

1 OH reactivity and concentrations of Biogenic Volatile Organic 2 Compounds in a Mediterranean forest of downy oak trees

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19 20 **Abstract**

21 Total OH reactivity, defined as the total loss frequency of the hydroxyl radical in the atmosphere,
22 has proved to be an excellent tool to identify the total loading of reactive species in ambient air.
23 High levels of unknown reactivity were found in several forests worldwide and were often higher
24 than at urban sites.

25 Our study presents atmospheric mixing ratios of biogenic compounds and total OH reactivity
26 measured during late spring 2014 at the forest of downy oak trees of the Observatoire de Haute
27 Provence, OHP, France. Air masses were sampled at two heights: 2 m, *i.e.* inside the canopy, and
28 10 m, *i.e.* above the canopy, where the mean canopy height is 5 m.

1 We found that the OH reactivity at the site mainly depended on the main primary biogenic species
2 emitted by the forest, which was isoprene and to a lesser extent by its degradation products and long
3 lived atmospheric compounds (up to 26% during daytime). During daytime, no significant missing
4 OH reactivity was reported at the site, neither inside, nor above the canopy. However, during two
5 nights we determined a missing fraction of OH reactivity up to 50%, possibly due to unmeasured
6 oxidation products. We confirmed that no significant oxidation of the primary species occurred
7 within the canopy: primary compounds emitted by the forest were fast transported to the
8 atmosphere. Finally, the OH reactivity at this site was maximum 69 s^{-1} , which is a high value for a
9 forest characterized by a temperate climate. Observations in various and diverse forests in the
10 Mediterranean region are therefore needed to better constrain the impact of reactive gases over this
11 area.

12

13 **1 Introduction**

14 The atmospheric oxidation of volatile organic compounds directly impacts the quality of air and
15 Earth's climate. Biogenic Volatile Organic Compounds (BVOCs) are globally the most abundant
16 class of reactive organic compounds in the troposphere. On a regional scale, such as in urban
17 environments, organic compounds emitted by anthropogenic sources may dominate the atmospheric
18 reactivity.

19 The dominant source of BVOCs is the foliage of terrestrial vegetation (Steiner and Goldstein,
20 2007), above all, trees provide the largest portion of emitted BVOCs (75%, Wiedinmyer et al.,
21 2004), followed by shrubs and grasslands and minor sources such as oceans and soils (Bonsang et
22 al., 1992; Guenther et al., 1995; Schade and Goldstein, 2001; Williams et al., 2004). Biogenic
23 VOCs include isoprenoids (isoprene, monoterpenes, sesquiterpenes etc.), alkanes, alkenes, alcohols,
24 carbonyls, esters, ethers and acids (Kesselmeier and Staudt, 1999). Among the biogenic compounds
25 isoprene and monoterpenes are the most studied, with a number of publications covering their
26 synthesis and emission factors (Laothawornkitkul et al., 2009), canopy fluxes (Rinne et al., 2002;
27 Karl et al., 2007), atmospheric mixing ratios (de Gouw and Warneke, 2007; Yáñez-Serrano et al.,
28 2015), and atmospheric role (Atkinson and Arey, 1998; Fuentes et al., 2000; Whalley et al., 2014)
29 currently available.

1 Isoprene alone represents half of all biogenic compounds emitted, and constitutes the largest single
2 source of VOCs in the atmosphere, with a current global estimate of about 500 TgC per year
3 (Guenther et al., 2006) and large uncertainties still associated (Sindelarova et al., 2014).

4 When isoprene is released into the atmosphere, it is rapidly oxidized by the hydroxyl radical (OH),
5 by ozone (O₃), by the nitrate radical (NO₃) during nighttime and occasionally by chlorine atoms.
6 The presence, position and number of double bonds determine its high reactivity as a molecule.
7 Atkinson and Arey (2003), have estimated lifetimes for isoprene ranging from a few hours with OH
8 and NO₃ to a few days with O₃, while monoterpenes and sesquiterpenes lifetimes can range from a
9 few minutes to hours with OH, NO₃ and O₃ (with mean concentrations of oxidants equal to 2 10⁶
10 molecules cm⁻³ for OH, 7 10¹¹ molecules cm⁻³ for ozone and 2.5 10⁸ molecules cm⁻³ for NO₃). By
11 comparison, anthropogenic emitted molecules have lifetimes that vary from hours to years
12 (Atkinson, 2000) which make biogenic compounds playing a dominant role in the lower
13 troposphere and atmospheric boundary layer.

14 The dominant loss of isoprene is the oxidation reaction with the OH radical, which involves the
15 formation of six isomeric peroxyradicals which in unpolluted environments further react forming
16 methyl vinyl ketone (MVK), methacrolein (MACR) and formaldehyde (HCHO) as primary
17 products in the highest yields (Jenkin et al., 1998). Other product intermediates and secondary
18 products in its oxidation pathway include hydroperoxides, hydroxyacetone, glyoxal, methylglyoxal,
19 3-methylfuran, acetic acid, glycolaldehyde and formic acid. Reactions with OH finally lead to the
20 production of carbon dioxide and water, including formation of ozone and low volatile products
21 which can partition to the particle phase. Significant production of ground level ozone on the
22 regional scale were reported by Hirsch et al., (1996); Tsigaridis and Kanakidou, (2002) for
23 northeastern USA and Europe, while production of Secondary Organic Aerosols was demonstrated
24 by Claeys et al., (2004).

25 Furthermore, isoprene and BVOCs emissions influence the oxidative capacity of the atmosphere,
26 impacting the lifetime of many species including long-lived species such as methane and
27 hydrofluorocarbons which are commonly depleted by OH.

28 Total OH reactivity is defined as the total loss of the hydroxyl radical due to the reaction with
29 ambient reactive molecules. It has demonstrated to be an excellent tool to provide indirect evidence
30 of the importance of reactive molecules in ambient air. In addition, when OH reactivity is measured
31 together with the concentration of trace compounds, it is possible to evaluate whether all the
32 reactive components in the studied environment are identified or not. Missing reactivity, which is

1 the fraction of measured OH reactivity not explained by complementary gas phase measurements,
2 has been already reported in several forested sites (di Carlo et al., 2004; Sinha et al., 2010; Nölscher
3 et al., 2013). It was found to be up to almost 90% (Nölscher et al., 2012a) and usually higher than
4 most of the urban sites investigated (Ren, 2003; Yoshino et al., 2006). Di Carlo and co-workers
5 were the first to report evidences of a missing biogenic source in a forest in Michigan, probably
6 associated to terpene-like emissions and not accounted for in trace gases analysis. Their work
7 pioneered and motivated the following studies of OH reactivity at other forested sites, including
8 boreal forests (Sinha et al., 2010; Nölscher et al., 2012a; Mogensen et al., 2011), temperate mixed
9 forests (Ren et al., 2006; Mao et al., 2012; Nölscher et al., 2013; Hansen et al., 2014 and Nakashima
10 et al., 2014), and tropical forests (Sinha et al., 2008; Ingham et al., 2009 and Edwards et al., 2013).

11 The Mediterranean alone emits about $40 \text{ t km}^{-2}\text{year}^{-1}$ of BVOCs, (as country specific emission
12 density considered for Portugal, Cyprus, Spain, Greece, Albania, Slovenia, Italy, Croatia and
13 Bosnia-Herzegovina, (Rainer Steinbrecher 2009)), its warm temperature and sunny conditions
14 trigger emissions of BVOCs, which have a clear light and temperature dependence. Global
15 warming is expected to impact the Mediterranean more than other areas in the world (Mellouki and
16 Ravishankara, 2007). Model predictions have shown that this area will be characterized by higher
17 temperatures, extended drought periods, enhanced ozone and particles levels (Giorgi, 2006; Giorgi
18 and Lionello, 2008; Giorgi et al., 2011) all which will influence BVOCs emissions in strength and
19 pattern (Laothawornkitkul et al., 2009). Such findings highlight the importance of conducting more,
20 intense and long-term field studies in the Mediterranean region.

21 Our study represents the first and only available to date study of OH reactivity in a Mediterranean
22 forest. It shows results of total OH reactivity and BVOCs concentration from a field experiment
23 conducted at two heights in the forest of the Observatoire de Haute Provence, France during late
24 spring 2014.

25 The site at Observatoire de Haute Provence (OHP) is a special forest in the Mediterranean basin,
26 located in the south east of France, poorly influenced by anthropogenic pollution and known for
27 being almost homogeneous in BVOCs emissions. The dominant tree species at the site is the downy
28 oak (*Quercus pubescens Willd.*), which has demonstrated to emit nearly exclusively isoprene in
29 large quantities (Kesselmeier et al., 1998; Genard-Zielinski et al., 2015). Recent studies at OHP
30 have shown evidences for large tree specific intra variability in emission strength, (Genard-Zielinski
31 et al., 2015) strong isoprene fluxes to the atmosphere (up $10.1 \text{ mg m}^{-2} \text{ h}^{-1}$) during summer 2010

1 (Baghi et al., 2012) and up to $9.7 \text{ mg m}^{-2}\text{h}^{-1}$ during spring 2012 (Kalogridis et al., 2014)) and low
2 intracanopy oxidation processes (Kalogridis et al., 2014).

3 OH reactivity was used as a tool to examine the reactive carbon budget, and help assess the
4 oxidative processes occurring through the canopy.

5 We measured total OH reactivity with the Comparative Reactivity Method (CRM, Sinha et al.,
6 2008) and used complementary measurements of trace gas concentrations to elucidate any missing
7 reactivity pattern. We determined the OH reactivity and the trace gases at the same time, and
8 investigated two canopy heights, one inside the forest at 2 m, a second one above the forest at 10 m.

9 **2 Methodology**

10 **2.1 Description of the field site**

11 We measured total OH reactivity and atmospheric gases concentrations at the oak observatory of
12 the field site of Observatoire de Haute Provence (OHP, <http://www.obs-hp.fr>), as part of the
13 CANOPEE project ([https://o3hp.obs-hp.fr/index.php/en/research/projects/121-canopee-anr-jc-2011-](https://o3hp.obs-hp.fr/index.php/en/research/projects/121-canopee-anr-jc-2011-en)
14 [en](https://o3hp.obs-hp.fr/index.php/en/research/projects/121-canopee-anr-jc-2011-en)). Observatoire de Haute Provence is located in the Mediterranean region, south east of France
15 ($5^{\circ} 42' 44''$ E, $43^{\circ} 55' 54''$ N, 650 m a.s.l.), with Marseille the closest largest city about 100 km
16 south (~ 1600000 inhabitants), and Manosque the closest town about 18 km south from the site (~
17 22000 inhabitants) (Fig. 1).

18 The oak observatory (O3HP, <https://o3hp.obs-hp.fr>) was installed in 2009 within the OHP site in
19 order to conduct field studies in ecology, plant phenology, microbiology and the atmosphere related
20 to the third most abundant tree species in the French Mediterranean region. A geophysical sciences
21 station (Gerard Megie) and an ICOS tower (Integrated Carbon Observation System, operative from
22 11/07/2014) also operate at OHP. The oak observatory is about 95 ha large and extends throughout
23 a deciduous ecosystem dominated by downy oaks (*Quercus pubescens Willd.*) and Montpellier
24 maple (*Acer monspessulanum L.*) which represent 75% and 25% respectively of the overstorey
25 canopy. Smokey bushes (*Cotinus coggygria Scop.*) and other grass species constitute the
26 understorey canopy. The whole canopy is about 5 m high with an average leaf area index (LAI)
27 measured during August 2010 of 2.4 (LAI-2000, Li-Cor, Lincoln, NE, USA). The climate at the site
28 is typical of the Mediterranean area, with dry and hot summers and humid cool winters.

1 Downy oak is a tree species known to emit almost exclusively isoprene (about 99%, see Genard-
2 Zielinski et al., (2015)) and due to its dominance in this forest it makes OHP a natural laboratory for
3 focused studies on isoprene.

4 Our field work took place during 29/05/2014- 12/06/2014 , as a follow up experimental study of
5 the works conducted during spring 2012 and published by Kalogridis et al., (2014) and Genard-
6 Zielinski et al., (2015).

7 **2.2 Ambient air sampling**

8 We measured the total OH reactivity together with the concentrations of BVOCs emitted by the
9 forest, their oxidation products and main atmospheric constituents. For these measurements we
10 deployed the following techniques: the Comparative Reactivity Method (CRM, home built), a
11 Proton Transfer Reaction Mass-Spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria), a Gas
12 Chromatography Flame Ionization Detector (GC-FID, Chromatotech, France), a formaldehyde
13 analyzer through the Hantzsch reaction (Aero-Laser GmbH, Germany), off-line analysis of sampling
14 tubes through Gas Chromatography Mass Spectrometry (GC-MS, 3800/2200 ion trap MS, Varian,
15 USA) and a NO_x detector (Thermo Scientific, USA).

16 We sampled simultaneously OH reactivity and concentrations of VOC through two PFA sampling
17 lines (OD 3/8'') collocated on a mast, which was erected downwind the oak observatory. The two
18 sampling lines, A and B, were directed to the main local A (Figure 1, number 4), and to a movable
19 trailer B (Figure 1, number 5), respectively. Both lines were ending with a manifold to provide the
20 sampling flows to all the instruments: sampling line A was split into lines directed to the PTR-MS,
21 the GC-FID and the Hantzsch analyser, which were all located in local A. On the other hand,
22 sampling line B was used for measuring OH reactivity and was split into a line for the zero air
23 generator of the CRM and another for the ambient air sampling of the CRM. The sampling flows
24 were driven by two pumps placed at the end of both manifolds. The flows and lines lengths were
25 adjusted in order to have a similar residence time of the species sampled through lines A and B,
26 which were respectively, 23 seconds and 13 seconds. The lines whole length was respectively 28 m
27 and 18 m for A and B; a joint union piece placed at 2 m on both lines allowed us to disconnect them
28 and perform sampling at two different heights along the forest canopy by using the same line.
29 Finally, both lines were insulated with black tubing and heated with a thermocouple type K by
30 about 1°C above ambient temperature, to prevent gases condensation. Measurements with this
31 sampling set-up were performed sequentially on different days over the campaign period

1 29/05/2014- 12/06/2014 at two heights: 2 m and 10 m. With an average canopy height of 5 m, air
2 collection conducted at 2 m and 10 m at OHP was used to elucidate the composition and reactivity
3 of air masses inside and above the whole forest.

4 Extra sampling lines were used for GC-MS offline analysis, ozone and NO_x detection.

5 An autosampler (Sypac V2, Tera Environnement, France) was used to adsorb air on packed
6 stainless steel sampling tubes with Tenax TA and Carboxen 1000 as sorbent, for GC-MS offline
7 analysis of monoterpenes levels. In this case we used an independent extra line that was placed at 2
8 m on the mast. The sampling was performed every three hours on specific days and relative
9 speciation among the detected monoterpenes (α -pinene, β -pinene, myrcene, limonene) was used to
10 determine the monoterpenes specific abundance and infer their amount from the total monoterpenes
11 concentration, which instead was measured by PTR-MS.

12 In addition, NO_x (NO+ NO₂) were sampled through an independent extra line placed on top of local
13 A, at 4.3 m from the ground, about 15 m away from the mast. Ozone was monitored by the regional
14 air quality network and its sampling line was placed a few hundred meters away from the main
15 sampling site at 4.3 m from the ground.

16 **2.3 Comparative Reactivity Method and instrument performance**

17 Measurements of total OH reactivity were performed with a Comparative Reactivity Method
18 instrument (home built CRM, see Sinha et al., (2008) and Nölscher et al., (2012b) for more details
19 on the CRM).

20 A CRM instrument consists of a glass flow reactor and a detector, in our case a commercial Proton
21 Transfer Reaction-Mass Spectrometer (PTR-MS quadrupole, Ionicon Analytik GmbH, Innsbruck,
22 Austria). The concept of CRM is to produce a competition between a reference molecule, pyrrole
23 (C₄H₅N) and reactive molecules in ambient air to react with OH radicals generated inside the glass
24 reactor. OH radicals are obtained from photolysis of water vapor with a pen ray Hg lamp which
25 emits at 184.9 nm placed inside one of the reactor arms. Pyrrole is first diluted in zero air and dry
26 nitrogen, and its concentration is monitored on the PTR-MS at the protonated *m/z* 68 (C0). When
27 the Hg lamp is switched on, pyrrole concentration decreases due to photolysis and its concentration
28 is monitored as C1. Then, the flow of nitrogen passes through a bubbler and water vapor is
29 transported to the lamp to achieve photolysis and production of OH; in this stage pyrrole reacts with
30 OH (rate coefficient= $1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 25°C, (Atkinson et al., 1984) and (Dillon et al.,

1 2012)) and C2 is monitored. A 4-way valve permits fast switches between zero air and ambient air,
2 when the latter dilutes pyrrole the competition for OH radicals takes place and C3 is the measured
3 concentration of pyrrole. C3 differs from C2 depending on the amount and type of reactive
4 molecules present in ambient air. Differences between C2 and C3 are used to determine the total
5 OH reactivity from the following equation:

$$6 \quad R_{air} = \frac{(C3 - C2)}{(C1 - C3)} \cdot k_{pyrrole+OH} \cdot C1 \quad (1)$$

8
9 Equation (1) assumes that the reaction between pyrrole and OH is in the pseudo first order kinetics,
10 *i.e.* [pyrrole] >> [OH].

11 Reactivity in ambient air is obtained every 10 minutes (calculated from 5 minutes on C2 and 5
12 minutes on C3) and raw values are corrected for humidity differences between the levels C2 and
13 C3, deviation from first order kinetics, and dilution inside the reactor (Zannoni et al., 2015).
14 Humidity differences between C2 and C3 can affect the concentration of OH radicals produced
15 inside the reactor and can lead to an underestimation or overestimation of the measured OH
16 reactivity. We generated zero air to produce C2 by sampling ambient air through a zero air
17 generator, which removes the VOCs present in ambient air and leaves the air flow with the same
18 humidity of ambient air. In our case, small differences in humidity were still observed and corrected
19 (13% decrease of the raw value).

20 We tested the performance of the CRM before and during the field campaign through injections of a
21 known amount of OH reactivity generated by external gas standards. For this purpose, we used a
22 standard of propane, which has a medium reactivity towards OH ($k_{propane+OH}=1.1 \cdot 10^{-12} \text{ cm}^3$
23 $\text{molecule}^{-1} \text{ s}^{-1}$, (Atkinson et al., 1997)); and isoprene, which instead is very reactive towards OH
24 ($k_{isoprene+OH}=1 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, (Atkinson, 1986)) and represents the main component of the
25 air parcels sampled in this specific forest. Injections were performed over a range of pyrrole/OH
26 ratio between 2 and 9, with 9 being the closest to pseudo first order kinetics regime. The reactivity
27 measured plotted versus the reactivity injected with the two mentioned standards gave a slope of
28 $1.01 \pm 0.04 (1\sigma)$ with an R^2 of 0.96 up to reactivity values of 500 s^{-1} . The correction factor (slope of
29 injected reactivity versus measured reactivity) is plotted versus the pyrrole-to-OH ratio and used to
30 correct the raw reactivity for deviations in the kinetics regime (see supplementary information). For
31 this study such correction determined a 47% decrease of the raw data of reactivity. Corrections for

1 humidity were obtained by averaging the results of three main tests conducted during the field
2 campaign and were comparable to the results obtained in the laboratory (19% standard deviation
3 among results). Calibrations of the PTR-MS for dry and wet pyrrole were carried out at the
4 beginning and end of the field campaign and showed a very good agreement between each other
5 (difference within 1% for the dry calibration factor and 4% for the wet calibration factor). It is
6 necessary to calibrate pyrrole at dry and wet conditions due to differences in sensitivity reported by
7 the PTR-MS operating at different ambient humidity (Sinha et al., 2010).

8 During the days dedicated to the sampling of trace gases, we measured OH reactivity for only five
9 days (three days inside the canopy and two days above the canopy) due to the time needed to
10 accurately test the performance of our instrument on the field, settings adjustment and tests needed
11 to process the raw data.

12 Our instrument performs measurements between the limit of detection (LoD) of the instrument (3 s^{-1}
13 1 , 3σ) up to 500 s^{-1} with an overall systematic uncertainty of 35% (1σ). More information on our
14 instrument can be found in Zannoni et al., 2015.

15 **2.4 Complementary measurements at the field site**

16 We measured the concentration of BVOCs emitted from the forest, their oxidation products and
17 main atmospheric constituents. Concentrations are used to calculate the OH reactivity at the site
18 with Eq. 2 and the species specific relative contribution.

$$19 \quad R = \sum_i k_{i+OH} \cdot X_i \quad (2)$$

20 with i being any measured compound listed in Table 1. The error on the calculated value of OH
21 reactivity is estimated by considering the propagation of the 1σ uncertainty on the rate constant of
22 reaction between OH and the measured compound and the 1σ uncertainty associated to the
23 concentration of the measured compound.

24 **2.4.1 Proton Transfer Reaction-Mass Spectrometer**

25 We used a Proton Transfer Reaction- Mass Spectrometer (PTR-MS, High sensitivity quadrupole,
26 from Ionicon Analytik, Austria) operated under standard conditions ($p_{\text{drift}}=2.2 \text{ mbar}$, $E/N=135 \text{ Td}$ (1
27 $\text{Td}=10^{-17} \text{ Vcm}^{-1}$), $T_{\text{inlet}}= 60^\circ\text{C}$) to record the concentrations of trace gases at the site, (Lindinger and
28 Jordan, 1998). We sampled the air masses in the scan mode, and inspected all species with
29 protonated mass from m/z 21 to m/z 138 with cycles of 5 minutes each. Sampling in the scan mode
30 procedure revealed to be a convenient way for analyzing unknown air parcels.

1 We calibrated the instrument using a gas calibration unit (GCU, Ionicon Analytik, Austria) with a
2 standard gas mixture (GCU, Ionicon Analytik, Austria) containing: methanol (m/z 33), acetonitrile
3 (m/z 42), acetaldehyde (m/z 45), acrolein (m/z 57), acetone (m/z 59), isoprene (m/z 69),
4 crotonaldehyde (m/z 71), methyl ethyl ketone (m/z 73), benzene (m/z 79), toluene (m/z 93), α -pinene
5 (m/z 137); see Table 2 for the list of compounds, their protonated mass, mean sensitivity from field
6 calibrations and masses LoD. Calibrations were run over the range 0-20 ppbv at the beginning and
7 at the end of the field campaign, with no significant change in the detector sensitivity (differences
8 up to 10% and for most species within 5%) therefore we used a mean calibration factor for the
9 whole campaign.

10 Volume mixing ratios for the calibrated species were obtained following the procedure of Taipale et
11 al., 2008. Mixing ratios for the non-calibrated species were obtained from the transmission curve of
12 the instrument and the species specific transmission coefficient. Correlations within mixing ratios
13 obtained from calibration and transmission coefficients for calibrated species showed a good/fair
14 agreement (R^2 for m/z 33, m/z 45 and m/z 69 respectively 0.81, 0.86 and 0.43).

15 We used a Gas Chromatography-Flame Ionization Detector to cross validate the concentration
16 obtained for isoprene, which is the dominant compound at the site, usually measured at the
17 protonated m/z 69 with the PTR-MS but often prone to fragmentation in the drift tube (see section
18 2.4.2). All the measured species, except isoprene, were not cross validated, and their mass
19 identification was conducted based on the existing literature at similar sites, *e.g.* Kalogridis et al.,
20 (2014); Holzinger et al., (2002); Warneke et al., (2001). This is the case in particular for masses
21 m/z 71 and m/z 73. The former has usually been attributed to the sum of methyl vinyl ketone
22 (MVK) and methacrolein (MACR), the most abundant oxidation products of isoprene. Recent
23 studies have highlighted that another group of compounds, the isoprene hydroperoxides
24 (ISOPOOH), mostly originated from isoprene oxidation in unpolluted environments can also
25 fragment at m/z 71 in the PTR-MS (Liu et al., 2013 and Rivera-Rios et al., 2014). Since we did not
26 separate between these compounds, and conducted our field work in an unpolluted environment,
27 where the ISOPOOH might have been produced, we will refer hereinafter to m/z 71 as the sum of
28 the isoprene oxidation products ISOP.OXs: methyl vinyl ketone (MVK) + methacrolein (MACR) +
29 isoprene hydroperoxides (ISOPOOH). Mass-to-charge 73, here reported as methyl ethyl ketone
30 (MEK) and calibrated as such, can have several interferences. Among the possible interferences we
31 speculate the presence of methylglyoxal, a compound generated during the degradation path of
32 isoprene, which is the most abundant compound measured at our site. A detailed discussion about

1 this compound and possible interferences at our site will be available in Yanez-Serrano et al., now
2 in preparation.

3 2.4.2 Gas Chromatography-Flame Ionization Detector

4 A gas chromatograph equipped with a flame ionization detector (GC-FID, airmoVOC C2-C6,
5 Chromatotec, Saint Antoine, France) was deployed to sample hydrocarbons in the fraction C2-C6,
6 with a time resolution of 30 minutes (10 minutes sampling followed by 20 minutes analysis). The
7 instrument sampled ambient air with a flow rate of 18 sccm via a stainless steel inlet. Ambient air
8 passed through a Nafion dryer, then to a preconcentration trap cooled down to -8°C, filled with
9 Carboxen, Carbopack B and Carbotrap C, and finally thermodesorbed at 220°C and injected on-
10 column into a metal capillary column (Porous Layer Open Tubular Column PLOT, Al₂O₃/KCl; 0.53
11 mm inner diameter and 25 m length, Varian Inc, USA). Calibrations were performed twice per
12 week with a certified standard VOCs mixture (National Physical Laboratory, UK). The overall
13 uncertainty was estimated to be 15% (1σ). Correlation between isoprene measured by GC-FID and
14 *m/z* 69 identified as the protonated isoprene mass over thirty minutes averaged data showed
15 differences within 14% among the two instruments ($\text{isoprene}_{\text{GC-FID}}=0.86(\text{isoprene}_{\text{PTR-MS}})$, $R^2=0.93$).

16 2.4.3 Formaldehyde analyzer

17 Formaldehyde (HCHO) was measured with a commercial Aerolaser analyzer (AL-4021, Aero-
18 Laser GmbH, Germany). The technique, a continuous liquid fluorimetry, has been described in
19 detail elsewhere (Dasgupta et al., 1988). Briefly, gaseous HCHO was scrubbed into a diluted
20 sulfuric acid solution in a stripping coil thermostated at +10 °C. A fluorescent compound was
21 quantitatively produced at +70 °C by the reaction of the liquid solution with the Hantzsch reagent
22 (*i.e.* a dilute mixture of acetyl acetone, acetic acid, and ammonium acetate) and subsequently
23 detected at 510 nm.

24 The working conditions applied to the AL 4021 for this study were similar to those applied
25 previously for the same device in two HCHO studies conducted in Antarctica (Preunkert and
26 Legrand, 2013; Preunkert et al., 2014). In brief, liquid reagents were prepared from analytical grade
27 chemicals (Merck, USA) and ultrapure water (18 MOhm, TOC<1 ppbv, Elga Labwater); the air
28 flow was kept at 1000 sccm which ensured a stripping efficiency of more than 99%. Raw data were
29 collected with a time resolution of 30 s. Gas standard calibrations and background levels took 50
30 min and 25 min and were performed every 12 h and 3 h, respectively. A mean detection limit of 42
31 ± 16 pptv is calculated as twice the standard deviation of the raw data (30 s) obtained during the

1 121 zero measurements made during the campaign, which was consistent with the typical LoD
2 achieved (~ 30 pptv) with the same analyzer in the previous studies above cited.

3 To minimize the effects of temperature changes on the field (see details in Preunkert et al., (2013)),
4 the instrument was placed in a thermostated box at 24°C. A Teflon filter (47 mm diameter) was
5 placed on the sampling line between the manifold (see section 2.2) and the HCHO analyzer to
6 prevent large particles (*e.g.* plant debris) entering the instrument. A comparison conducted on the
7 field between line A (see section 2.2, including the Teflon filter) and a 3 m long PTFE line (OD
8 1/4") connected directly to the analyzer confirmed that no significant contamination or loss of
9 HCHO was present with this set up.

10 2.4.4 NO_x analyzer

11 Nitrogen oxides were measured with a commercial instrument (17i model, Thermo Scientific,
12 USA), based on chemiluminescence. Its calibration was performed after the field campaign, where a
13 LoD of 0.3 ppbv (2σ) and a precision of +/- 0.4 ppbv were estimated.

14 Nitrogen oxides were sampled at 15 m from the main sampling site, hence we assumed that their
15 concentration inside and above the canopy was not affected by any significant change.

16 2.4.5 GC-MS offline analysis

17 Adsorbing stainless steel sampling tubes with Tenax TA and Carbopack X as sorbents were used to
18 sample monoterpenes as α-pinene, β-pinene, β-myrcene and limonene for off-line analysis with a
19 Gas Chromatograph-Mass Spectrometer (GC-MS, 3800/2200 ion trap MS, Varian, USA). Sampling
20 was conducted at ambient temperature with an autosampler (Sypac V2, Tera Environnement,
21 France) every three hours, tubes were then stored at 4°C and analyzed within one month in the
22 laboratory. Ozone was removed from the tubes prior to the sampling procedure by using MnO₂-
23 coated copper nets, according to the procedure reported in Larsen et al., (1997). Concentrations of
24 individual monoterpenes were then used to infer their relative abundance from the total
25 monoterpenes concentration obtained with the PTR-MS and calculate their contribution to the OH
26 reactivity.

27 2.4.6 O₃, CH₄, CO

28 Ozone is constantly monitored at OHP from the regional Air quality network Air-Paca, France
29 (<http://www.atmopaca.org/>). The monitor is placed in a container located at a distance of a few

1 hundred meters from the sampling site. Methane and carbon monoxide mean concentrations were
2 derived based on measurements conducted during spring 2012 and considered to be 1900 ppbv and
3 108 ± 16 ppbv respectively.

4 2.4.7 Meteorological parameters

5 Meteorological parameters such as temperature, relative humidity (CS215, Campbell Scientific,
6 UK), Photosynthetic Active Radiation (PAR) (LI-190, Li-Cor, Lincoln, NE, USA) , wind speed
7 and wind direction were acquired through sensors already available at the measurements site (O₃HP
8 website: <https://o3hp.obs-hp.fr/index.php/fr/>). In this work we used data collected at 2 m and at 6 m
9 to help with discussion of the results inside the canopy and above the canopy respectively.

10

11 3 Results

12 3.1 Trace gases mixing ratio

13 During the first campaign week we observed some peaks of contamination for about one hour every
14 morning due to emissions from car exhausts. Such data points were filtered from the data sets that
15 will be discussed in this section.

16 Figures 2 and 3 illustrate diurnal profiles and time series of m/z 69, identified as isoprene, its main
17 degradation products m/z 71, identified as MVK+MACR+ISOPOOH and here referred as
18 ISOP.OXs (isoprene oxidation products), and formaldehyde (HCHO), together with meteorological
19 parameters as air temperature and PAR, at both sampling heights. Figure 2 shows that these
20 compounds have clear diurnal profiles, but while isoprene has similar profiles to PAR and
21 temperature, its degradation products tend to increase after isoprene increases, which confirms the
22 main secondary origin of such species. Isoprene mean values peak when temperature is highest:
23 during the afternoon inside the canopy (2 PM, left panel) and during the late afternoon above the
24 canopy (8 PM, right panel). The latter peak measured so late above the canopy is driven by the
25 enhanced ambient temperature measured on 8/06/2014 (represented in fig. 6). Formaldehyde
26 mixing ratios are higher than m/z 71 for both heights; inside the canopy its profile is clearly diurnal,
27 while above the canopy it looks more stable, mostly because of the higher nighttime level reached
28 on 8/6/2014, see Fig. 3.

29 Time series are reported in Fig. 3 for the whole campaign period, from 29/05/2014 to 12/06/2014,
30 with different colors indicating the air masses sampled at 2 m (data reported with the green line),

1 and at 10 m (data reported with the blue line). All species show a progressive increase towards the
2 end of the field campaign, when air temperature at the site was higher compared to the first days of
3 measurements. Data collected between 07/06/2014-12/06/2014 above and inside the canopy can be
4 directly compared, based on similar conditions of temperature and solar radiation. Maximum values
5 for isoprene inside and above the canopy are close (maximum at 10 m is 19 ppbv, maximum at 2 m
6 is 23 ppbv) and small differences can be explained mainly on a dilution basis, a better mixing of air
7 masses reached above the canopy height due to the sparse canopy structure. Interestingly, high
8 levels of m/z 71 and HCHO were recorded during the nights between 07/06 and 08/06 and between
9 11/06 and 12/06. Such high nighttime concentrations are also observed for other chemical species
10 (see text below). Figure 4 illustrates time series for masses m/z 33, m/z 45, m/z 59, m/z 73 and m/z
11 137; identified respectively as methanol, acetaldehyde, acetone, methyl ethyl ketone and sum of
12 monoterpenes. Monoterpenes are primary emitted biogenic compounds while the other species can
13 have both primary and secondary origins (Jacob et al., 2002; Jacob et al., 2005 and Millet et al.,
14 2010). Methanol has a daily maximum of 14 ppbv (inside the canopy), which makes it the second
15 most abundant compound measured at OHP after isoprene (daily max inside the canopy 23 ppbv),
16 followed by acetone, acetaldehyde, monoterpenes, ISOP.OXs, toluene and benzene, in order of
17 abundance (Table 3). Over 24 hours, methanol is instead the first most abundant compound at OHP,
18 followed by isoprene, acetone and acetaldehyde. Both methanol and isoprene have a diurnal profile,
19 but methanol has a longer lifetime compared to isoprene (estimated to be 12 days and 1.4 hours
20 respectively, see Atkinson and Arey, 2003) therefore over 24 hours the former shows less
21 variability in the atmosphere.

22 During the two nights mentioned above (08/06 and 12/06) the concentration of the oxygenated
23 compounds was higher compared to the other nights. More discussion on this behaviour is provided
24 in section 3.4.

25 Anthropogenic hydrocarbons mixing ratios in the fraction C2-C6 were individually below 1.5 ppbv,
26 with ethane being the most abundant (mean over the campaign= 0.9 ± 0.2 ppbv), followed by
27 acetylene, ethylene and iso-pentane. Anthropogenic tracers measured by PTR-MS showed the same
28 trend and confirmed the poor anthropogenic influence at this forested site: benzene maximum was
29 0.41 ppbv, the mean over 24 hours was 0.04 ppbv, toluene was maximum 0.69 ppbv and its mean
30 over 24 hours was 0.05 ppbv. Concentrations of NO and NO₂ were maximum 1.7 ppbv and 5
31 ppbv with a mean value of 0.45 ± 0.38 ppbv and 3.4 ± 0.49 ppbv during the whole campaign,
32 respectively. Ozone concentration ranged within 21-78 ppbv, with a mean value of 47 ± 10 ppbv.

1 The highest values of ozone, often observed in the afternoon, are due to regional transport from air
2 masses impacted by anthropogenic emissions (usually from the area of Marseille). Therefore the
3 site can be, depending on air mass origin, regionally influenced by anthropogenic plumes.
4 Nevertheless, the low levels of anthropogenic primary compounds suggest that this anthropogenic
5 contribution is low. Additionally, we noticed that, during the campaign the dominant wind direction
6 was from north, hence the site was mostly exposed to the influence of the oak forest.

7 Values discussed herein can be compared to values measured during the field work conducted at
8 OHP during spring 2012 (compare table 3 in this work with table 2 in Kalogridis et al., (2014)).
9 Both field works were conducted during the same season (late spring, beginning of June), with the
10 site exposed to slightly different temperature levels (daily maximum in 2012 30°C, daily maximum
11 in 2014 31.5°C), but the sampling was performed in different portions of the forest, with a distance
12 between each other of a few hundreds of meters. It is interesting to notice that atmospheric levels of
13 VOCs are close only for anthropogenic species while all biogenic species and oxygenated
14 compounds have almost doubled from 2012 to 2014. The same isoprene-temperature dependence
15 was achieved during the two experimental works, which demonstrates that the higher mean
16 concentration of biogenic compounds observed in 2014 was probably due to the higher mean
17 temperature during the second campaign.

18 **3.2 Total OH reactivity**

19 Figures 5 and 6 report thirty-minute averaged values of total OH reactivity inside and above the
20 canopy during 11-12/06/2014 and 7-8/06/2014, respectively, with the black line and associated
21 error bars (overall uncertainty 35%, 1σ). At 2 m OH reactivity varied between the instrumental LoD
22 up to 69 s^{-1} , and was on average $26 \pm 19 \text{ s}^{-1}$. At 10 m it varied between the LoD and a maximum of
23 68 s^{-1} and was on average $24 \pm 14 \text{ s}^{-1}$. OH reactivity had the same trend of temperature and PAR,
24 with a diurnal profile that demonstrates its dependency on the emission and profile of biogenic
25 compounds emitted by the forest, released when sunrise started and temperature increased. During
26 11/06/2014 OH reactivity started to increase at 6:00 AM (CEST) when the sun rose up and it
27 reached a maximum around 10.30 AM, then again around 4:00 PM, associated to more intense solar
28 radiation. It decreased after sunset, at 8:00 PM when also temperature and light reduced.
29 Remarkably, the profile of OH reactivity resembled the one of isoprene concentration, except for
30 the morning peak (10.30 AM) which could be possibly associated to the release in the atmosphere
31 of oxygenated molecules. The OH reactivity sampled at 10 m had also a diurnal profile. Compared

1 to the OH reactivity measured at 2 m, here the profile resulted slightly shifted due to enhanced
2 ambient temperature during the late afternoon on both sampling days. On 7/06/2014 it started to
3 increase at 6.30 AM, had its maximum around 6.30 PM and decreased at 9:30 PM. On 8/06/2014 it
4 increased at 6:30 AM and reached its maximum at 2.15 PM.

5 **3.3 Measured and Calculated OH reactivity**

6 We compared the total OH reactivity measured with the CRM instrument with the one calculated
7 from the concentrations of the measured trace gases and their rate coefficients with OH. Table 1
8 illustrates the classes and species measured by ancillary methods deployed on the field and used to
9 compute their relative contribution to the OH reactivity. It has to be noticed that due to instruments
10 availability and the relative homogeneity of species emitted by the forest, only a few primary
11 emitted compounds and main atmospheric species were measured and used to calculate the OH
12 reactivity. For methane and carbon monoxide we derived a mean value from measurements run in
13 2012, respectively 1900 ppbv and 180 ppbv. The OH reactivity given by the oxidation products of
14 isoprene (ISOP.OXs) was calculated from their measured total concentration and the mean rate
15 coefficient of the reaction of MVK and MACR with OH. Since we did not separate the different
16 ISOP.OXs, we could not determine the exact fraction of MVK and MACR contributing to the OH
17 reactivity, which leads to a slight overestimation of the calculated reactivity (Rivera-Rios et al.,
18 2014); in our case such overestimation is not significant due to the higher abundance of isoprene.

19 The calculated OH reactivity was between 5 and 58 s⁻¹ and on average 24 ± 19 s⁻¹ between 11-
20 12/06/2014 at 2 m inside the canopy. At 10 m, above the canopy height, it varied between 3 and 55
21 s⁻¹, being on average 19 ± 12 s⁻¹.

22 Figures 5 and 6 show the covariation between measured (black line) and calculated (green line) OH
23 reactivity during 11-12/06/2014 at 2 m and during 7-8/06/2014 at 10 m, with associated error bars
24 (35% for the measured reactivity and 25% for the calculated reactivity, 1σ).

25 For both time series, during daytime, inside and above the canopy height, the measured OH
26 reactivity agreed very well with the calculated one within the instrumental uncertainties. Since there
27 was not a significant difference between the two values we can conclude that no significant missing
28 reactivity was observed in this specific ecosystem in the Mediterranean basin during our
29 measurement campaign. In addition, the precise characterization of the composition of air even at
30 10 m height corroborates the weak oxidation of primary compounds within the canopy (Kalogridis
31 et al., 2014).

1 Simultaneous ancillary measurements of trace gases permit to resolve the total OH reactivity into
2 the relative contributions of the individual species. Figures 7 and 8 show the breakdown of reactive
3 components in OH reactivity during daytime and nighttime at the two heights considered. In all
4 cases the dominant reactive species was isoprene. Isoprene is among the most reactive compounds
5 towards OH, the most abundant compound in this forest and nearly the only compound emitted by
6 downy oak trees which constitute the large majority of tree species accounted in this ecosystem.
7 Hence, we expected its large contribution to the reactivity. At 2 m, isoprene represented from 28%
8 to 83% of the total OH reactivity during nighttime (total mean 6 s^{-1}) and daytime (total mean 29 s^{-1})
9 respectively. At 10 m, it constituted from 24% during nighttime to 74% during daytime of the total
10 reactivity (total means 6 s^{-1} and 20 s^{-1} , respectively). The impact of isoprene on OH reactivity
11 between the two heights of sampling differs only of 9%. If we consider that, at 2 m the data of
12 alkanes+alkenes are missing and similar air temperature was measured at the two heights (30°C
13 temperature maximum at 2 m, and 32°C maximum at 10 m), we can conclude that no substantial
14 difference in the atmospheric composition in terms of reactive gases existed between the two
15 heights of sampling. Inside the canopy during daytime, all the measured species apart from
16 isoprene, contributed in total to about 17% to the OH reactivity. Carbon monoxide, HCHO and NO_2
17 were the second most important species accounting for 3% each, followed by acetaldehyde,
18 MVK+MACR and monoterpenes with 2% each and all the other compounds less than this. During
19 nighttime, the concentration of isoprene reduced to a few pptv and other species such as CO and
20 methane which are more stable in the atmosphere became more important, contributing to 16% and
21 5% respectively. Formaldehyde, NO_2 , acetaldehyde, MVK+MACR and monoterpenes represented
22 respectively 11%, 16%, 8%, 5% and 4%. Above the canopy during daytime the second most
23 reactive species were CO, NO_2 , HCHO and MVK+MACR (5%, 5%, 4% and 3%). Still above the
24 canopy but during nighttime, CO, NO_2 , HCHO, alkanes+alkenes, MVK+MACR, methane and
25 acetaldehyde weighted respectively 17%, 15%, 14%, 6%, 5%, 5% and 5%. Monoterpenes weighted
26 about 2-1% during daytime and 4% during night in both cases. Monoterpenes are also very reactive
27 BVOCs towards OH, when present in the atmosphere they can compete with isoprene in terms of
28 reactivity. At OHP, monoterpenes mixing ratios were low (see Table 3), they did not constitute a
29 major class of compounds in the area and by consequence their contribution to the OH reactivity
30 was poor.

1 3.4 Nighttime missing reactivity

2 During the nights between 07/06/2014 and 08/06/2014 and between 11/06/2014 and 12/06/2014,
3 the measured total OH reactivity and the calculated reactivity reported some discrepancies (Fig. 5
4 and 6). For the results above the canopy such discrepancy was visible around midnight, and
5 significant differences were observed from 1 AM to 4.30 AM (Fig. 6). Inside the canopy, the signal
6 of total OH reactivity started to scatter around 11.30 PM, then again at 2 AM and decreased back to
7 the signal of calculated OH reactivity around 4.30 AM (Fig. 5). Both differences were respectively
8 13- 14 s⁻¹ and accounted for a fraction higher than 50% of missing OH reactivity. Such values of
9 missing reactivity are comparable to values of total OH reactivity measured in boreal and temperate
10 forests (Sinha et al., 2010; Ren et al., 2006).

11 To investigate the molecules responsible for the missing OH reactivity, we examined the variability
12 of the calculated and measured OH reactivity, along with primary biogenic compounds,
13 anthropogenic tracers, OVOCs and ozone concentrations, and ISOP.OXs/isoprene ratio. It is
14 striking noticing that whereas isoprenoids exhibited a regular diurnal cycle, all OVOCs showed
15 increased nighttime values (Fig. 3 and 4). Species profiles as reported in Fig. 3 show that on
16 07/06/2014 ISOP.OXs and HCHO started to increase during the day, around 1 PM, reached a
17 maximum around 7.30 PM and then decreased during the night. While isoprene concentration is
18 flatter much faster due to its higher reaction rate, its oxidation products reacted slower, which
19 explains the higher ISOP.OXs/isoprene ratio observed. Indeed, higher variability was observed on
20 short time scale for isoprene compared to ISOP.OXs (0.9 and 0.5 respectively, relative standard
21 deviation over the mean value during 07/06/2014). The ISOP.OXs/isoprene ratio had the same
22 magnitude and trend for both missing reactivity events and reached a maximum during these two
23 specific nights compared to the rest of the campaign period (Fig. 3). Interestingly,
24 ISOP.OXs/isoprene increases when ozone decreases, especially for measurements at 10 m (Fig. 9
25 and 10). Profiles of other measured OVOCs (*m/z* 45, *m/z* 59, *m/z* 73, Fig. 4) show higher
26 concentrations around midnight of both nights, suggesting an accumulation of oxygenated
27 compounds and an intense nighttime chemistry. Indeed, meteorological parameters as wind speed
28 and wind direction for data collected at 10 m help to notice that during the night between
29 07/06/2014 and 08/06/2014 the wind blew from the same direction with low speed, suggesting more
30 stable meteorological conditions which could have favoured nighttime chemistry (Fig. 10). Daytime
31 air temperature on these two days was also the highest registered over the whole measurement
32 campaign (Fig. 3). During nighttime, the atmospheric boundary layer is shallower, producing two

1 main effects evident in Fig. 9 and 10; on one hand it favors ozone deposition on leaves surface,
2 which could be the main reason of the observed decrease of ozone concentration; on the other hand
3 it concentrates the atmospheric species present in ambient air, resulting in higher concentration of
4 the compounds more stable in the atmosphere.

5 Several evidences make us believe that the production of OVOCs was linked to the oxidation of
6 biogenic molecules. First, common anthropogenic tracers such as acetonitrile and benzene did not
7 show any particular increase during these events, supporting the idea that such nighttime higher
8 concentrations of oxidized compounds in the atmosphere was associated to local drivers rather than
9 transport. Secondly, we observed an increase in atmospheric levels of some masses measured by the
10 PTR-MS and not used before to calculate the OH reactivity, such as: m/z 47, m/z 61, m/z 75, m/z 83,
11 m/z 87 and m/z 101. According to the existing literature, these protonated masses can be identified
12 as oxidation products resulting from the degradation of isoprene and associated respectively to:
13 formic acid, acetic acid, hydroxyacetone, 3-methylfuran and other unsaturated C5, methacrylic acid
14 and isoprene hydroperoxides (Warneke et al., 2001; Holzinger et al., 2002). We estimated roughly
15 the contribution of such species to the calculated OH reactivity and found out that only a small
16 fraction of the missing OH reactivity could be explained. Therefore there must be other unmeasured
17 species that were formed locally, very likely OVOCs that were present during those nights.

18 Gas phase chemistry during nighttime is usually initiated by ozone and the nitrate radical. The low
19 levels of NO_x observed at the site (nighttime NO was maximum 0.8 ppbv and on average $0.14 \pm$
20 0.13 ppbv) indicate that nitrate chemistry is not a probable source of such oxidized compounds; on
21 the other hand ozone isoprene chemistry is slow and cannot explain alone their production in the
22 gas phase (isoprene lifetime with nitrate is 1.6 hours while with ozone is calculated to be 1.3 days
23 (Atkinson and Arey, 2003)). If the unmeasured OVOCs were neither generated exclusively from
24 isoprene, nor had anthropogenic precursors, we speculate that these unmeasured OVOCs must have
25 been a combination of higher generation products derived from isoprene oxidation and OVOCs
26 resulting from reactive primary biogenic precursors, other than isoprene, and more reactive towards
27 ozone. We can expect that these biogenic precursors were larger molecules that could not be
28 measured by our instrumentation.

29 Holzinger et al., (2005) measured a whole class of oxidation products in a pine forest and suggested
30 that they must have formed from reactions of ozone with very reactive terpene-like compounds. He
31 estimated these compounds to be emitted approximately 6-30 times more than the emission of the
32 observed monoterpenes above his forest. Karl et al., (2005) have identified the same oxygenated

1 compounds for different pine species and speculated their production at the leaf level, rather than in
2 the gas phase. Recent experiments on leaves of tobacco plants have identified the unsaturated
3 semivolatile compounds undergoing reactions on the leaves surface (Jud et al., 2015). Those
4 compounds once deposited on the leaves quickly undergo surface oxidation reactions with ozone
5 releasing volatile products into the gas phase. Oxidation reactions are favored by higher ambient
6 RH, high ozone levels and can also occur when leaves stomata are closed. Measuring the species
7 initiating these surface reactions is extremely difficult with the instruments we had on the field,
8 therefore we do not have more clues to support this hypothesis nor exclude it has occurred in the
9 forest of OHP. Focused studies on the leaves of downy oak trees with branch enclosure techniques
10 would be of help to elucidate it.

11 **3.5 OH reactivity at other biogenic sites**

12 Our results of reactivity from OHP constitute the first data set of total OH reactivity measured in a
13 Mediterranean forest. Nevertheless, several observations to study the emissions from different plant
14 species and their evolution due to natural factors such as light and air temperature in other forested
15 sites exist to date. OH reactivity observations have been of great help in the years to elucidate the
16 presence of unknown compounds and to eventually assess BVOCs oxidation patterns which were
17 not before characterized (Nakashima et al., 2012; Nölscher et al., 2014). In addition, biogenic
18 species constitute a class of compounds with the highest reactivity towards the hydroxyl radical.
19 OH reactivity during springtime and summertime in forests is usually higher than in metropolitan
20 areas which are often polluted by less reactive hydrocarbons.

21 Figure 11 illustrates all the existing studies of OH reactivity conducted in biogenic environments
22 with their corresponding references. Colored bars show the range of reactivity measured at the site;
23 while colors refer to different types of climatic zones to which the studied forests belong. The
24 reader has to notice that not all the studies were carried out using the same method (see figure's
25 caption for more details).

26 The forest at OHP is among the investigated biogenic sites producing the highest OH reactivity
27 worldwide. The only two sites where a higher reactivity was reached is the tropical rainforest of
28 Borneo (Edwards et al., 2013), where a maximum of 84 s^{-1} was reported and the tropical rainforest
29 of Suriname with a maximum of 72 s^{-1} (Sinha et al., 2008) . Tropical forests are usually more
30 heterogeneous in plants species and BVOCs emission patterns compared to the forest at OHP,
31 which is particularly homogeneous also compared to other Mediterranean forests. In Borneo, the

1 dominant primary species to the OH reactivity was also isoprene (relative contribution of 36.8%),
2 but terpenes made up 7% and the largest portion of reactivity was attributed to the oxidation
3 products of BVOCs and products intermediates (47.1%). In conclusion, on one hand the intense
4 temperature and solar radiation result in similar emission strength and reactivity, while on the other
5 hand, biodiversity and canopy structure draw the major differences between the two sites. Indeed,
6 the forest at OHP besides being homogeneous is also shorter and sparser compared to tropical
7 forests, such structure allows a better mixing of the air masses and a faster transport of the primary
8 species to the atmosphere.

9 By comparison, the investigated mixed temperate forests and boreal forests produced lower OH
10 reactivity, which can also be attributed to the lower temperature and less intense solar radiation
11 leading to weaker emissions from the local canopies.

12

13 **4 Summary and conclusion**

14 During late spring 2014 at the downy oaks forest of the site Observatoire de Haute Provence we
15 found that the total OH reactivity was maximum 69 s^{-1} at 2 m (inside the canopy), and 68 s^{-1} at 10 m
16 (above the canopy). Interestingly, during daytime, at both heights the measured OH reactivity was
17 in good agreement, within the measurements uncertainties, with the calculated OH reactivity
18 obtained from the suite of measurements of trace gases concentration available during our field
19 experiment. Hence, we did not observe any missing OH reactivity neither inside nor above the
20 forest.

21 In addition, considered the homogeneity of the forest and strong reactivity of isoprene, we expected
22 isoprene to be the species contributing mostly to the OH reactivity, at least for measurements at 2 m
23 high. We found indeed that inside the canopy during daytime, isoprene contributed to the OH
24 reactivity at 83%, followed by CO, NO₂ and HCHO. Above the canopy height, isoprene made up to
25 74%, followed by CO, NO₂, HCHO and MVK+MACR. Such results indicate that there was not a
26 significant difference in the speciation inside and above the canopy. During nighttime, when
27 isoprene emissions stopped and atmospheric concentrations were a few pptv, long lived species
28 such as CO and methane contributed to about 16-17% and 5% for both inside and above the canopy.
29 Still, even by night, isoprene accounted for the largest portion of OH reactivity.

30 The low levels of isoprene oxidation products observed during the day indicate that the intracanopy
31 oxidation is low, and almost all the isoprene emitted by the canopy is transported to the atmosphere,

1 which confirms the previous experimental work on isoprene fluxes conducted during spring 2012.
2 The fact that no missing OH reactivity was observed, especially above the canopy, additionally
3 corroborates the fact that no significant unmeasured compound, product of the oxidation of
4 isoprene, was present.

5 During the nights between 07/06/2014-08/06/2014 and 11/06/2014-12/06/2014 from sampling
6 above and inside the canopy respectively, the total OH reactivity we measured was significantly
7 higher compared to the calculated OH reactivity. Such missing reactivity accounted for more than
8 50% and can be explained by locally produced unmeasured oxidation products. We speculate that
9 unmeasured OVOCs represent a mixture of species including higher generation products resulting
10 from isoprene oxidation and products of the reaction between reactive biogenic precursors and
11 ozone.

12 Our work represents the first and unique data set to date of total OH reactivity measured in a
13 Mediterranean forest. In a worldwide perspective, the investigated forest of downy oaks at OHP
14 produces an OH reactivity among the highest measured. Remarkably, only tropical forests showed
15 to be as much reactive as OHP. Lower OH reactivity was measured in boreal and mixed temperate
16 forests, due to the lower temperature and solar radiation and possibly to the more heterogeneous-
17 like forests (*i.e.* less abundance of isoprene).

18 The Mediterranean region is rich in biodiversity, and biogenic activity is enhanced by its
19 characteristic climate. Out of 2 million km² of surface only about 100 thousands remain undisturbed
20 by human activity. We expect therefore that OH reactivity in the Mediterranean can vary much
21 depending on the type of vegetation, its extension and interaction with pollutants derived by human
22 activity. In addition, the Mediterranean is also a hotspot for climate change. This issue will certainly
23 impact the biogenic emissions strength and pattern which therefore will influence the total OH
24 reactivity. We would therefore pose the interest with our work to initiate studies of OH reactivity
25 and BVOCs levels at diverse biogenic sources in the Mediterranean area for extensive periods.

26

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Table 1. Measured species (except for CO and methane whose concentrations were assumed) used for calculating OH reactivity.

Family group	Species name
alkanes	methane; ethane; propane; n-butane; i-butane; n-pentane; i-pentane; 2,2-dimethylbutane; cyclohexane; hexane
alkenes	ethylene; propene; 1-butene; i-butene; cis-2-butene; 1,3-butadiene; trans-2-pentene; 1-pentene; cis-2-pentene; trans-2-butene
alkynes	acetylene
aromatics	benzene; toluene
biogenics	isoprene; MVK+MACR+ISOPOOH; α -pinene; β -pinene; myrcene; limonene
oxygenates	formaldehyde; acetaldehyde; methanol; acetone; methyl ethyl ketone
inorganics	CO; NO; NO ₂

Table 2. Name and mass of VOCs included in the standard mixture used for calibrating the PTR-MS. Reported sensitivities correspond to mean values of calibrations performed during the campaign. Limit of detections (LoD) correspond to 3σ of the standard deviation.

VOCs contained in the calibration gas standard			
<i>m/z</i>	Identified compound	S_{norm} (<i>ncps ppbv⁻¹</i>)	LoD (<i>ppbv</i>)
33	Methanol	11.0	0.72
42	Acetonitrile	19.0	0.12
45	Acetaldehyde	16.5	0.26
57	Ethylketone	17.6	0.09
59	Acetone	20.9	0.15
69	Isoprene	6.6	0.19
71	Crotonaldehyde	21.0	0.22
73	MEK	18.6	0.11
79	Benzene	9.9	0.13
93	Toluene	10.5	0.08
137	α -pinene	2.7	0.08

Table 3. Volume mixing ratios inside and above the canopy of targeted molecules sampled with the PTR-MS.

<i>m/z</i>	Identified compound	Volume mixing ratios inside the canopy (2 m) (ppbv)				Volume mixing ratios above the canopy (10m) (ppbv)			
		Mean 24 h	Mean day (06:30 – 22:00)	Mean night (22:00 – 06:30)	Daily max	Mean 24 h	Mean day (06:30 – 22:00)	Mean night (22:00 – 06:30)	Daily max
33	Methanol	5.4±0.7	5.4±0.5	4.4±0.4	2.8 – 13.5	5.5±0.1	5.7±0.4	4.8±0.2	7.9 – 11.2
45	Acetaldehyde	1.2±0.1	1.2±0.2	0.9±0.1	1.2 – 5	1±0.08	1.2±0.1	1±0.09	1.8 – 6.4
59	Acetone	2.4±0.7	2.4±0.6	2.2±0.2	2.3 – 10	2.1±0.2	2±0.3	2.1±0.1	2 – 7.1
69	Isoprene	2.5±1.8	3.5±1.5	0.5±0.2	1.2 – 22.8	2.3±1.7	2.8±1.5	0.4±0.2	5.1 – 19
71	ISOP.OXs	0.3±0.1	0.4±0.1	0.2±0.03	0.1 – 1.6	0.4±0.08	0.4±0.1	0.28±0.05	0.4 – 1.4
79	Benzene	0.04±0.02	0.04±0.01	0.03±0.01	0.1 – 0.4	0.07±0.01	0.11±0.01	0.07±0.01	0.1 – 0.4
93	Toluene	0.05±0.01	0.05±0.01	0.04±0.01	0.08 – 0.7	0.06±0.01	0.07±0.02	0.05±0.01	0.2 – 0.5
137	Monoterpenes	0.18±0.07	0.21±0.08	0.11±0.03	0.3 – 1.8	0.14±0.05	0.15±0.05	0.08±0.01	0.4 – 0.9

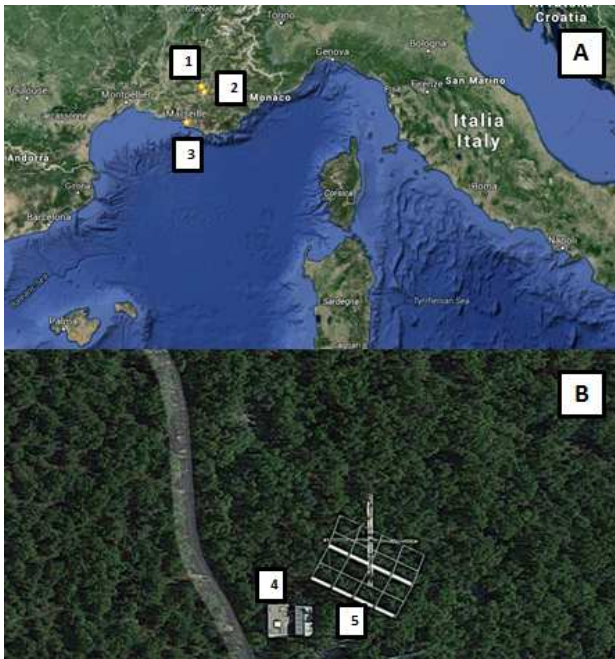


Figure 1. Site of Observatoire de Haute Provence (OHP) in the European map (panel A) and seen from above (panel B). Numbers refer to: (1) OHP field site, (2) town of Manosque, (3) city of Marseille, (4) room for instruments measuring trace gases, (5) movable trailer for measuring OH reactivity.

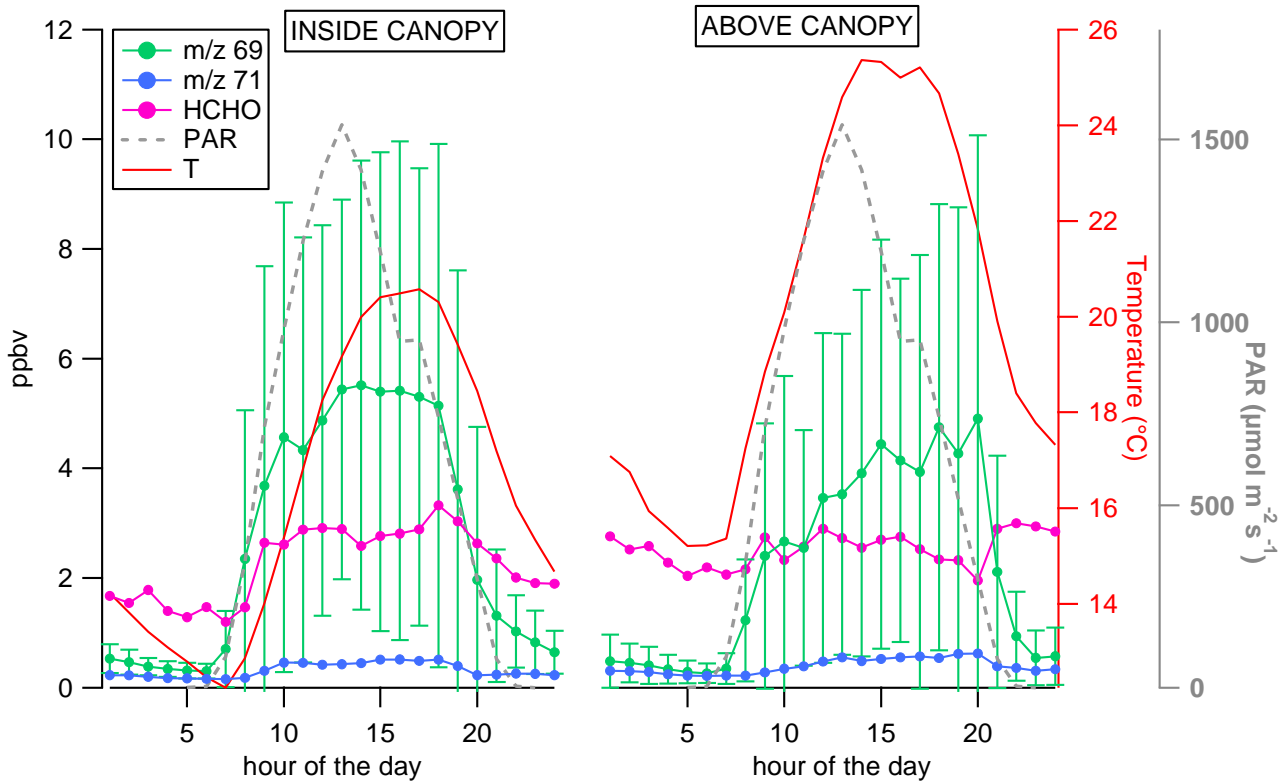


Figure 2. Daily mean of m/z 69, m/z 71, HCHO (ppbv), temperature and PAR for days of measurements at 2 m (left panel) and at 10 m (right panel) of the field campaign. Bars on m/z 69 correspond to $\pm 1\sigma$ standard deviation. PAR data were collected at 6 m for both cases. Temperature data were collected at 2 m and at 6.15 m.

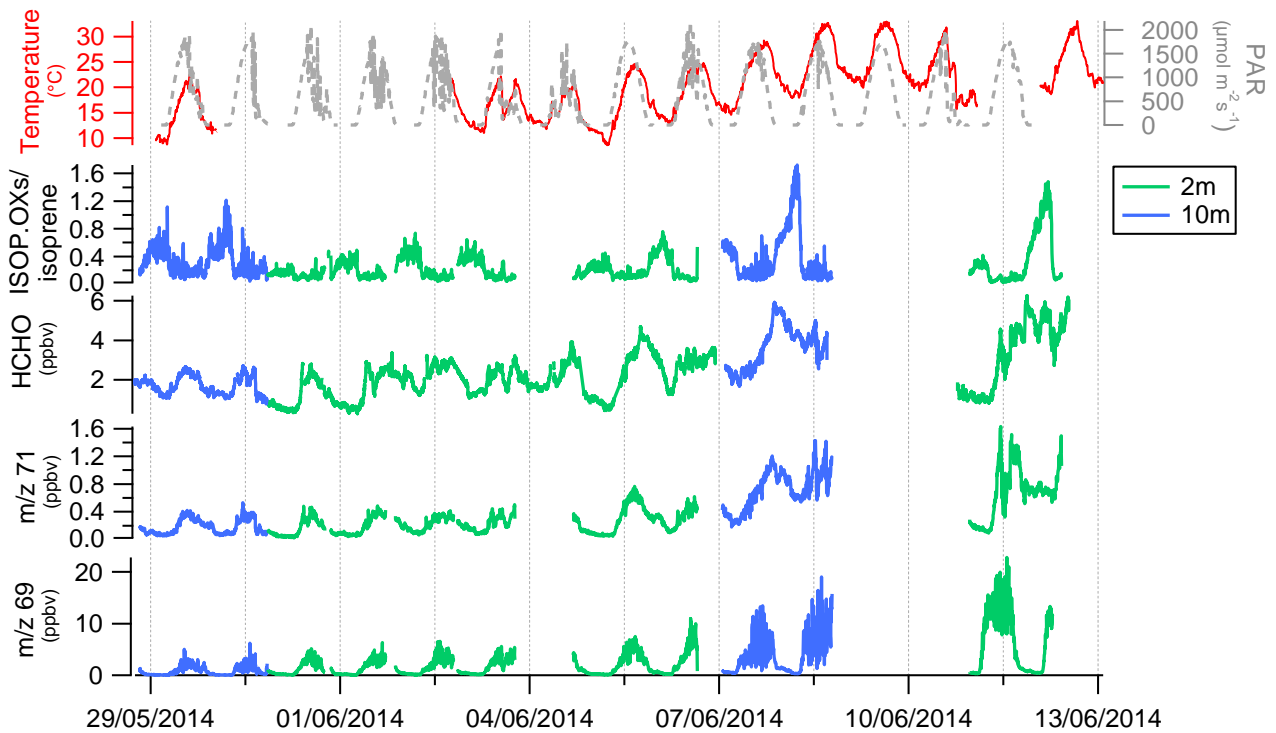


Figure 3. Time series of m/z 69 (isoprene), m/z 71 (ISOP.OXs=MVK+MACR+ISOPOOH), HCHO and ISOP.OXs/isoprene during the field campaign at OHP. Data were collected inside the canopy (2m, green line) and above the canopy (10m, blue line) on different days. Temperature and PAR measured at 6 m are reported as reference on the top panel.

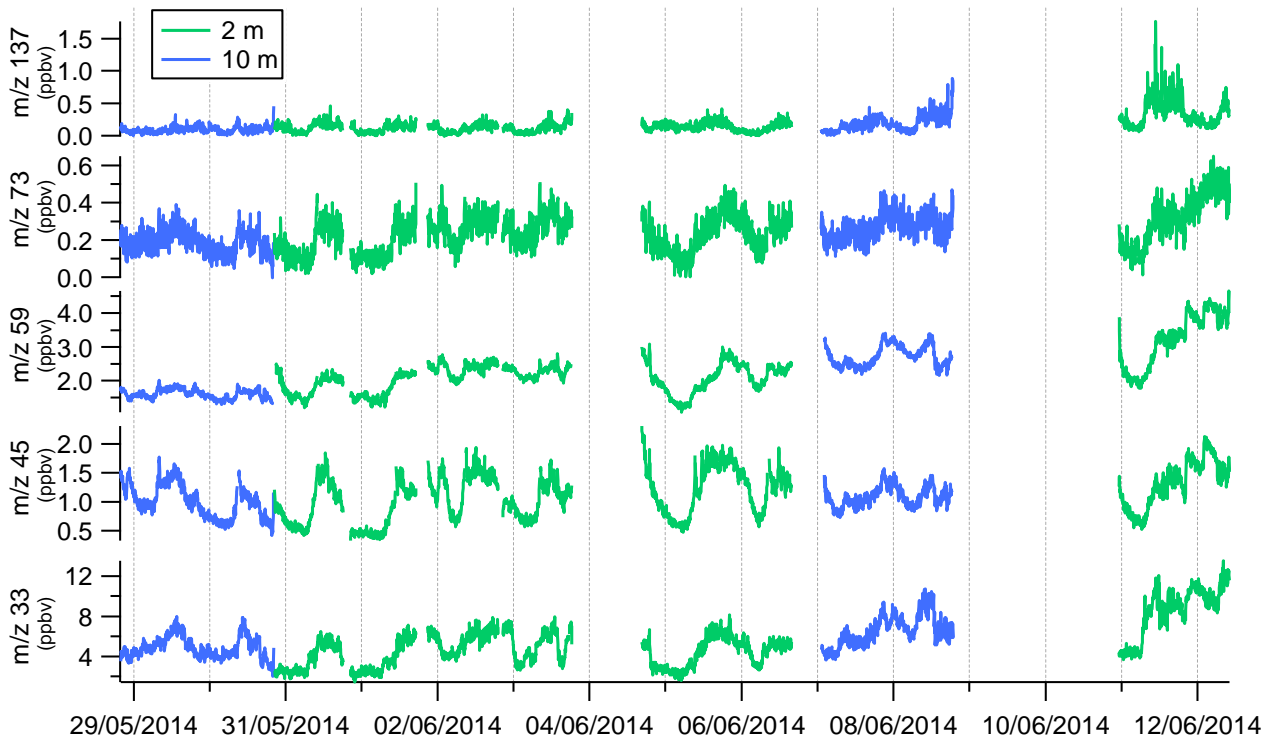


Figure 4. Time series of m/z 33 (methanol), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 73 (methyl ethyl ketone), m/z 137 (monoterpenes) inside (2 m, green line) and above (10 m, blue line) the canopy at OHP.

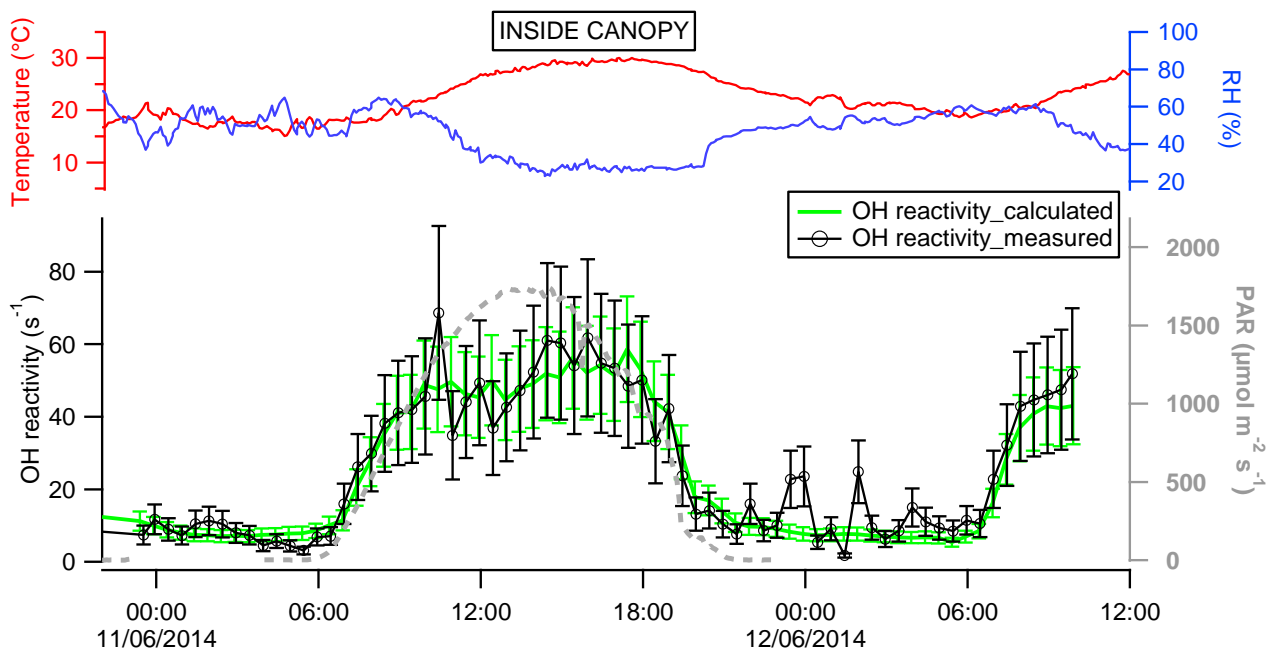


Figure 5. Total OH reactivity measured (black line and markers) with the Comparative Reactivity Method (CRM) and calculated OH reactivity from measured concentrations of trace gases (green line) on the left axes, Photosynthetic Active Radiation on the right axes (gray dashed line),

temperature and Relative Humidity on the left and right upper axes (red and blue lines). Data points represent thirty minutes averages of the sampled data and error bars correspond to 35% and 25% (1σ) instrumental uncertainties. Data refer to air sampled inside the canopy at 2 m height.

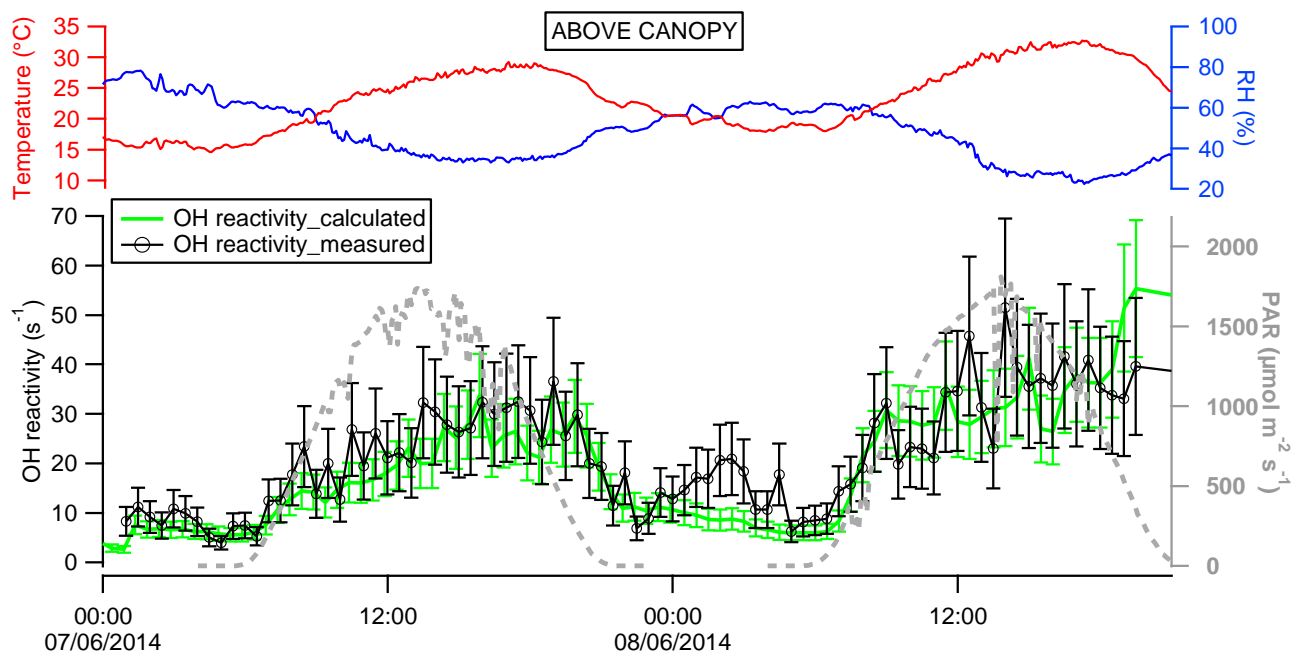


Figure 6. Total OH reactivity measured (black line and markers) and OH reactivity calculated (green line) above the canopy at 10 m height. Temperature (red line), RH (blue line) and PAR (gray dashed line) are reported for reference. Data points represent thirty minutes averages over the data collected. Uncertainties correspond to 35% and 25% for the measured and calculated reactivity respectively (1σ).

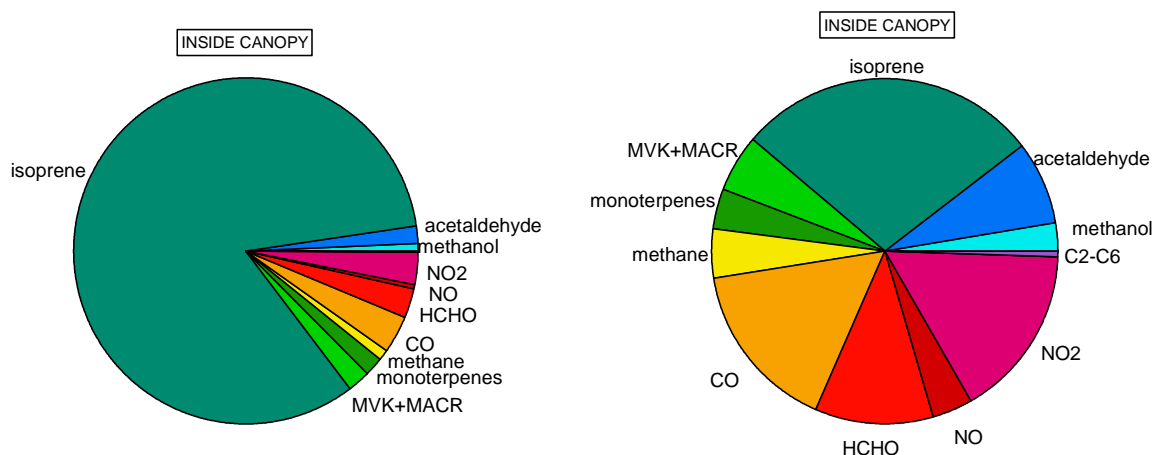


Figure 7. The components of OH reactivity inside the canopy (2 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 11-12/06/2014. Total OH reactivity was 29 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value).

All compounds reported in Table 1 were used to calculate their relative contributions. C2-C6 refer to alkanes and alkenes in the fraction C2-C6.

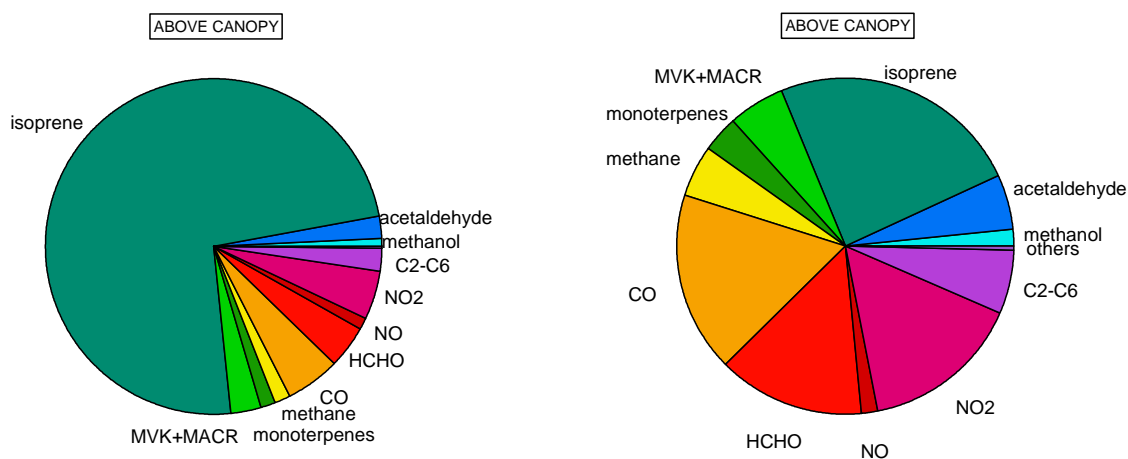


Figure 8. The components of OH reactivity above the canopy (10 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 07-08/06/2014. Total OH reactivity was 20 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. C2-C6 refer to alkanes and alkenes in the fraction C2-C6. Others refer to the sum of the contributions of: acetonitrile, acetone, MEK, benzene and toluene.

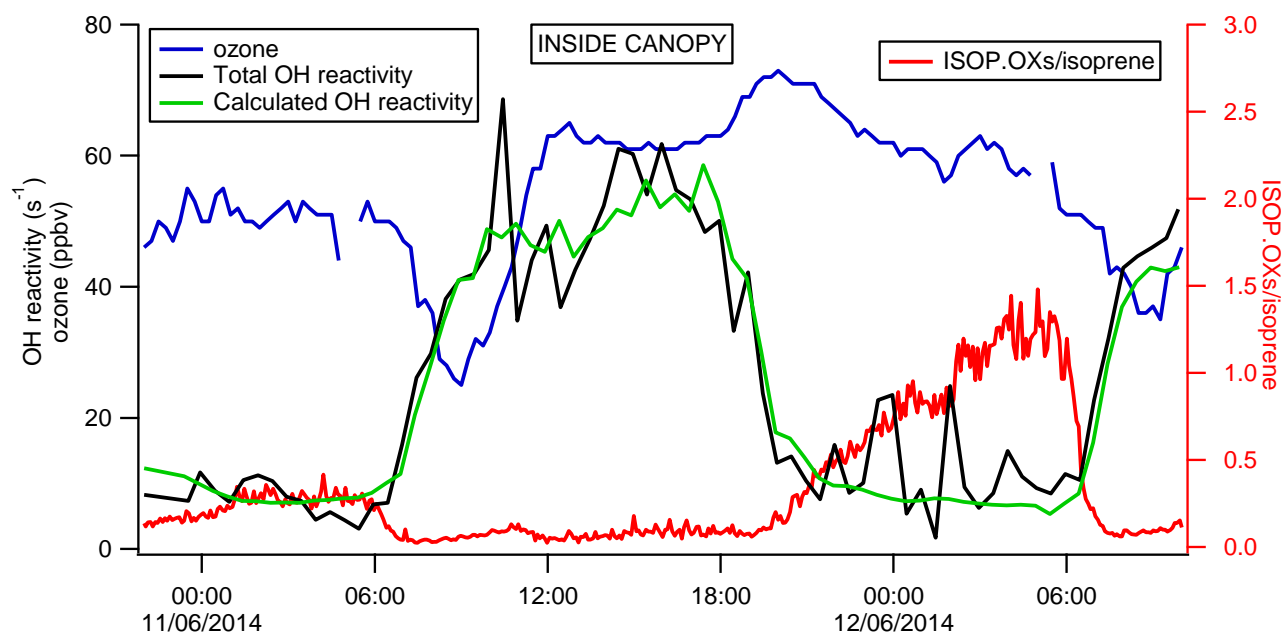


Figure 9. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 2 m height. Ozone data were acquired a few hundred meters away from the sampling area.

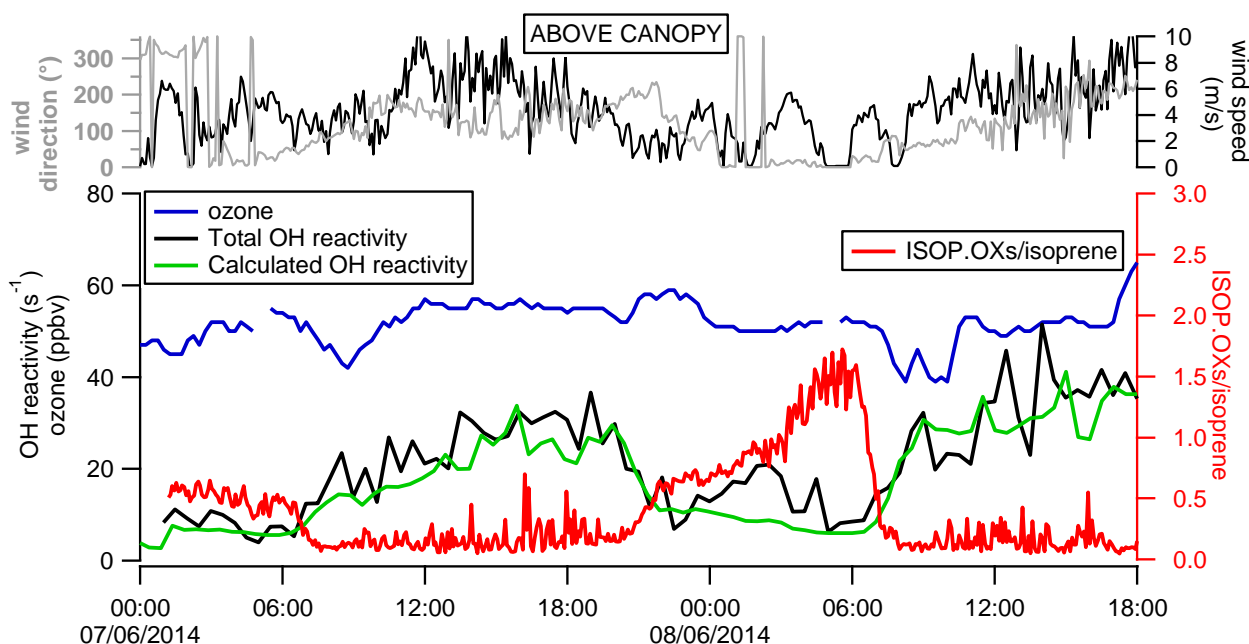


Figure 10. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 10 m height. Ozone data were acquired a few hundred meters away from the sampling area. The upper panel shows wind direction and wind speed data.

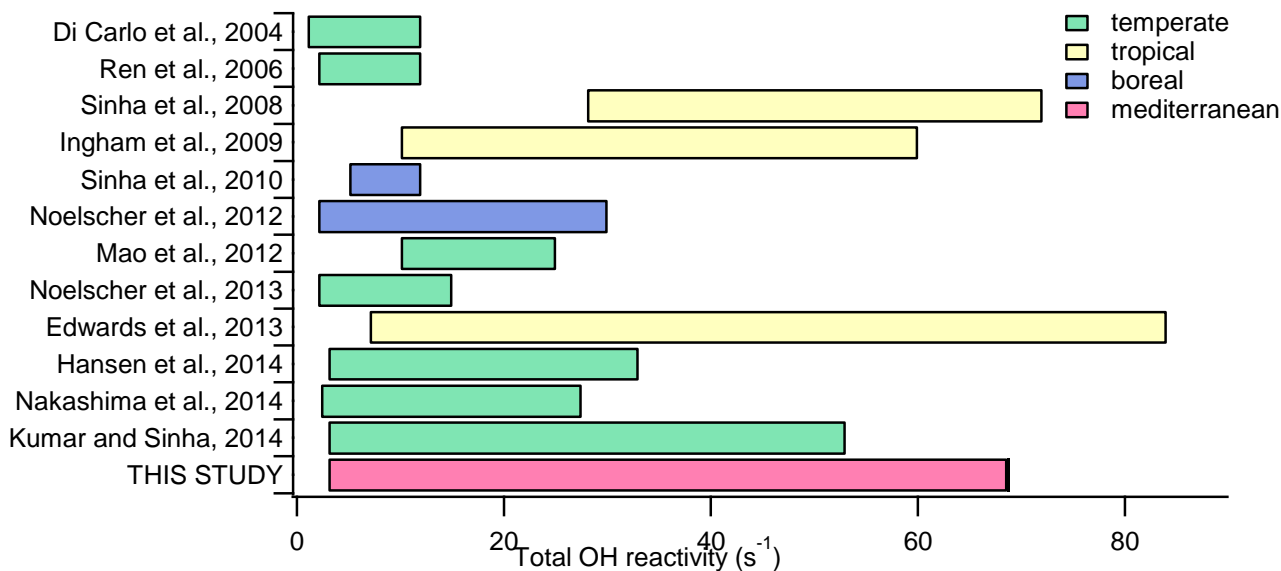


Figure 11. Total OH reactivity results from all the published experiments conducted worldwide at forested sites. Bars refer to the ranges observed between the minimum (often corresponding to the instrumental LoD) and the maximum values published. Studies were all conducted during spring-summer time. This study and those from Sinha and Noelscher adopted the Comparative Reactivity

Method; while di Carlo, Ren, Mao, Ingham, Edwards and Hansen used a Total OH Loss Rate Measurement based on Laser Induced Fluorescence; Nakashima deployed a Laser Induced Fluorescence Pump and Probe Technique (see references for instrumental details).