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

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Abstract

Understanding the processes between the biosphere and the atmosphere is challenged by the difficulty to determine with enough accuracy the composition of the atmosphere.

Total OH reactivity, which is defined as the total loss of the hydroxyl radical in the atmosphere, has proved to be an excellent tool to identify indirectly the important reactive species in ambient air. High levels of unknown reactivity were found in several forests worldwide and were often higher than at urban sites. Such results demonstrated the importance of OH reactivity for characterizing two of the major unknowns currently present associated to forests: the set of primary emissions from the canopy to the atmosphere and biogenic compounds oxidation pathways. Previous studies also highlighted the need to quantify OH reactivity and missing OH reactivity at more forested sites.

Our study presents results of a field experiment conducted during late spring 2014 at the forest site at the Observatoire de Haute Provence, OHP, France. The forest is mainly composed of downy oak trees, a deciduous tree species characteristic of the Mediterranean region. We deployed the Comparative Reactivity Method and a set of state-of-the-art techniques such as Proton Transfer Reaction-Mass Spectrometry and Gas Chromatography to measure the total OH reactivity, the concentration of volatile organic compounds and main atmospheric constituents at the site. We sampled the air masses at two heights: 2 m, i.e. inside the canopy, and 10 m, i.e. above the canopy, where the mean canopy height is 5 m. We found that the OH reactivity at the site mainly depended on the main primary biogenic species emitted by the forest, which was isoprene and to a lesser extent by its degradation products and long lived atmospheric compounds (up to 26 % during daytime). We determined that the daytime total measured reactivity equaled the calculated reactivity obtained from the concentrations of the compounds measured at the site. Hence, no significant missing reactivity is reported in this specific site, neither inside, nor above the canopy. However, during two

nights we reported a missing fraction of OH reactivity up to 50 %, possibly due to un-measured oxidation products.

Our results confirm the weak intra canopy oxidation, already suggested in a previous study focused on isoprene fluxes. They also demonstrate how helpful can be the OH re-activity as a tool to clearly characterize the suite of species present in the atmosphere. We show that our result of reactivity is among the highest reported in forests worldwide and stress the importance to quantify OH reactivity at more and diverse Mediterranean forests.

1 Introduction

Biogenic Volatile Organic Compounds (BVOCs) are the most important class of reactive organic compounds in the troposphere, once emitted they can be rapidly oxidized into other forms which have important feedbacks on air quality and climate.

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

Isoprene alone makes up half of all biogenic compounds emitted, and the largest single source of VOCs in the atmosphere, with a current global estimate of about 500 TgC

per year (Guenther et al., 2006) and large uncertainties still associated (Sindelarova et al., 2014).

When isoprene is released into the atmosphere, it is rapidly oxidized by the hydroxyl radical (OH), by ozone (O_3), by the nitrate radical (NO_3) during nighttime and occasionally by chlorine atoms. What determines its high reactivity as molecule is the presence, position and number of the double bonds. Atkinson and Arey (2003), have estimated lifetimes for isoprene ranging from a few hours with OH and NO_3 to a few days with O_3, while monoterpenes and sesquiterpenes lifetimes can range from few minutes to hours with OH, NO_3 and O_3 (with mean concentrations of oxidants equal to 2×10^6 molecules cm^{-3} for OH, 7×10^{11} molecules cm^{-3} for ozone and 2.5×10^8 molecules cm^{-3} for NO_3). By comparison, anthropogenic emitted molecules have lifetimes that vary between hours to years (Atkinson, 2000) which make biogenic compounds playing a dominant role in the lower troposphere and atmospheric boundary layer.

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

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

Total OH reactivity is defined as the total loss of the hydroxyl radical due to reaction with ambient reactive molecules. It has demonstrated to be an excellent tool to provide indirect evidence of the importance of reactive molecules in ambient air. In addition, when OH reactivity is measured together with the concentration of trace compounds, it is possible to evaluate whether all the reactive components in the studied environment are identified or not. Missing reactivity, which is the fraction of measured OH reactivity not explained by complementary gas phase measurements, has been already reported in several forested sites (di Carlo et al., 2004; Sinha et al., 2010; Nölscher et al., 2013), up to almost 90 % (Nölscher et al., 2012a) and usually higher than most of the urban sites investigated (Ren, 2003; Yoshino et al., 2006). Di Carlo and co-workers were the first to report evidences of a missing biogenic source in a forest in Michigan, probably associated to terpene-like emissions and not accounted from trace gases analysis. Their work pioneered and motivated the following studies of OH reactivity at other forested sites, including boreal forests (Sinha et al., 2010; Nölscher et al., 2012a; Mogensen et al., 2011), temperate mixed forests (Ren et al., 2006; Mao et al., 2012; Nölscher et al., 2013; Hansen et al., 2014 and Nakashima et al., 2014), and tropical forests (Sinha et al., 2008; Ingham et al., 2009 and Edwards et al., 2013).

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

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

The site at Observatoire de Haute Provence (OHP) is a special forest in the Mediterranean basin, located in the south east of France, poorly influenced by anthropogenic pollution and known for being almost homogeneous in BVOCs emissions. The dominant tree species at the site is the downy oak (*Quercus pubescens Willd.*), which has demonstrated to emit nearly exclusively isoprene in large quantities (Kesselmeier et al., 1998; Genard-Zielinski et al., 2015). Recent studies at OHP have shown evidences for large tree specific intra variability in emission strength (Genard-Zielinski et al., 2015) strong isoprene fluxes to the atmosphere (up $10.1\,\mathrm{mg\,m^{-2}\,h^{-1}}$ during summer 2010 (Baghi et al., 2012) and up to $9.7\,\mathrm{mg\,m^{-2}\,h^{-1}}$ during spring 2012 (Kalogridis et al., 2014) and low intracanopy oxidation processes (Kalogridis et al., 2014).

OH reactivity was used as a tool to close the reactive carbon budget, and help assessing the oxidative processes occurring through the canopy. We measured total OH reactivity with the Comparative Reactivity Method (CRM, Sinha et al., 2008) and used complementary measurements of trace gases concentration to elucidate any missing reactivity pattern. We sampled OH reactivity and trace gases concentration at the same time, and investigated two canopy heights, one inside the forest at 2 m, a second one above the forest at 10 m.

2 Methodology

2.1 Description of the field site

We measured total OH reactivity and atmospheric gases concentrations at the oak observatory of the field site of Observatoire de Haute Provence (OHP, http://www.obs-hp.fr), as part of the CANOPEE project

(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 (5°42′44″ E, 43°55′54″ N, 650 m a.s.l.), with Marseille the closest largest city about 100 km south, and Manosque the closest town about 18 km south from the site (Fig. 1).

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

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

Our field work took place during 29 May 2014–12 June 2014, as a follow up experimental study of the works conducted during spring 2012 and published by Kalogridis et al. (2014) and Genard-Zielinski et al. (2015).

2.2 Ambient air sampling

We measured the total OH reactivity together with the concentrations of BVOCs emitted by the forest, their oxidation products and main atmospheric constituents. For these measurements we deployed the Comparative Reactivity Method (CRM, home built),

a Proton Transfer Reaction Mass-Spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria), a Gas Chromatography Flame Ionization Detector (GC-FID, Chromatotech, France), a formaldehyde analyzer through the Hantzch reaction (Aero-Laser GmbH, Germany), off-line analysis of sampling tubes through Gas Chromatography Mass Spectrometry (GC-MS, 3800/2200 ion trap MS, Varian, USA) and a NO_x detector (Thermo Scientific, USA). We sampled simultaneously OH reactivity and VOCs levels through two PFA sampling lines (OD 3/8″) collocated on a mast. Measurements were performed sequentially at two heights inside and above the canopy (respectively 2 and 10 m), during 29 May 2014–12 June 2014. With an average canopy height of 5 m, air collection conducted at 2 and 10 m at OHP was used to elucidate the composition and reactivity of air masses inside and above the whole forest. The sampling lines were insulated with black tubing and slightly heated with a thermocouple type K (1 °C above ambient temperature) to prevent losses along the tubes. Ambient air sampled from the two lines was directed to the two main trailers were the instruments were placed. Ambient air from sampling line A was divided through a manifold into four lines, directed respectively to PTR-MS, GC-FID, an HCHO analyzer and a main driving pump. Sampling line B was used for OH reactivity measurements and the manifold separated the flows to measure C2 (background pyrrole signal for OH reactivity), C3 (ambient air signal for OH reactivity) and a second driving pump. Flows to the main pumps were adjusted to achieve residence times differing about 10 s maximum between the two sampling lines (residence time for CRM of 13 s and for the other instruments of 23 s).

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

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In addition, NO_x ($NO + NO_2$) were monitored from sampling through an independent extra line placed 15 m away from the main sampling site. Ozone was monitored by the regional air quality network and its sampling line was placed a few hundred meters away the main sampling site.

2.3 Comparative Reactivity Method and instrument performance

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

A CRM instrument consists of a glass flow reactor and a detector, in our case a commercial Proton Transfer Reaction-Mass Spectrometer (PTR-MS quadrupole, Ionicon Analytik GmbH, Innsbruck, Austria). The concept of CRM is to produce a competition between a reference molecule, pyrrole (C_4H_5N) and reactive molecules in ambient air to take up OH radicals generated inside the glass reactor. OH radicals are obtained from photolysis of water vapor with a pen ray Hg lamp which emits at 184.9 nm placed inside one of the reactor arms. Pyrrole is first diluted in zero air and dry nitrogen, and its concentration is monitored on the PTR-MS at the protonated m/z 68 (C0). When the Hg lamp is switched on, pyrrole concentration decreases due to photolysis and its concentration is monitored as C1. Then, the flow of nitrogen passes through a bubbler and water vapors are transported to the lamp to achieve photolysis and production of OH; in this stage pyrrole reacts with OH (rate coefficient = 1.2×10^{-10} cm^3 molecule^{-1} s^{-1} at 25 °C, (Atkinson et al., 1984) and (Dillon et al., 2012) and C2 is monitored. A 4-way valve permits fast switches between zero air and ambient air, when the latter dilutes pyrrole the competition for OH radicals takes place and C3 is the measured concentration of pyrrole. C3 differs from C2 depending on the amount and type of reactive molecules present in ambient air. Differences between C2 and C3 are used to determine the total

OH reactivity from the following equation:

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

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

Reactivity in ambient air is obtained every 10 min and raw values are corrected for humidity differences between the levels C2 and C3, deviation from first order kinetics, and dilution inside the reactor (Zannoni et al., 2015).

We qualified the performance of the CRM before and during the field campaign through injections of a known amount of reactivity generated by external gas standards. For this purpose, we used a standard of propane, which has a medium reactivity towards OH ($k_{propane+OH} = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, (Atkinson et al., 1997) and can therefore represent a proxy of an unknown air matrix; and isoprene, which instead is very reactive towards OH ($k_{isoprene+OH} = 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, (Atkinson, 1986) and represents the main component of the air parcels sampled in this specific forest. Injections were performed over a range of pyrrole/OH between 2 and 9, with 9 being the closest to pseudo first order kinetics regime. The reactivity measured plotted versus the reactivity injected with the two mentioned standards gave a slope of 1.01 ± 0.04 (1σ) and an R^2 of 0.96 up to reactivity values of 500 s^{-1}. The correction factor (slope of injected reactivity versus measured reactivity) is plotted versus the pyrrole-to-OH ratio and used to correct the raw reactivity for deviations in the kinetics regime. Corrections for humidity were obtained by averaging the results of three main tests conducted during the field campaign and were comparable to the results obtained in the laboratory (19 % standard deviation among results). Calibrations of the PTR-MS for pyrrole dry and wet were carried out at the beginning and end of the field campaign and showed a very good agreement between each other (difference within 1 % for the dry calibration factor and 4 % for the wet calibration factor).

During the days dedicated to the sampling of trace gases, we measured OH reactivity only for five days (three days inside the canopy and two days above the canopy) due

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to time needed to accurately qualify the performance of our instrument on the field, settings adjustment and tests needed to process the raw data.

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

2.4 Complementary measurements at the field site

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

$$R = \sum_i k_{i+\mathrm{OH}} \cdot X_i \tag{2}$$

with i any measured compound listed in Table 1.

2.4.1 Proton Transfer Reaction-Mass Spectrometer

We used a Proton Transfer Reaction-Quadrupole Mass Spectrometer (PTR-QMS, Ionicon Analytik, Austria) operated under standard conditions (p_{drift} = 2.2 mbar, E/N = 130 Td (1 Td = $10^{-17}\,V\,cm^{-1}$), T_{inlet} = 60 °C) to record the concentrations of trace gases at the site, (Lindinger and Jordan, 1998). We sampled the air masses in the scan mode, and inspected all species with protonated mass from m/z 21 to m/z 138 with cycles of 5 min each. Sampling in the scan mode procedure revealed to be a convenient way for analyzing unknown air parcels.

We calibrated the instrument using a gas calibration unit (GCU, Ionicon Analytik, Austria) with a standard gas mixture (GCU, Ionicon Analytik, Austria) containing: methanol (m/z 33), acetonitrile (m/z 42), acetaldehyde (m/z 45), acrolein (m/z 57), acetone (m/z 59), isoprene (m/z 69), crotonaldehyde (m/z 71), methyl ethyl ketone (m/z 73), benzene (m/z 79), toluene (m/z 93), α-pinene (m/z 137); see Table 2 for

the list of compounds, their protonated mass, mean sensitivity from field calibrations and masses LoD. Calibrations were run over the range 0–20 ppbv at the beginning and at the end of the field campaign, with no significant change in the detector sensitivity (differences up to 10 % and for most species within 5 %) therefore we used a mean calibration factor for the whole campaign.

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

We used a Gas Chromatography-Flame Ionization Detector to cross validate the concentration obtained for isoprene, which is the dominant compound at the site, usually measured at the protonated m/z 69 with the PTR-MS but often prone to fragmentation in the drift tube (see Sect. 2.4.2). All the measured species, except isoprene, were not cross validated, and their mass identification was conducted based on the existing literature at similar sites, e.g. Kalogridis et al. (2014); Holzinger et al. (2002); Warneke et al. (2001). This is the case in particular for masses m/z 71 and m/z 73. Previous studies highlighted the presence of isoprene hydroperoxides (ISOPOOH) fragmenting at m/z 71 in the PTR-MS, and representing a major yield from isoprene oxidation for low NO_x environments, such as our case study (Liu et al., 2013 and Rivera-Rios et al., 2014). Since we did not separate between these compounds, we will therefore refer hereinafter to m/z 71 as the sum of the isoprene oxidation products ISOP.OXs: methyl vinyl ketone (MVK) + methacrolein (MACR) + isoprene hydroperoxides (ISOPOOH). Mass-to-charge 73, here reported as MEK and calibrated as such, can have several interferences. Among the possible interferences we speculate the presence of methylglyoxal, a compound generated during the degradation path of isoprene, which is the most abundant compound measured at our site. A detailed discussion about this compound and possible interferences at our site will be available in Yanez-Serrano et al. (2015).

2.4.2 Gas chromatography-flame ionization detector

A gas chromatograph equipped with a flame ionization detector (GC-FID, airmoVOC C2–C6, Chromatotec, Saint Antoine, France) was deployed to sample hydrocarbons in the fraction C2–C6, with a time resolution of 30 min (10 min sampling followed by 20 min analysis). The instrument sampled ambient air with a flow rate of 18 sccm via a stainless steel inlet. Ambient air passed through a Nafion dryer, then to a preconcentration trap cooled down to −8 °C, filled with Carboxen, Carbopack B and Carbotrap C, and finally thermodesorbed 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., USA). Calibrations were performed twice per week with a certified standard VOCs mixture (National Physical Laboratory, UK). The overall uncertainty was estimated to be 15 % (1σ). Correlation between isoprene measured by GC-FID and m/z 69 identified as the protonated isoprene mass over thirty minutes averaged data showed differences within 14 % among the two instruments (isoprene$_{GC-FID}$ = 0.86(isoprene$_{PTR-MS}$), R^2 = 0.93).

2.4.3 Formaldehyde analyzer

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

The working conditions applied to the AL 4021 for this study were similar to those applied previously for the same device in two HCHO studies conducted in Antarctica (Preunkert and Legrand, 2013; Preunkert et al., 2015). In brief, liquid reagents were prepared from analytical grade chemicals (Merck, USA) and ultrapure water (18 MOhm,

TOC < 1 ppbv, Elga Labwater); the air flow was kept at 1000 sccm which ensured a stripping efficiency of more than 99 %. Raw data were collected with a time resolution of 30 s. Gas standard calibrations and background levels took 50 and 25 min and were performed every 12 and 3 h, respectively. A mean detection limit of 42 ± 16 pptv is calculated as twice the standard deviation of the raw data (30 s) obtained during the 121 zero measurements made during the campaign, which was consistent with the typical LoD achieved (~ 30 pptv) with the same analyzer in the previous studies above cited.

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

2.4.4 NO$_x$ analyzer

Nitrogen oxides were measured with a commercial instrument (17i model, Thermo Scientific, USA), based on chemiluminescence. Its calibration was performed after the field campaign, where a LoD of 0.3 ppbv (2σ) and a precision of ±0.4 ppbv were estimated. Nitrogen oxides were sampled at 15 m from the main sampling site, hence we assumed that their concentration inside and above the canopy was not affected by any significant change.

2.4.5 GC-MS offline analysis

Adsorbing sampling tubes in stainless steel with Tenax TA and Carbopack X as sorbents were used to sample monoterpenes as α-pinene, β-pinene, β-myrcene and limonene for off-line analysis with a Gas Chromatograph-Mass Spectrometer (GC-MS,

3800/2200 ion trap MS, Varian, USA). Sampling was conducted at ambient temperature with an autosampler (Sypac V2, Tera Environnement, France) every three hours, tubes were then stored at 4 °C and analyzed within one month in the laboratory. Concentrations of individual monoterpenes were then used to infer their relative abundance from the total monoterpenes concentration obtained with the PTR-MS and calculate their contribution to the OH reactivity.

2.4.6 O_3, CH_4, CO

Ozone is constantly monitored at OHP from the regional Air quality network Air-Paca, France (http://www.atmopaca.org/). The monitor is placed in a container located a few hundred meters distant from the sampling site. Methane and carbon monoxide mean concentrations were derived based on measurements conducted during spring 2012 and considered to be 1900 and 180 ppbv respectively.

2.4.7 Meteorological parameters

Meteorological parameters such as temperature, relative humidity (CS215, Campbell Scientific, UK), Photosynthetical Active Radiation (PAR) (LI-190, Li-Cor, Lincoln, NE, USA), wind speed and wind direction were acquired through sensors already available at the measurements site (O_3HP website: https://o3hp.obs-hp.fr/index.php/fr/). In this work we used data collected at 2 m and at 6 m to help discussing results inside the canopy and above the canopy respectively.

3 Results

3.1 Trace gases profiles and atmospheric regime

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

Figures 2 and 3 illustrate diurnal profiles and time series of m/z 69, identified as isoprene, its main degradation products m/z 71, identified as MVK+MACR+ISOPOOH and here referred as ISOP.OXs (isoprene oxidation products), and formaldehyde (HCHO), together with meteorological parameters as air temperature and PAR, at both sampling heights. Figure 2 shows that these compounds have clearly diurnal profiles, but while isoprene covariates perfectly with PAR and temperature, its degradation products tend to increase after isoprene increases, which confirms the main secondary origin of such species. Isoprene peaks when temperature is highest in both cases: during the afternoon inside the canopy (left panel), during the late afternoon above the canopy (right panel). Formaldehyde mixing ratios are higher than m/z 71 for both the heights; inside the canopy its profile is clearly diurnal, while above the canopy it looks more stable, mostly because of the higher nighttime level reached on 8 June 2014, see Fig. 3.

Time series are reported in Fig. 3 for the whole campaign period, from 29 May 2014 to 12 June 2014, and distinguished between air masses sampled at 2 m (data reported with the green line), and at 10 m (data reported with the blue line), on different days. All species show a progressive increase towards the end of the field campaign, when air temperature at the site was higher compared to the first days of measures. Data collected between 7–12 June 2014 above and inside the canopy can be directly compared, based on similar conditions of temperature and solar radiation. Maximum values for isoprene inside and above the canopy are close (maximum at 10 m is 19 ppbv, maximum at 2 m is 23 ppbv) and small differences can be explained mainly on a dilution basis, a better mixing of air masses reached above the canopy height due to the sparse

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canopy structure. Interestingly, high levels of m/z 71 and HCHO were recorded during the nights between 7 and 8 June and between 11 and 12 June. Such high nighttime concentrations are also observed for other chemical species (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 137; iden-
tified respectively as methanol, acetaldehyde, acetone, methyl ethyl ketone and sum of monoterpenes. Monoterpenes are primary emitted biogenic compounds while the other species can have both primary and secondary origins (Jacob et al., 2002, 2005 and Millet et al., 2010). Methanol has a daily maximum of 14 ppbv (inside the canopy), which makes it the second most abundant compound measured at OHP after isoprene
(daily max inside the canopy 23 ppbv), followed by acetone, acetaldehyde, monoterpenes, ISOP.OXs, toluene and benzene, in order of abundance (Table 3). Based on a 24 h statistics, methanol is instead the first most abundant compound at OHP, followed by isoprene, acetone and acetaldehyde. Both methanol and isoprene have a diurnal profile, but methanol has a longer lifetime compared to isoprene (estimated to
be 12 days and 1.4 h respectively, see Atkinson and Arey (2003) therefore over 24 h the former shows less variability in the atmosphere.

During the two nights mentioned above (8 and 12 June) the concentration of the oxygenated compounds was higher compared to the other nights. More discussion on this behaviour is provided in Sect. 3.4.

Anthropogenic hydrocarbons mixing ratios in the fraction C2–C6 were individually below 1.5 ppbv, with ethane the most abundant (mean over the campaign = 0.9 ± 0.2 ppbv), followed by acetylene, ethylene and iso-pentane. Anthropogenic tracers measured by PTR-MS showed the same trend and confirmed the poor anthropogenic influence at this forested site: benzene maximum was 0.41 ppbv, with a 24 h
statistics mean of 0.04 ppbv, toluene was maximum 0.69 ppbv and its mean over 24 h was 0.05 ppbv. Concentrations of NO and NO_2 were maximum 1.7 and 5 ppbv with a mean value of 0.45 ± 0.38 and 3.4 ± 0.49 ppbv during the whole campaign, respectively. Ozone concentration ranged within 21–78 ppbv, with a mean value of 47 ± 10 ppbv.

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

3.2 Total OH reactivity

Figures 5 and 6 report thirty-minutes averaged values of total OH reactivity inside and above the canopy during 11–12 June 2014 and 7–8 June 2014 with the black line and associated error bars (overall uncertainty 35 %, 1σ). At 2 m OH reactivity varied between the instrumental LoD up to $69\,s^{-1}$, and was on average $26 \pm 19\,s^{-1}$. At 10 m it varied between the LoD and a maximum of $68\,s^{-1}$ and was on average $24 \pm 14\,s^{-1}$. OH reactivity had the same trend of temperature and PAR, with a diurnal profile that demonstrates its dependency on the emission and profile of biogenic compounds emitted by the forest, released when sunrise started and temperature increased. During 11 June 2014 OH reactivity started to increase at 6 a.m. (CEST) when the sun rose up and it reached a maximum around 10:30 a.m., then again around 4 p.m., associated to more intense solar radiation. It decreased after sunset, at 8 p.m. when also temperature and light reduced. Reactivity sampled at 10 m had also a diurnal profile. On 7 June 2014 it started to increase at 6:30 a.m., had its maximum around 6:30 p.m. and decreased at 9:30 p.m. On 8 June 2014 it increased at 6:30 a.m. and reached its maximum at 2:15 p.m.

3.3 Measured and calculated OH reactivity

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

Calculated OH reactivity was determined to be between 5 and 58 s^{-1} and on average 24 ± 19 s^{-1} between 11–12 June 2014 at 2 m inside the canopy. At 10 m, above the canopy height, it varied between 3 and 55 s^{-1}, being on average 19 ± 12 s^{-1}.

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

For both time series, during daytime, inside and above the canopy height, the measured OH reactivity agreed very well with the calculated one within the instrumental uncertainties. Since there was not a significant difference between the two values we can conclude that no significant missing reactivity was observed in this specific ecosystem in the Mediterranean basin during our measurement campaign. In addition, the precise

characterization of the composition of air even at 10 m height corroborates the weak oxidation of primary compounds within the canopy.

Simultaneous ancillary measurements of trace gases permit to resolve the total OH reactivity into the relative contributions of the individual species. Figures 7 and 8 show the breakdown of OH reactivity into the main contributors during daytime and nighttime at the two heights considered. In all cases the dominant reactive species was isoprene. Isoprene is among the most reactive compounds towards OH, the most abundant compound in this forest and nearly the only compound emitted by downy oak trees which constitute the large majority of tree species accounted in this ecosystem. Hence, we expected its large contribution to the reactivity. Isoprene made up from 28 to 83 % of the total OH reactivity during nighttime (total mean $6\,s^{-1}$) and daytime (total mean $29\,s^{-1}$) respectively at 2 m high. It made up from 24 % during night to 74 % during the day of the total reactivity (total means 6 and $20\,s^{-1}$ respectively) at 10 m. Assuming the same OH reactivity inside and above the canopy during those days of measurements (30° temperature maximum at 2 m, and 32° maximum at 10 m) the weight of isoprene between the two heights differs only of 9 points percentage, considered that at 2 m data of alkanes+alkenes are missing, we can conclude that there was not a substantial difference between the two heights. Inside the canopy during daytime, all the measured species apart from isoprene, contributed in total about 17 % to the OH reactivity. Carbon monoxide, HCHO and NO_2 were the second important species accounting for 3 points percentage each, followed by acetaldehyde, MVK+MACR and monoterpenes with 2 points percentage each and all the other compounds less than this. During nighttime, the concentration of isoprene reduced to a few pptv and other species such as CO and methane which were more stable in the atmosphere became more important, contributing to 16 and 5 % respectively. Formaldehyde, NO_2, acetaldehyde, MVK+MACR and monoterpenes made up respectively 11, 16, 8, 5 and 4 %. Above the canopy during daytime the second most reactive species were CO, NO_2, HCHO and MVK+MACR (5, 5, 4 and 3 %). Still above the canopy but during nighttime, CO, NO_2, HCHO, alkanes+alkenes, MVK+MACR, methane and acetaldehyde

weighted respectively 17, 15, 14, 6, 5, 5 and 5 %. Monoterpenes weighted about 2–1 % during daytime and 4 % during night in both cases. Monoterpenes are also very reactive BVOCs towards OH, when present they can definitely compete with isoprene in terms of reactivity. At OHP, monoterpenes mixing ratios were low (see Table 3), they did not constitute a major class of compounds of the area and by consequence their contribution to the OH reactivity was poor.

3.4 Nighttime missing reactivity

During the nights between 7 June 2014 and 8 June 2014 and between 11 June 2014 and 12 June 2014, the measured total OH reactivity and the calculated reactivity reported some discrepancies (Figs. 5 and 6). For the results above the canopy such discrepancy was visible around midnight, and significant differences were observed from 1 a.m. to 4:30 a.m. (Fig. 6). Inside the canopy, the signal of total OH reactivity started to scatter around 11:30 p.m., then again at 2 a.m. and flattered back to the signal of calculated OH reactivity around 4:30 a.m. (Fig. 5). Both differences were respectively 13–14 s^{-1} and accounted for a fraction higher than 50 % of missing OH reactivity. Such values of missing reactivity are comparable to values of total OH reactivity measured in boreal and temperate forests (Sinha et al., 2010; Ren et al., 2006).

To investigate the molecules responsible for the missing OH reactivity, we examined the variability of the calculated and measured OH reactivity, along with primary biogenic compounds, anthropogenic tracers, OVOCs and ozone concentrations, and ISOP.OXs / isoprene ratio. It is striking noticing that whereas isoprenoids exhibited a regular diurnal cycle, all OVOCs showed increased nighttime values (Figs. 3 and 4). Species profiles as reported in Fig. 3 show that on 7 June 2014 ISOP.OXs and HCHO started to increase during the day, around 1 p.m., reached a maximum around 7:30 p.m. and then decreased during the night. While isoprene concentration flattered much faster due to its higher reaction rate, its oxidation products reacted slower, which explains the higher ISOP.OXs / isoprene ratio observed. The ISOP.OXs / isoprene ratio had the same magnitude and trend for both missing reactivity events and reached

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a maximum during these two specific nights compared to the rest of the campaign period (Fig. 3). Interestingly, ISOP.OXs / isoprene well anticovaried with ozone's decrease (Figs. 9 and 10). Profiles of other measured OVOCs (m/z 45, m/z 59, m/z 73, Fig. 4) show higher concentrations around the midnight of both nights, suggesting an accumulation of oxygenated compounds and an intense nighttime chemistry. Indeed, meteorological parameters as wind speed and wind direction for data collected at 10 m help noticing that during the night between 7 and 8 June 2014 the wind blew from the same direction with low speed, suggesting more stable meteorological conditions which could have favored some nighttime chemistry (Fig. 10). Daytime air temperature for these two days was also the highest registered over the whole measurement campaign (Fig. 3).

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

Gas phase chemistry during nighttime is usually initiated by ozone and the nitrate radical. The low levels of NO_x observed at the site (nighttime NO was maximum 0.8 ppbv and on average 0.14 ± 0.13 ppbv) indicate that nitrate chemistry is not a proba-

ble source of such oxidized compounds; on the other hand ozone isoprene chemistry is slow and cannot explain alone their production in the gas phase (isoprene lifetime with nitrate is 1.6 h while with ozone is calculated to be 1.3 days (Atkinson and Arey, 2003). If the unmeasured OVOCs were not generated exclusively from isoprene, neither had anthropogenic precursors, we speculate that they must have been a combination of higher generation products derived from isoprene oxidation and OVOCs resulting from reactive primary biogenic precursors, other than isoprene, and more reactive towards ozone. We can expect that these biogenic precursors were larger molecules that could not be measured with our means.

Holzinger et al. (2005) measured a whole class of oxidation products in a pine forest and suggested that they must have formed from reactions of ozone with very reactive terpene-like compounds. He estimated these compounds to be emitted about 6–30 times more the emission of the observed monoterpenes above his forest. Karl et al. (2005) have identified the same oxygenated compounds for different pine species and speculated their production at the leaf level, rather than in the gas phase. Recent experiments on leaves of tobacco plantations have identified the unsaturated semivolatile compounds undergoing leaves reactions (Hansel et al., oral presentation EGU 2015). Those compounds once deposited on the leaves quickly undergo surface oxidation reactions with ozone releasing volatile products into the gas phase. Oxidation reactions are favored by higher ambient RH, high ozone levels and can also occur when leaves stomata are closed. Measuring the species initiating these surface reactions is extremely difficult with the instruments we had on the field, therefore we do not have more clues to support this hypothesis nor exclude it has occurred in the forest of OHP. Focused studies on the leaves of downy oak trees with branch enclosure techniques would be of help to elucidate it.

3.5 OH reactivity at other biogenic sites

Our results of reactivity from OHP constitute the first data set of total OH reactivity measured in a Mediterranean forest. Nevertheless, several observations in other forested

sites exist to date. Such environments constitute perfect laboratories to study the emissions from different plant species and their evolution due to natural factors such as light and air temperature. OH reactivity observations have been of great help in the years to elucidate the presence of unknown compounds and to eventually assess BVOCs oxidation patterns which were not before characterized (Nakashima et al., 2012; Nölscher et al., 2014). In addition, biogenic species constitute a class of compounds with the highest reactivity towards the hydroxyl radical. OH reactivity during springtime and summertime in forests is usually higher than in metropolitan areas which are often polluted by less reactive hydrocarbons.

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

The forest at OHP is among the investigated biogenic sites producing the highest OH reactivity worldwide. The only two sites where a higher reactivity was reached is the tropical rainforest of Borneo (Edwards et al., 2013), where a maximum of $84\,s^{-1}$ was reported and the tropical rainforest of Suriname with a maximum of $72\,s^{-1}$ (Sinha et al., 2008). Tropical forests are usually more heterogeneous in plants species and BVOCs emission patterns compared to the forest at OHP, which is particularly homogeneous also compared to other Mediterannean forests. In Borneo, the dominant primary species to the OH reactivity was also isoprene (relative contribution of 36.8 %), but terpenes made up 7 % and the largest portion of reactivity was attributed to the oxidation products of BVOCs and products intermediates (47.1 %). In conclusion, on one side the intense temperature and solar radiation result in similar emission strength and reactivity, while on the other side, biodiversity and canopy structure draw the major differences between the two sites. Indeed, the forest at OHP besides being homogeneous is also shorter and sparser compared to tropical forests, such structure allows

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a better mixing of the air masses and a faster transport of the primary species to the atmosphere.

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

4 Summary and conclusion

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

In addition, considered the homogeneity of the forest and strong reactivity of isoprene, we expected isoprene to be the species contributing mostly to the OH reactivity, at least for measurements at 2 m high. We found indeed that inside the canopy during daytime, isoprene contributed to the OH reactivity at the 83 %, followed by CO, NO_2 and HCHO. Above the canopy height, isoprene made up 74 %, followed by CO, NO_2, HCHO and MVK+MACR. Such results indicate that there was not a significant difference in the speciation inside and above the canopy. During nighttime, when isoprene emissions arrested and atmospheric concentrations were a few pptv, long lived species such as CO and methane contributed to about 16–17 and 5 % for both inside and above the canopy. Still, even by night, isoprene accounted for the largest portion of OH reactivity.

The low levels of isoprene oxidation products observed during the day indicate that the intracanopy oxidation is low, and almost all the isoprene emitted by the canopy is transported to the atmosphere, which confirms the previous experimental work on

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isoprene fluxes conducted during spring 2012. The fact that no missing OH reactivity was observed, especially above the canopy, additionally corroborates the fact that any unmeasured compound, product of the oxidation of isoprene was present.

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

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

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

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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			
m/z	Identified compound	S_{norm} (ncps ppbv^{-1})	LoD (ppbv)
33	Methanol	11.0	0.72
42	Acenotrile	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.

m/z	Identified compound	Volume mixing ratios inside the canopy			(2 m) (ppbv)	Volume mixing ratios above the canopy (10 m) (ppbv)			
		Mean 24 h statistics	Mean day (06:30–22:00)	Mean night (22:00–06:30)	Daily max	Mean 24 h statistics	Mean day (06:30–22:00)	Mean night (22:00–06:30)	Daily max
33	Methanol	5.41	5.35	4.44	2.80–13.51	5.47	5.72	4.81	7.87–11.16
45	Acetaldehyde	1.20	1.20	0.94	1.21–5.01	1.03	1.18	1	1.77–6.41
59	Acetone	2.39	2.37	2.20	2.33–10.03	2.08	2.04	2.06	2.02–7.12
69	Isoprene	2.54	3.54	0.47	1.17–22.77	2.26	2.80	0.42	5.11–19.02
71	ISOP.OXs	0.33	0.36	0.20	0.14–1.63	0.40	0.41	0.28	0.44–1.43
79	Benzene	0.04	0.04	0.03	0.12–0.36	0.07	0.11	0.07	0.14–0.41
93	Toluene	0.05	0.05	0.04	0.08–0.69	0.06	0.07	0.05	0.17–0.48
137	Monoterpenes	0.18	0.21	0.11	0.25–1.76	0.14	0.15	0.08	0.35–0.89
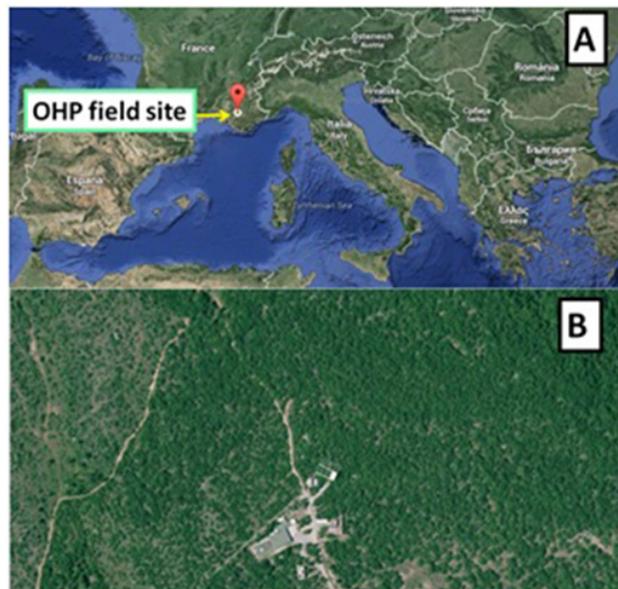
Figure 1. Site of Observatoire de Haute Provence (OHP) in the European map **(a)** and seen from above **(b)**.
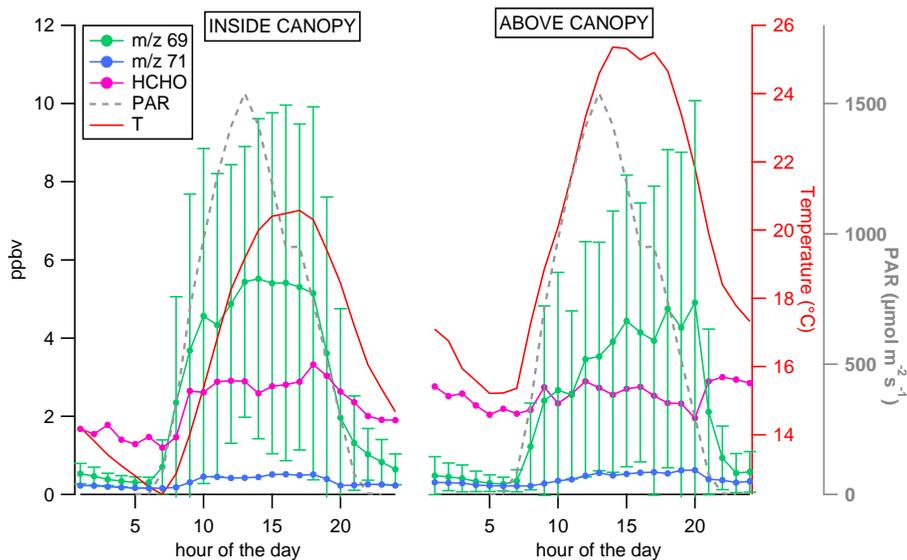
Figure 2. Diurnal profile of m/z 69, m/z 71, HCHO, temperature and PAR for days of measurements at 2 m (left panel) and at 10 m (right panel) of the field campaign. Bars on m/z 69 correspond to $\pm 1\sigma$ standard deviation. PAR data were collected at 6 m for both cases.

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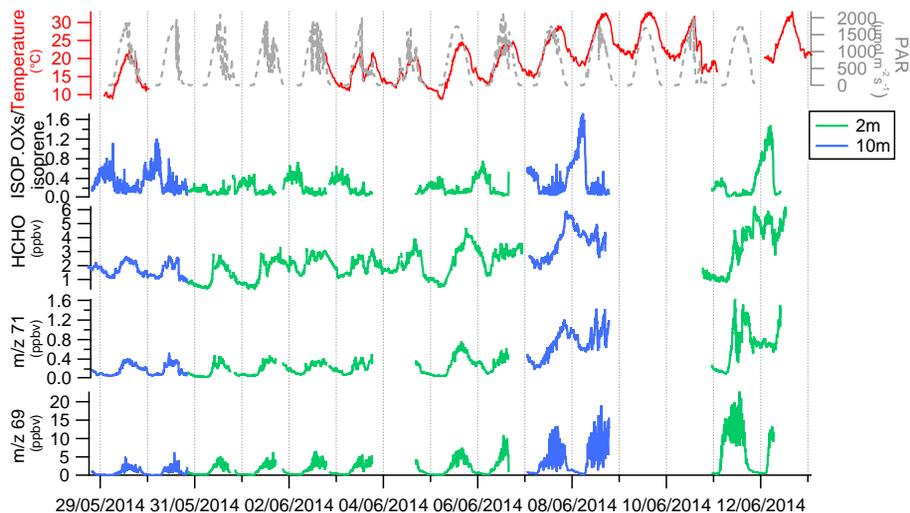
Figure 3. Time series of m/z 69 (isoprene), m/z 71 (ISOP.OXs=MVK+MACR+ISOPOOH), HCHO and ISOP.OXs / isoprene during the field campaign at OHP. Data were collected inside the canopy (2 m, green line) and above the canopy (10 m, blue line) on different days. Temperature and PAR measured at 6 m are reported as reference on the top panel.
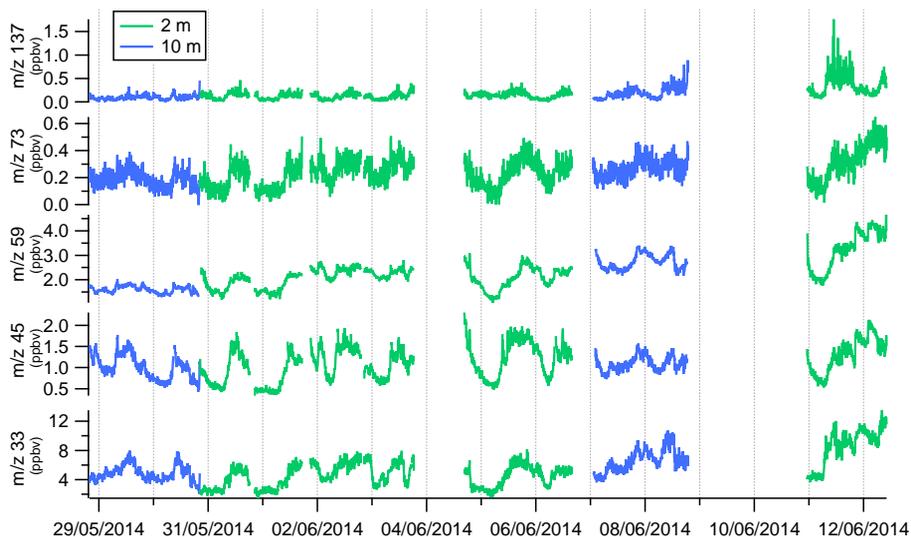
Figure 4. Time series of m/z 33 (methanol), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 73 (methyl ethyl ketone), m/z 137 (monoterpenes) inside (2 m, green line) and above (10 m, blue line) the canopy at OHP.

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OH reactivity and concentrations of Biogenic Volatile Organic Compounds

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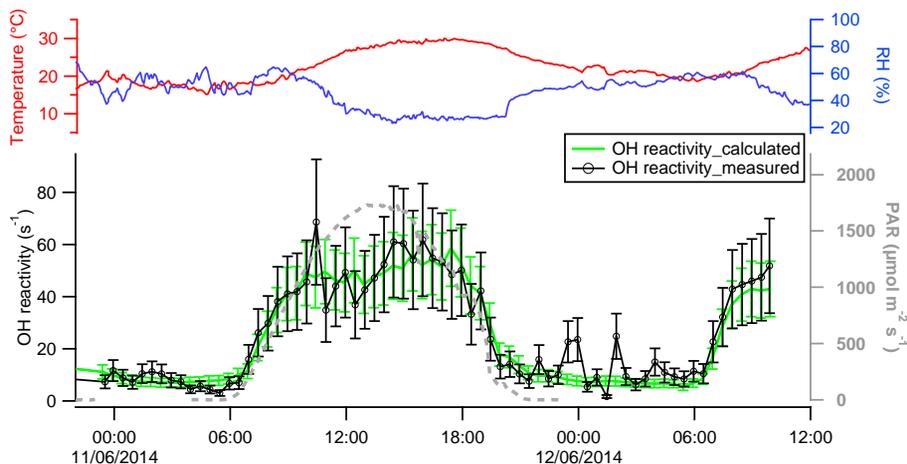
Figure 5. Total OH reactivity measured (black line and markers) with the Comparative Reactivity Method (CRM) and calculated OH reactivity from measured concentrations of trace gases (green line) on the left axes, Photosynthetical Active Radiation on the right axes (gray dashed line), temperature and 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.
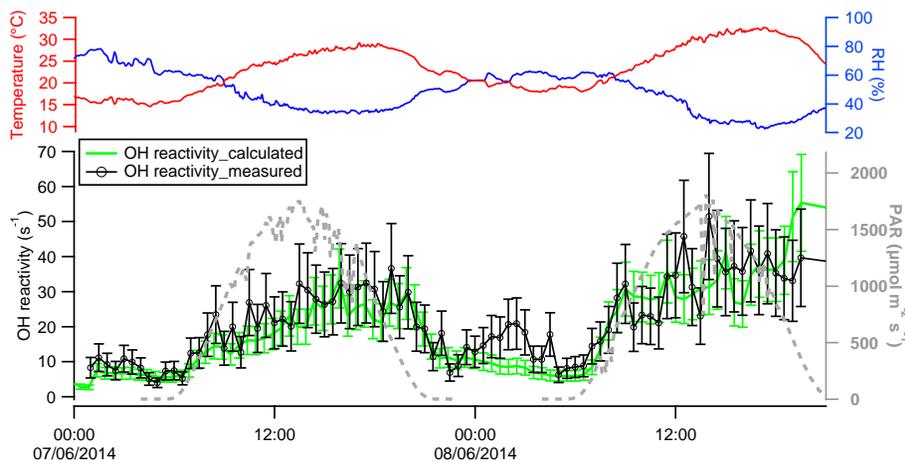
Figure 6. Total OH reactivity measured (black line and markers) and OH reactivity calculated (green line) above the canopy at 10 m height. Temperature (red line), RH (blue line) and PAR (gray dashed line) are reported for reference. Data points represent thirty minutes averages over the data collected. Uncertainties correspond to 35 and 25 % for the measured and calculated reactivity respectively (1σ).

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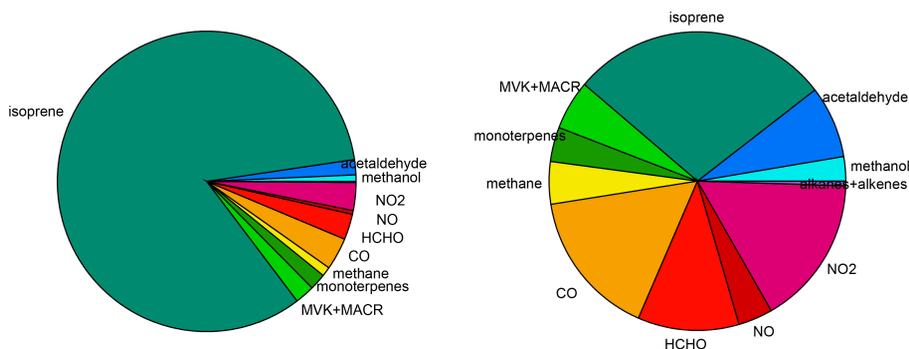
Figure 7. Total OH reactivity speciation inside the canopy (2 m height) during daytime (left pie chart **a**) and during nighttime (right pie chart **b**). Data refer to air masses sampled at OHP during 11–12 June 2014. Total OH reactivity was 29 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions.

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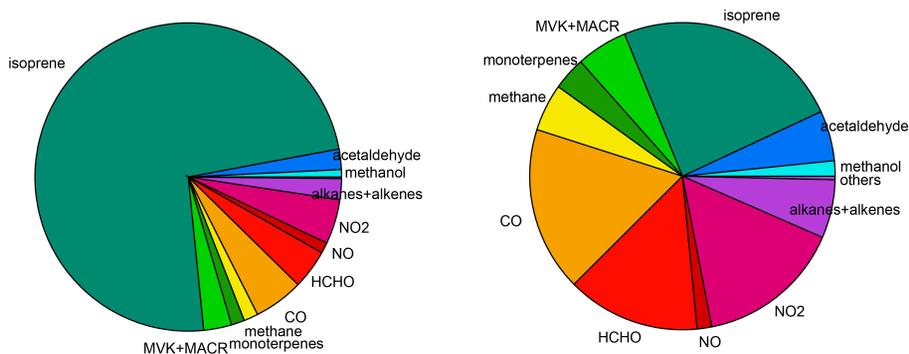
Figure 8. Total OH reactivity speciation above the canopy (10 m height) during daytime (left pie chart **a**) and during nighttime (right pie chart **b**). Data refer to air masses sampled at OHP during 7–8 June 2014. Total OH reactivity was 20 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. Others refer to the sum of the contributions of: acetonitrile, acetone, MEK, benzene and toluene.
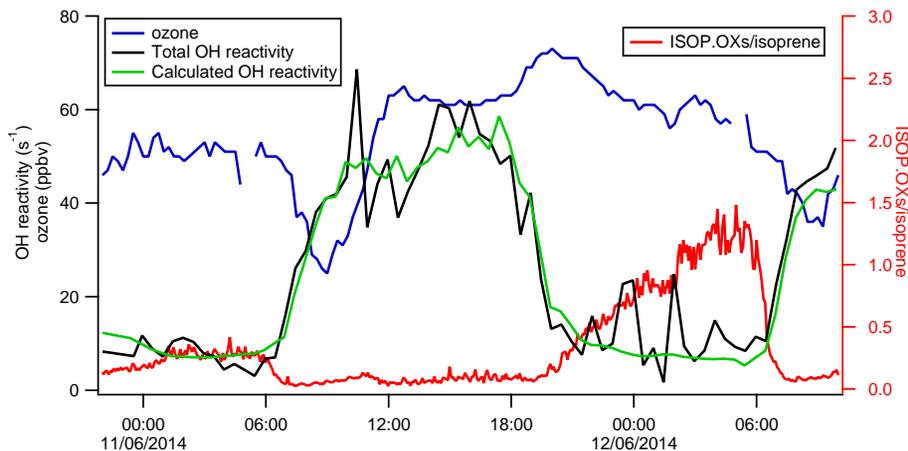
Figure 9. Total OH reactivity, calculated reactivity and ISOP.OXs / isoprene ratio at 2 m height. Ozone data were acquired a few hundred meters away from the sampling area.
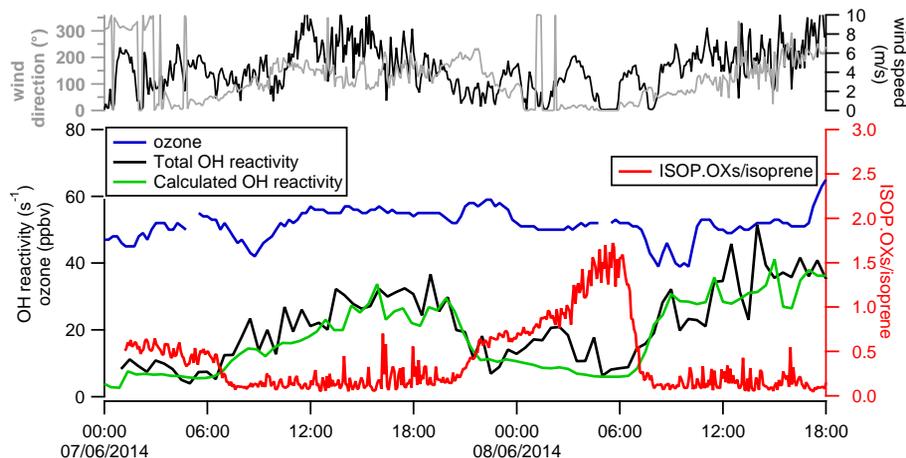
Figure 10. Total OH reactivity, calculated reactivity and ISOP.OXs / isoprene ratio at 10 m height. Ozone data were acquired a few hundred meters away from the sampling area. The upper panel shows wind direction and wind speed data.
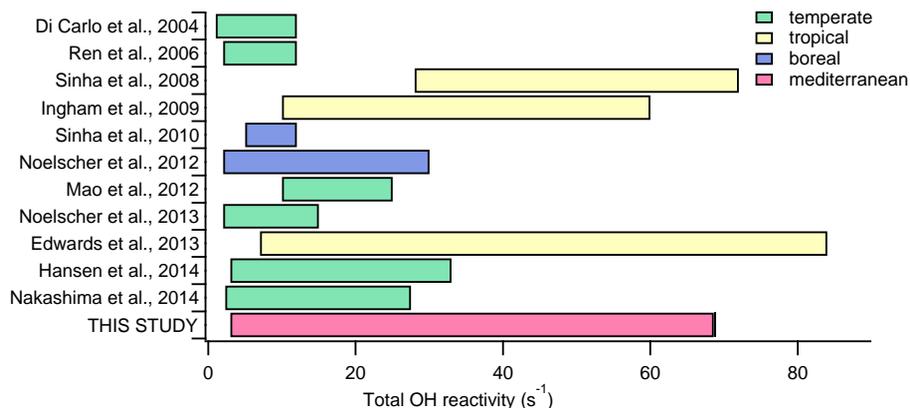
Figure 11. Total OH reactivity results from all the published experiments conducted worldwide at forested sites. Bars refer to the ranges observed between the minimum (often corresponding to the instrumental LoD) and the maximum values published. Studies were all conducted during spring- summer time. 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).