limit, were recorded above the canopy. From these observations we concluded that isoprene oxidation within the canopy was weak and did not significantly affect the air composition above the forest. *Q.pubescens* was found to be a weak monoterpene emitter, and, as a result, ambient concentrations of monoterpenes were close to the detection limits. OxVOCs were abundant at the site with mean daytime concentration of 2.48, 1.35 and 0.42 ppbv for methanol, acetone and acetaldehyde respectively. Of these compounds, only methanol exhibited significant fluxes, indicating a primary source inside the canopy. Daytime methanol maximum fluxes ranged between 0.15–0.4 mg m^{-2} h^{-1}, and were therefore about 5 to 20 times lower than isoprene fluxes.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/871/2014/acpd-14-871-2014-supplement.pdf.

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Table 1. Normalized sensitivities derived from the gas calibration or using the transmission factors and reaction rate coefficients (k) given by Zhao and Zhang (2004). Limit of detections calculated as 2 times the standard deviation of the noise (ncps) divided by the normalised sensitivity.

VOC present in the calibration gas standard				VOC NOT present in the calibration gas standard					
m/z	Identified compound	S_{norm} (ncps ppbv^{-1}) (dwell = 0.5 s)	LOD (ppbv)	m/z	Identified Compound	Transmission factor	k (10^{-9} cm^3 s^{-1})	$S_{\text{norm-calculated}}$ (ncps ppbv^{-1})	LOD (ppbv)
33	Methanol	17.2	0.31	61	Acetic Acid	0.91	2.27	14.5	0.16
45	Acetaldehyde	21.6	0.13	75	Hydroxyacetone	0.96	2.20	14.9	0.05
59	Acetone	22.9	0.05	81	MT fragment	0.98	2.40	16.6	0.03
69	Isoprene	9.8	0.07						
71	MVK+MACR	27.4	0.03						
73	MEK	22.5	0.05						
79	Benzene	11.8	0.04						
[*]87	MBO	12.0	0.08						
93	Toluene	12.4	0.07						
137	Monoterpens	4.0	0.04						

[*] Mass calibration of m/z 87 was achieved by interpolation of calibration factors between m/z 79 and m/z 93.

Table 2. Statistical summary of volume mixing ratios (ppbv) and fluxes of 12 targeted VOC above the canopy (10 m) of the Oak Observatory of the Observatoire de Haute Provence.

m/z	Identified compound	Mean VMR [ppbv] 24 h-statistics	Mean VMR [ppbv] (10:00–17:00)	Daily-Max VMR [ppbv]	Mean Flux [$\mathrm{mg\,m^{-2}\,h^{-1}}$] (10:00–17:00)	Maximum Flux [$\mathrm{mg\,m^{-2}\,h^{-1}}$]
33	Methanol	2.28	2.48	1.5–5.4	0.2	0.2–0.4
45	Acetaldehyde	0.38	0.42	0.2–1.4		
59	Acetone	1.28	1.35	1.0–2.5		
61	Acetic Acid	0.20	0.23	0.11–0.59		
69	Isoprene	1.19	2.09	1.7–5	2	2–8
71	MVK+MACR	0.21	0.28	0.1–0.8	0.035	0.1
*73	MEK	0.14	0.16	0.15–0.51		
*75	Hydroxyacetone	0.14	0.18	0.11–0.52		
*79	Benzene	0.07	0.08	0.11–0.75		
*81	Monoterpens fragment	0.05	0.06	0.10–0.18		
87	MBO	0.12	0.15	0.06–0.3		
*93	Toluene	0.05	0.09	0.13–1.37		
137	Monoterpens	0.06	0.06	0.06–0.25		

* Derived from 5 min hourly mass scans.

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Table 3. Quality assessment of isoprene, methanol and MVK+MACR fluxes.

Quality Tests	Passed all the tests	Failed at least one test		
		Turbulence test failed ($u^* < 0.15\,\mathrm{m\,s^{-1}}$)	LOD Test failed ($F <$ LOD)	Stationary Test failed ($\Delta s > 60\,\%$)
Isoprene Fluxes	77 %	12 %	11 %	1 %
Methanol Fluxes	78 %	13 %	10 %	0 %
MVK+MACR	40 %	20 %	37 %	3 %

Table 4. Non exhaustive overview of above-canopy isoprene fluxes in different ecosystems of the world.

Site	Method	Mean Fluxes [$\mathrm{mg\,m^{-2}\,h^{-1}}$]		Max [$\mathrm{mg\,m^{-2}\,h^{-1}}$]	Season	
Mediterranean						
Haute Provence, France downy oaks	DEC	Mean daytime: 1000 µmol $\mathrm{m^{-2}\,s^{-1}}$; 30 °C	2.0 6.6	8	Spring 2013	This study
Haute-Provence, France downy oaks	DEC	Midday:	5.4–10	10.1	Summer 2010	Baghi et al. (2012)
Western Italy, macchia ecosystem	DEC	Median daytime: 1000 µmol $\mathrm{m^{-2}\,s^{-1}}$; 30 °C	0.097/0.016/0.032 0.4		Spring 2007	Davison et al. (2009b)
Tropical						
Malaysia borneo oil plantation	DEC	Mean daytime:	9.7	28.94	Spring 2008	Misztal et al. (2011)
Malaysia Rainforest	DEC	Mean 24 h	0.93	3.7	Spring-summer 2008	Langford et al. (2010)
Central Amazon mature lowland	REA	Mean daytime:	2.4	6.1	Summer 2001	Kuhn et al. (2007)
La Selva, Costa Rica oil tree	DEC	Mean daytime:	1.3	2.9	Spring 2003	Karl et al. (2004)
Tabajos, Brazil terra firme	EC	1000 µmol $\mathrm{m^{-2}\,s^{-1}}$; 30 °C	2.4	2.0	Spring 2000	Rinne et al. (2002)
Temperate						
Central Massachusetts, mixed canopy	DEC	Mean daytime:	4.4	~ 13	Spring 2007	McKinney et al. (2011)
Germany mixed deciduous: beech, birch, oak	DEC	Mean daytime:	3.4	10.8	Summer 2003	Spirig et al. (2005)
Eastern Belgium mixed coniferous species	DEC	1000µmol $\mathrm{m^{-2}\,s^{-1}}$; 20 °C	2–3.3	7.1	Summer 2009	Laffineur et al. (2011)

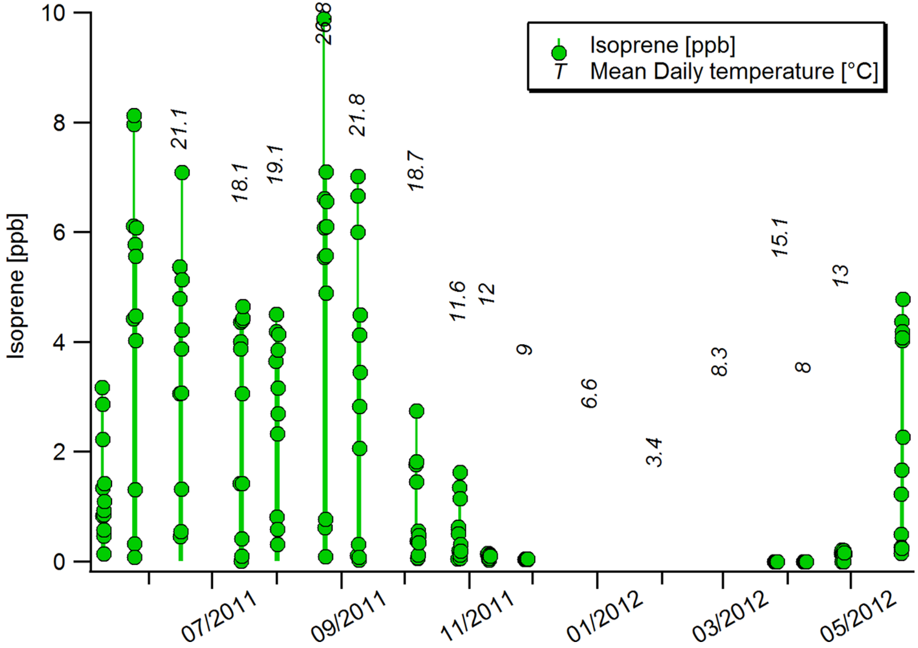

Fig. 1. Seasonal variation of isoprene concentrations (3 m above ground) at the O_3HP, May 2011 to December 2011 and from April 2012 to June 2012. Measurement derived from cartridge samples and analysed by GC-MS.

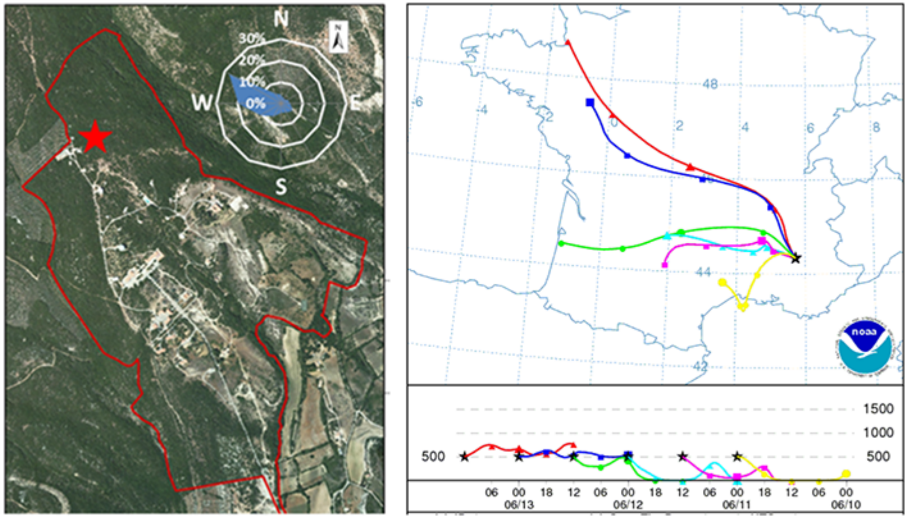

Fig. 2. (left) Satellite photo of the Observatoire of Haute Provence. The red star represents the location of the measurements. wind rose: wind direction origins (%) from the 4 until the 17 June 2012. (right) Location of the O_3HP in the southeast of France. 24 h duration backward trajectories ending at 00.00 UTC 14 June 2012 (NOAA HYSPLIT MODEL).

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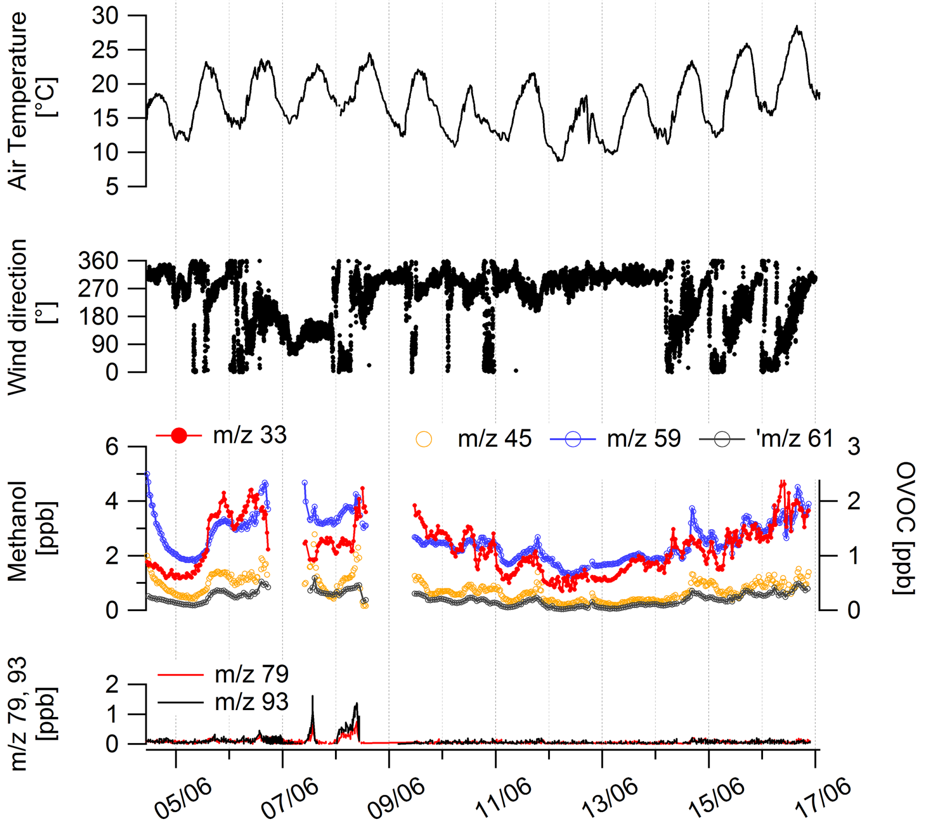

Fig. 3. Time series of benzene (m/z 79) and toluene (m/z 93), methanol (m/z 33), acetaldehyde (m/z 45), acetone (m/z 59) and acetic acid (m/z 61) recorded from 4 to 16 June above the canopy along with temperature and wind direction.

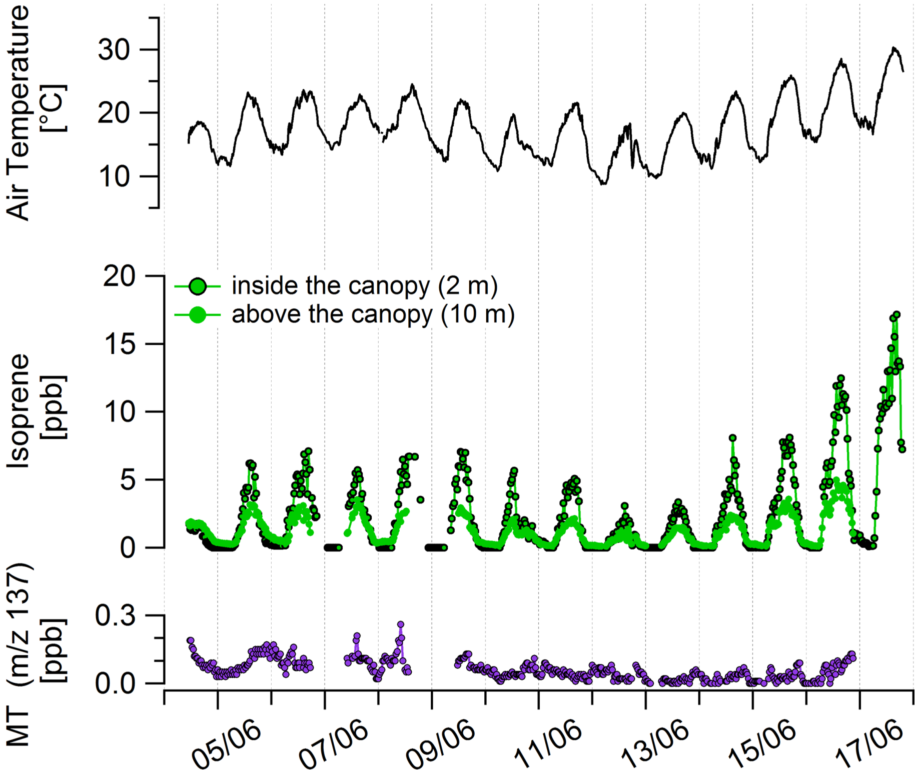

Fig. 4. Time series of total monoterpenes (MT) followed at the ion channel *m*/*z* 137, isoprene inside and above the canopy along with air temperature recorded between the 4–17 June 2012 at the O_3HP.

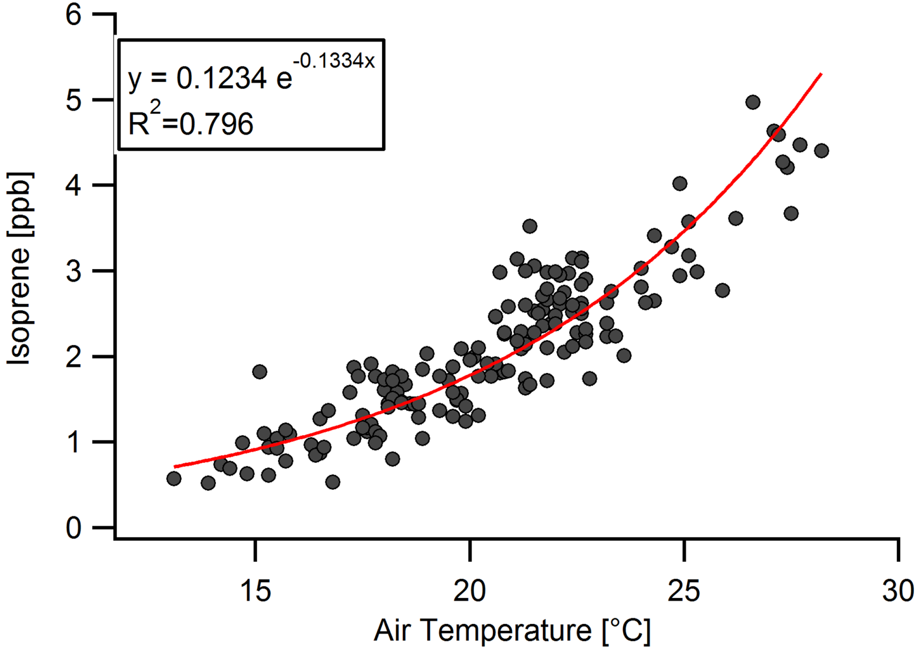

Fig. 5. Relationship between daytime isoprene mixing ratios (ppbv) at 10 m measured by PTR-MS and air temperature (°C).

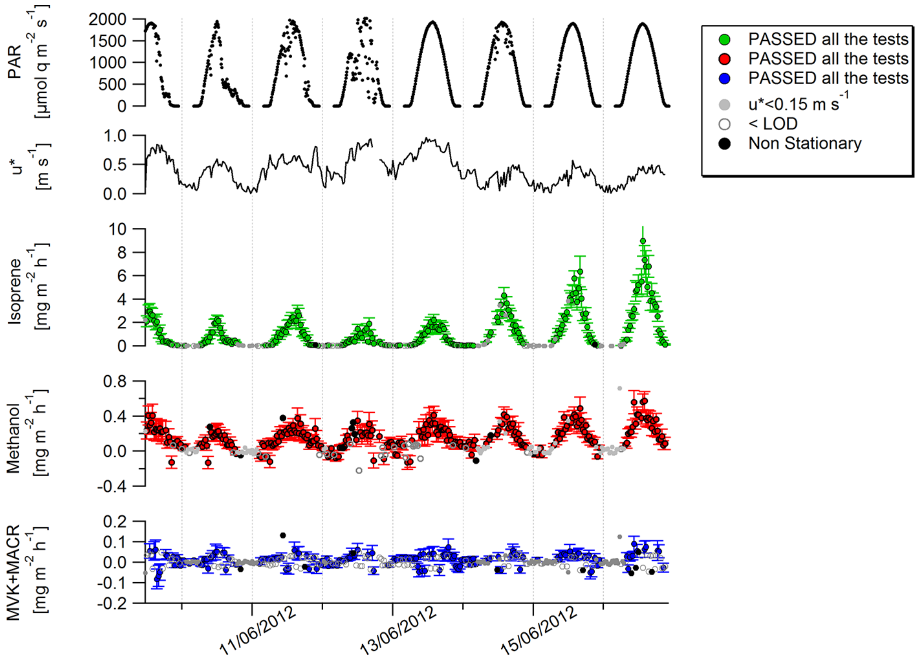

Fig. 6. Time series of methanol fluxes, isoprene fluxes, friction velocity and PAR above the canopy at the O_3HP from the 4 to the 16 June. Error bars show ± standard deviation.

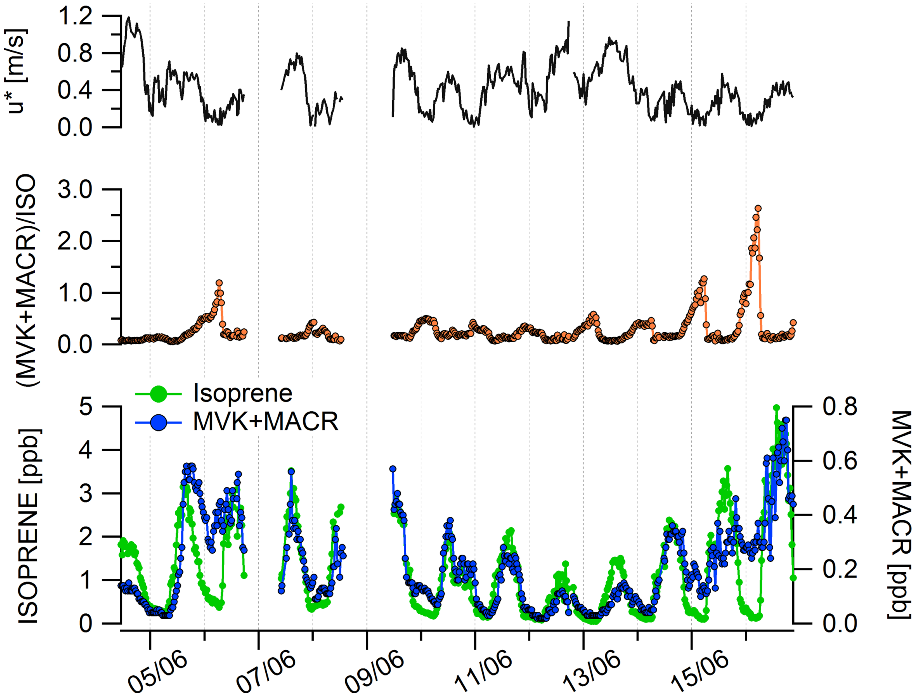

Fig. 7. Time series of MVK+MACR and isoprene concentrations, [MVK+MACR]/isoprene ratio along with friction velocity above the canopy of the O_3HP.

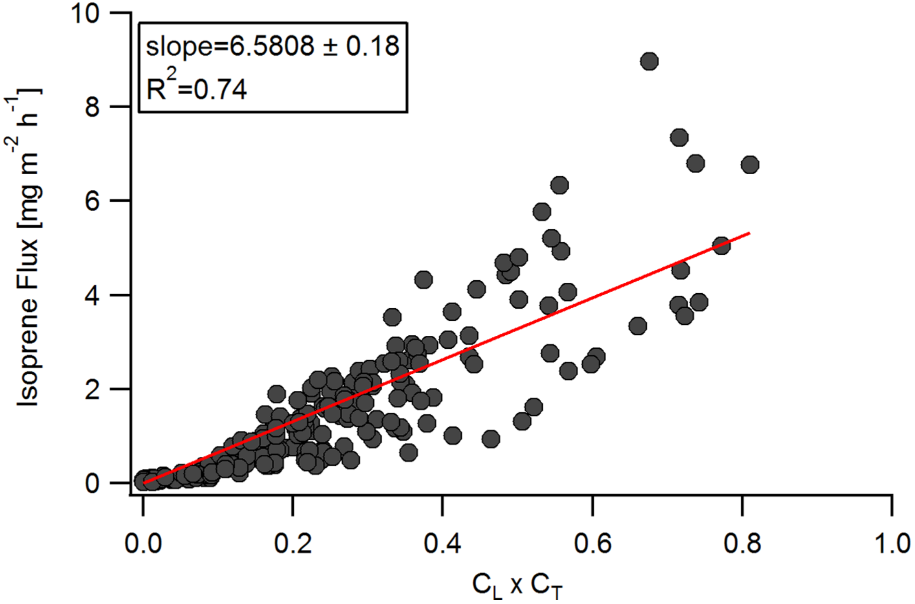

Fig. 8. (Right) Isoprene fluxes against the combined temperature and light scaling factors (C_L, C_T): $e^{\frac{C_{T1}(T-T_s)}{RTT_s}} / 1 + e^{\frac{C_{T2}(T-T_M)}{RTT_s}}$, $C_\mathrm{L} = \alpha C_\mathrm{L1} L / \sqrt{(1+a^2L^2)}$ with L = Photosynthetically Active Radiation (PAR) in µmol(photon) $\mathrm{m^{-2}\,s^{-1}}$, $a = 0.0027\,\mathrm{m^2\,s\,µmol^{-1}}$, CL1 = 1.066 units, CT1 = 95 000 $\mathrm{J\,mol^{-1}}$, CT2 = 230 000 $\mathrm{J\,mol^{-1}}$, T_S = standard temperature in Kelvin (303 K to 30 °C), T_M = 314 K.

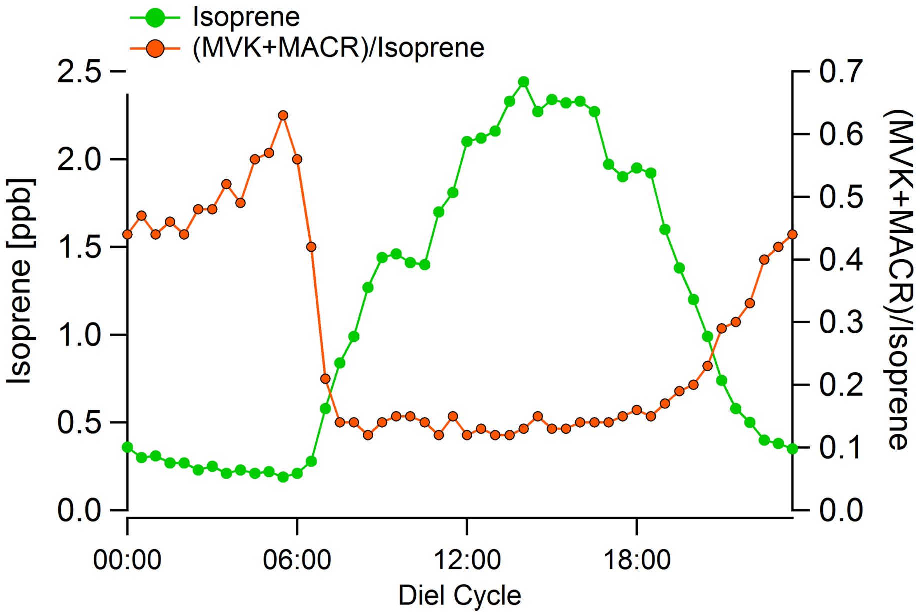

Fig. 9. Averaged diel cycles of isoprene concentrations and [MVK+MACR]/isoprene ratio measured above the canopy of the O_3HP from the 4 June to the 16 June.