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

Our study presents atmospheric mixing ratios of biogenic compounds and total OH reactivity measured during late spring 2014 at the forest of downy oak trees of the Observatoire de Haute Provence (OHP), France. Air masses were sampled 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). During daytime, no significant missing OH reactivity was reported at the site, either inside or above the canopy. However, during two nights we determined a missing fraction of OH reactivity up to 50 %, possibly due to unmeasured oxidation products. We confirmed that no significant oxidation of the primary species occurred within the canopy; primary compounds emitted by the forest were fast transported to the atmosphere. Finally, the OH reactivity at this site was maximum 69 s^{-1} , which is a high

value for a forest characterized by a temperate climate. Observations in various and diverse forests in the Mediterranean region are therefore needed to better constrain the impact of reactive gases over this area.

1 Introduction

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

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 represents half of all biogenic compounds emitted and constitutes the largest single source of VOCs in the atmosphere, with a current global estimate of about 500 TgC yr^{-1} (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), ozone (O_3), the nitrate radical (NO_3) during nighttime and occasionally chlorine atoms. The presence, position and number of double bonds determine its high reactivity as a molecule. 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 a few minutes to hours with OH, NO_3 and O_3 (with mean concentrations of oxidants equal to $2 \times 10^6 \text{ molecules cm}^{-3}$ for OH, $7 \times 10^{11} \text{ molecules cm}^{-3}$ for ozone and $2.5 \times 10^8 \text{ molecules cm}^{-3}$ for NO_3). By comparison, anthropogenic emitted molecules have lifetimes that vary from hours to years (Atkinson, 2000), resulting in biogenic compounds playing a dominant role in the lower troposphere and atmospheric boundary layer.

The dominant loss of isoprene is the oxidation reaction with the OH radical, which involves the formation of six isomeric peroxy radicals that further react in unpolluted environments, 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 the formation of ozone and low volatile products which can partition to the particle phase. Significant production of ground-level ozone on the regional scale was reported by Hirsch et al. (1996) and in northeastern USA and Europe by Tsigaridis and Kanakidou (2002), 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 the reaction with ambient reactive molecules. It has been demonstrated to be an excellent tool for providing indirect evidence of the importance of reactive molecules in ambient air. In addition, when OH reac-

tivity 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). It was found to be 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 coworkers were the first to report evidences of a missing biogenic source in a forest in Michigan, probably associated with terpene-like emissions and not accounted for in trace gas analysis. Their work pioneered and motivated followup 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 $40 \text{ t km}^{-2} \text{ yr}^{-1}$ 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) all which will influence BVOCs emissions in strength and pattern (Laothawornkitkul et al., 2009). Such findings highlight the importance of conducting more intense and long-term field studies in the Mediterranean region.

Our study represents the first and only study to date 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 (OHP), France, during late spring 2014.

The site at OHP is a special forest in the Mediterranean basin, located in the southeast 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 been demonstrated to emit nearly exclusively isoprene in large quantities (Kesselmeier et al., 1998; Genard-Zielinski et al., 2015). Recent studies at OHP have shown evidence of large tree-specific intra-variability in emission strength (Genard-Zielinski et al., 2015), strong isoprene fluxes to the atmosphere (up $10.1 \text{ mg m}^{-2} \text{ h}^{-1}$) during summer 2010 (Baghi et al., 2012) and up to $9.7 \text{ mg m}^{-2} \text{ h}^{-1}$ dur-

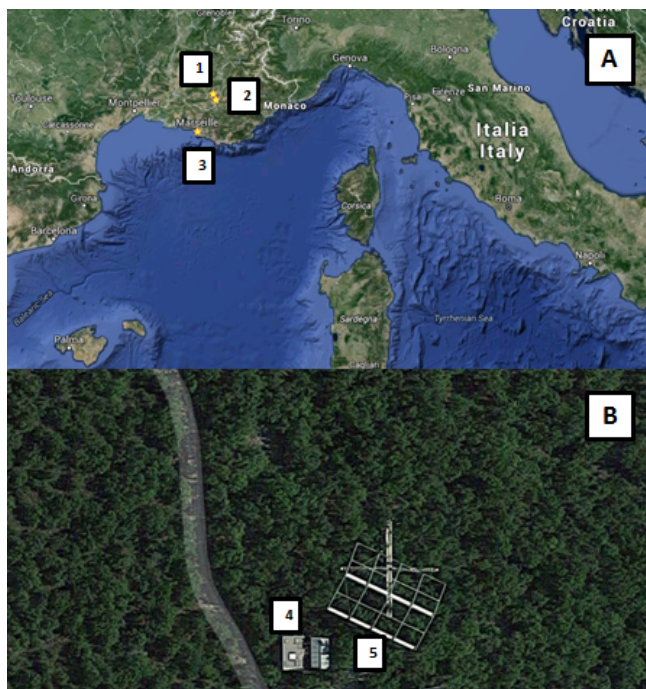


Figure 1. Site of Observatoire de Haute Provence (OHP) in the European map (a) and seen from above (b). Numbers refer to (1) OHP field site, (2) town of Manosque, (3) city of Marseille, (4) room for instruments measuring trace gases and (5) movable trailer for measuring OH reactivity.

ing spring 2012 (Kalogridis et al., 2014) and low intracanalopy oxidation processes (Kalogridis et al., 2014).

OH reactivity was used as a tool to examine the reactive carbon budget and help assess 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 gas concentrations to elucidate any missing reactivity pattern. We determined the OH reactivity and the trace gases at the same time and investigated two canopy heights: one inside the forest at 2 m and 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 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, southeast of France ($5^{\circ}42'44''$ E, $43^{\circ}55'54''$ N; 650 m a.s.l.); Marseille is the closest largest city, about 100 km south ($\sim 1\,600\,000$

inhabitants), and Manosque is the closest town, about 18 km south from the site ($\sim 22\,000$ inhabitants; 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 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 due to its dominance in this forest it makes OHP a natural laboratory for focused studies on isoprene.

Our field work took place during 29 May–12 June 2014, as a followup 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 following techniques: the CRM (home built), a PTR-MS (Ionicon Analytik GmbH, Austria), a gas chromatography/flame ionization detector (GC-FID, Chromatotech, France), a formaldehyde analyzer through the Hantzsch reaction (Aero-Laser GmbH, Germany), offline analysis of sampling tubes through GC-MS (3800/2200 ion trap MS, Varian, USA) and a NO_x detector (Thermo Scientific, USA).

We sampled simultaneously OH reactivity and concentrations of VOC through two PFA sampling lines (OD 3/8") collocated on a mast, which was erected downwind the oak observatory. The two sampling lines, A and B, were directed to the main local A (Fig. 1, number 4) and to a movable trailer B (Fig. 1, number 5), respectively. Both lines ended with a manifold to provide the sampling flows to all the instruments. Sampling line A was split into lines directed to the PTR-MS, the GC-FID and the Hantzsch analyzer, which were all located in local A. Sampling line B was used for measuring OH reactivity and was split into a line for the zero air generator of the CRM and another for the ambient air sampling of the CRM. The sampling flows were driven by

two pumps placed at the end of both manifolds. The flows and lines lengths were adjusted in order to have similar residence times of the species sampled through lines A and B that were, respectively, 23 and 13 s. The lines' entire lengths were, respectively, 28 and 18 m for A and B; a joint union piece placed at 2 m on both lines allowed us to disconnect them and perform sampling at two different heights along the forest canopy by using the same line. Finally, both lines were insulated with black tubing and heated with a thermocouple type K by about 1 °C above ambient temperature in order to prevent gases condensation. Measurements with this sampling setup were performed sequentially on different days over the campaign period 29 May–12 June 2014 at two heights: 2 and 10 m. 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.

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

An autosampler (Sypac V2, Tera Environnement, France) was used to adsorb air on packed stainless steel sampling tubes 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 2 m on the mast. The sampling was performed every 3 h 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.

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

2.3 Comparative reactivity method and instrument performance

Measurements of total OH reactivity were performed with a CRM 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 PTR-MS (quadrupole, Ionicon Analytik GmbH, Innsbruck, Austria). The concept of CRM is to produce a competition between a reference molecule, pyrrole (C₄H₅N) and reactive molecules in ambient air to react with 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 vapor is transported to the lamp to achieve photolysis and production of OH; in this stage pyrrole reacts with OH (rate coefficient = 1.2×10^{-10} cm³ molecule⁻¹ s⁻¹ at 25 °C; Atkinson et al., 1984 and Dillon et al., 2012) and C2 is monitored. A four-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:

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

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

Reactivity in ambient air is obtained every 10 min (calculated from 5 min on C2 and 5 min on C3) 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). Humidity differences between C2 and C3 can affect the concentration of OH radicals produced inside the reactor and can lead to an underestimation or overestimation of the measured OH reactivity. We generated zero air to produce C2 by sampling ambient air through a zero air generator, which removes the VOCs present in ambient air and leaves the air flow with the same humidity of ambient air. In our case, small differences in humidity were still observed and corrected (13 % decrease of the raw value).

We tested the performance of the CRM before and during the field campaign through injections of a known amount of OH reactivity generated by external gas standards. For this purpose, we used a standard of propane, which has a medium reactivity towards OH ($k_{\text{propane+OH}} = 1.1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; Atkinson et al., 1997), and isoprene, which instead is very reactive towards OH ($k_{\text{isoprene+OH}} = 1 \times 10^{-10}$ cm³ 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 ratio between 2 and 9, with 9 being the closest to pseudo-first-order kinetics regime. The reactivity measured plotted against the reactivity injected with the two mentioned standards gave a slope of 1.01 ± 0.04 (1σ) with 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 (see Supplement). For this study such correction determined a 47 % decrease of the raw data of reactivity. 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 dry and wet pyrrole 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). It is necessary to calibrate pyrrole at dry and wet conditions due to differences in sensitivity reported by the PTR-MS operating at different ambient humidity (Sinha et al., 2010).

During the days dedicated to the sampling of trace gases, we measured OH reactivity for only 5 days (3 days inside the canopy and 2 days above the canopy) due to the time needed to accurately test 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.

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

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

2.4.1 Proton transfer reaction/mass spectrometer

We used a PTR-MS (high-sensitivity quadrupole, Ionicon Analytik, Austria) operated under standard conditions ($p_{\text{drift}} = 2.2\text{ mbar}$, $E/N = 135\text{ Td}$ ($1\text{ Td} = 10^{-17}\text{ cm}^{-1}$), $T_{\text{inlet}} = 60\text{ }^\circ\text{C}$) 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 was revealed to be a convenient way to analyze 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) and α -pinene (m/z 137); see Table 2 for the list of compounds, their protonated mass, mean sensitivity from field calibrations and mass 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 was, respectively, 0.81, 0.86 and 0.43).

We used a GC/FID 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 obtained according to the existing studies conducted 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. The former has usually been attributed to the sum of MVK (methyl vinyl ketone) and MACR (methacrolein), the most abundant oxidation products of isoprene. Recent studies have highlighted that another group of compounds, the isoprene hydroperoxides (ISOPOOH), mostly originated from isoprene oxidation in unpolluted environments can also fragment at m/z 71 in the PTR-MS (Liu et al., 2013; Rivera-Rios et al., 2014). Since we did not separate these compounds, and we conducted our field work in an unpolluted environment where the ISOPOOH might have been produced, we will refer hereinafter to m/z 71 as the sum of the isoprene oxidation products ISOPOXs: MVK + MACR + isoprene hydroperoxides (ISOPOOH). Mass-to-charge 73, here reported as methyl ethyl ketone (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.

2.4.2 Gas chromatography/flame ionization detector

A gas chromatograph equipped with a 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

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. Limits of detection (LoDs) 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	Acetonitrile	19.0	0.12
45	Acetaldehyde	16.5	0.26
57	Ethyl ketone	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

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, Al₂O₃/KCl; 0.53 mm inner diameter and 25 m length, Varian Inc, USA). Calibrations were performed twice per week with a certified standard VOC 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 30 min averaged data showed differences within 14 % among the two instruments ($\text{isoprene}_{\text{GC-FID}} = 0.86$ ($\text{isoprene}_{\text{PTR-MS}}$), $R^2 = 0.93$).

2.4.3 Formaldehyde analyzer

Formaldehyde (HCHO) was measured with a commercial Aero-Laser 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 $+10^{\circ}\text{C}$. A fluorescent compound was quantitatively produced at $+70^{\circ}\text{C}$ 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 megohm, 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 above-cited previous studies.

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 setup.

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 stainless steel sampling tubes 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 GC-MS (3800/2200 ion trap MS, Varian, USA). Sampling was conducted at ambient temperature with an autosampler (Sypac V2, Tera Environnement, France) every 3 h, tubes were then stored at 4 °C and analyzed within 1 month in the laboratory. Ozone was removed from the tubes prior to the sampling procedure by using MnO₂-coated copper nets according to the procedure reported in Larsen et al. (1997). 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 O₃, CH₄, 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 at a distance of a few hundred meters from the sampling site. Methane and carbon monoxide mean concentrations were derived based on measurements conducted during spring 2012 and considered to be 1900 ppbv and 108 ± 16 ppbv, respectively.

2.4.7 Meteorological parameters

Meteorological parameters such as temperature, relative humidity (CS215, Campbell Scientific, UK), photosynthetic 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 (O₃HP website: <https://o3hp.obs-hp.fr/index.php/fr/>). In this work we used data collected at 2 and at 6 m to help with discussion of the results inside the canopy and above the canopy, respectively.

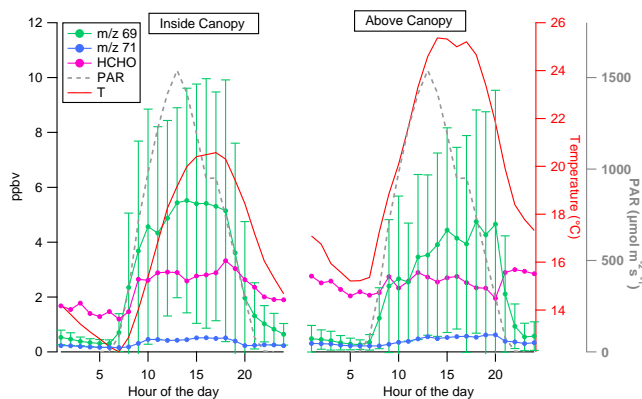


Figure 2. Daily mean of m/z 69, m/z 71, HCHO (ppbv), temperature and PAR for days of measurements at 2 m (left panel) and at 10 m (right panel) of the field campaign. Bars on m/z 69 correspond to $\pm 1\sigma$ standard deviation. PAR data were collected at 6 m for both cases. Temperature data were collected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

3 Results

3.1 Trace gas mixing ratio

During the first campaign week we observed some peaks of contamination for about 1 h every morning due to emissions from car exhausts. 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 to as ISOP.OXs (isoprene oxidation products), and HCHO, together with meteorological parameters as air temperature and PAR, at both sampling heights. Figure 2 shows that these compounds have clear diurnal profiles; however, while isoprene has similar profiles to PAR and temperature, its degradation products tend to increase after isoprene increases, which confirms the main secondary origin of such species. Isoprene mean values peak when temperature is highest: during the afternoon inside the canopy (14:00 CEST, left panel) and during the late afternoon above the canopy (20:00, right panel). The latter peak measured so late above the canopy is driven by the enhanced ambient temperature measured on 8 June 2014 (represented in Fig. 6). Formaldehyde mixing ratios are higher than m/z 71 for both 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 to 12 June 2014, with different colors indicating the air masses sampled at 2 m (data reported with the green line) and at 10 m (data reported with the blue line). 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 measurements. Data

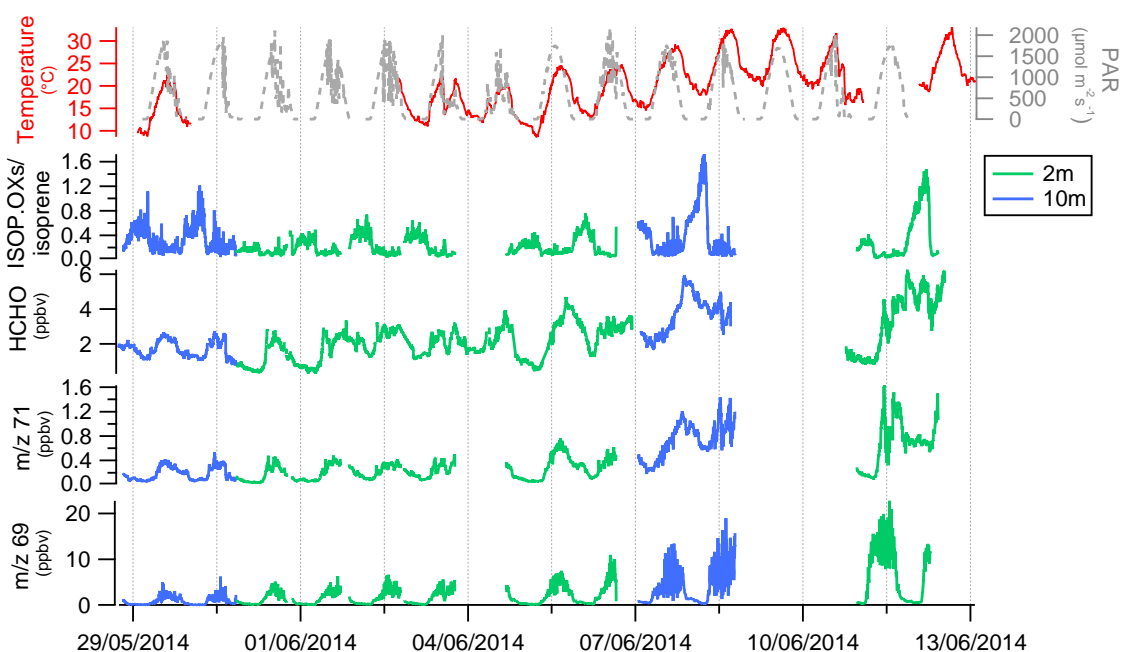


Figure 3. Time series of m/z 69 (isoprene), m/z 71 (ISOP.OXs = MVK+MACR+ISOPOOH), HCHO and ISOP.OXs/isoprene during the field campaign at OHP. Data were collected inside the canopy (2 m, green line) and above the canopy (10 m, blue line) on different days. Temperature and PAR measured at 6 m are reported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

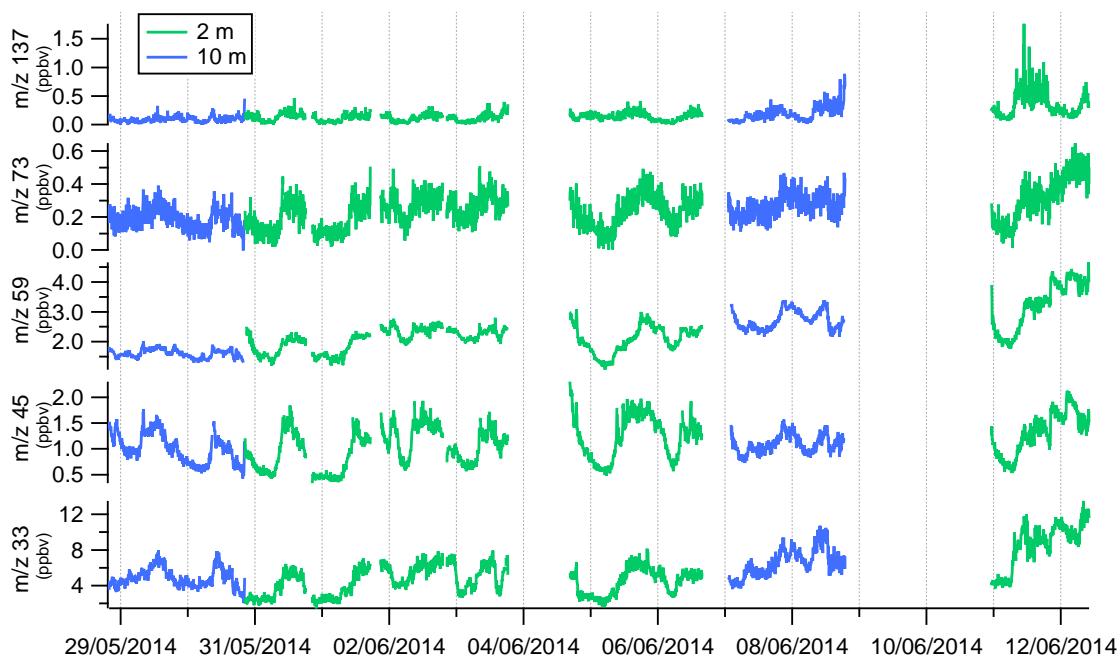


Figure 4. Time series of m/z 33 (methanol), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 73 (methyl ethyl ketone) and m/z 137 (monoterpenes) inside (2 m, green line) and above (10 m, blue line) the canopy at OHP.

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 (10 m; 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

collected between 7 and 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 canopy structure. Interestingly, high levels of *m/z* 71 and HCHO were recorded during the nights between 7 and 8 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, identified, 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; 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). Over 24 h, 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 behavior is provided in Sect. 3.4.

Anthropogenic hydrocarbons mixing ratios in the fraction C2–C6 were individually below 1.5 ppbv, with ethane being the most abundant (mean over the campaign = 0.9 ± 0.2 ppbv), followed by acetylene, ethylene and isopentane. 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, the mean over 24 h was 0.04 ppbv,

toluene was maximum 0.69 ppbv and its mean over 24 h was 0.05 ppbv. Concentrations of NO and NO₂ were maximum 1.7 and 5 ppbv with a mean value of 0.45 ± 0.38 ppbv 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. The highest values of ozone, often observed in the afternoon, are due to regional transport from air masses impacted by anthropogenic emissions (usually from the area of Marseille). Therefore the site can be, depending on air mass origin, regionally influenced by anthropogenic plumes. Nevertheless, the low levels of anthropogenic primary compounds suggest that this anthropogenic contribution is low. Additionally, we noticed that during the campaign the dominant wind direction was from north; hence the site was mostly exposed to the influence of the oak forest.

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 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 in different portions of the forest, with a distance between each other of 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 30 min averaged values of total OH reactivity inside and above the canopy during 11–12 and 7–8 June 2014, respectively, with the black line and associated error bars (overall uncertainty 35 %, 1σ). At 2 m OH reactivity varied between the instrumental LoD and 69 s⁻¹ and was on average 26 ± 19 s⁻¹. At 10 m it varied between the LoD

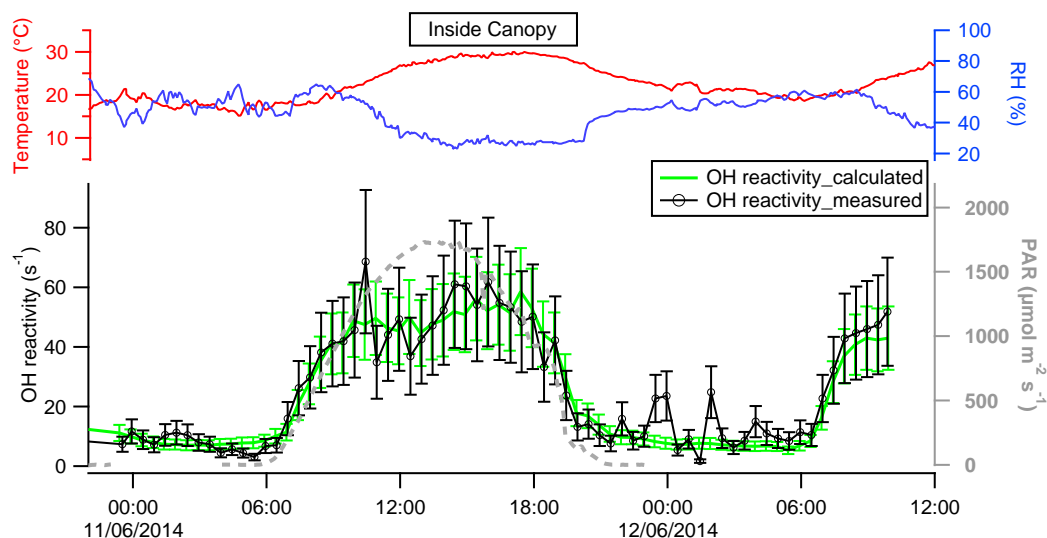


Figure 5. Total OH reactivity measured (black line and markers) with the comparative reactivity method (CRM) and calculated OH reactivity from measured concentrations of trace gases (green line) on the left axes, photosynthetic active radiation on the right axes (gray dashed line) and temperature and relative humidity on the left and right upper axes (red and blue lines). Data points represent 30 min 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.

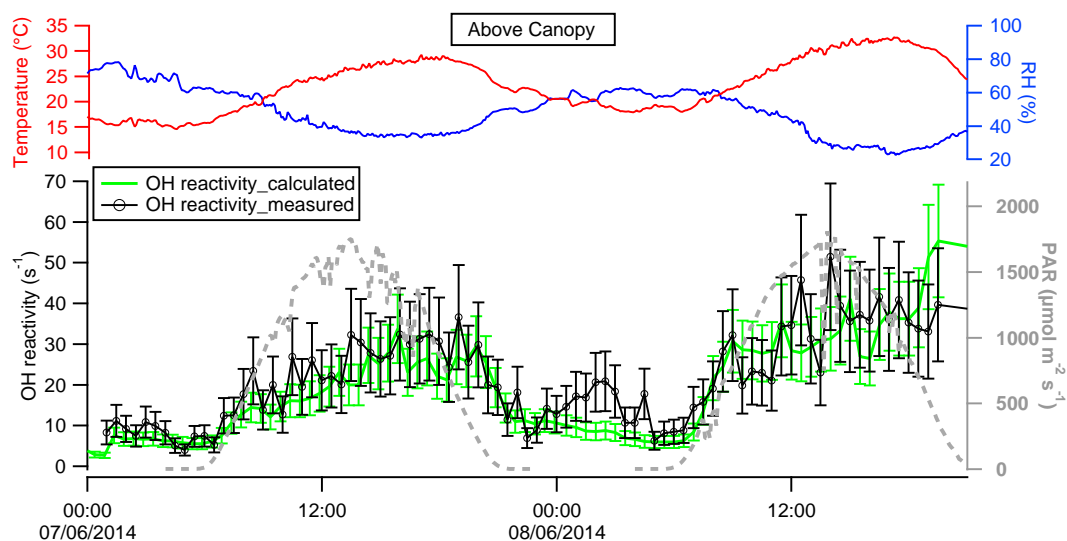


Figure 6. Total OH reactivity measured (black line and markers) and OH reactivity calculated (green line) above the canopy at 10 m height. Temperature (red line), RH (blue line) and PAR (gray dashed line) are reported for reference. Data points represent 30 min averages over the data collected. Uncertainties correspond to 35 and 25 % for the measured and calculated reactivity, respectively (1σ).

and a maximum of 68 s^{-1} and was on average $24 \pm 14\text{ s}^{-1}$. 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 6:00 when the sun rose and reached a maximum around 10:30 and again around 16:00, associated with more

intense solar radiation. It decreased after sunset, at 20:00 when temperature and light also reduced. Remarkably, the profile of OH reactivity resembled that of isoprene concentration, except for the morning peak (10:30), which could be possibly associated with the release in the atmosphere of oxygenated molecules. The OH reactivity sampled at 10 m had also a diurnal profile. Compared to the OH reactivity measured at 2 m, here the profile resulted slightly shifted due

to enhanced ambient temperature during the late afternoon on both sampling days. On 7 June 2014 it started to increase at 06:30, had its maximum around 18:00 and decreased at 21:30. On 8 June 2014 it increased at 06:30 and reached its maximum at 14:15.

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 deployed on the field and used to compute their relative contribution to the OH reactivity. It has to be noted that due to instrument 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: 1900 and 180 ppbv, respectively. The OH reactivity given by the oxidation products of isoprene (ISOP.OXs) 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.

The calculated OH reactivity was between 5 and 58 s^{-1} and on average $24 \pm 19\text{ s}^{-1}$ between 11 and 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 $19 \pm 12\text{ s}^{-1}$.

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 (Kalogridis et al., 2014).

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 reactive components in OH reactivity 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 majority of tree species accounted for in this ecosystem. Hence, we expected its large contribution to the reactivity. At 2 m, isoprene represented 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 10 m, it constituted from 24 % during nighttime to 74 % during daytime of the total reactivity (total means 6 and 20 s^{-1} , respectively). The impact of isoprene on OH reactivity between the two heights of sampling differs by only 9 %. When we consider that at 2 m the data of alkanes+alkenes are missing and similar air temperature was measured at the two heights (30°C temperature maximum at 2 m and 32°C maximum at 10 m), we can conclude that no substantial difference in the atmospheric composition in terms of reactive gases existed between the two heights of sampling. 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 most important species, accounting for 3 % each, followed by acetaldehyde, MVK+MACR and monoterpenes with 2 % each and all the other compounds with less. During nighttime, the concentration of isoprene reduced to a few pptv and other species such as CO and methane which are more stable in the atmosphere became more important, contributing to 16 and 5 %, respectively. Formaldehyde, NO_2 , acetaldehyde, MVK+MACR and monoterpenes represented, 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 %). 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 the night in both cases. Monoterpenes are also very reactive BVOCs towards OH; when present in the atmosphere they can 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 in the area and by consequence their contribution to the OH reactivity was poor.

3.4 Nighttime missing reactivity

During the nights between 7 and 8 and between 11 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 01:00 to 04:30 (Fig. 6). Inside the canopy, the signal of total OH reactivity started to scatter around 23:30, again at 02:00 and decreased back to the signal of calculated OH reactivity around 04:30 (Fig. 5). Both differences were $13\text{--}14\text{ s}^{-1}$ and accounted for a fraction higher than 50 % of missing OH reactivity. Such values of missing reactivity are com-

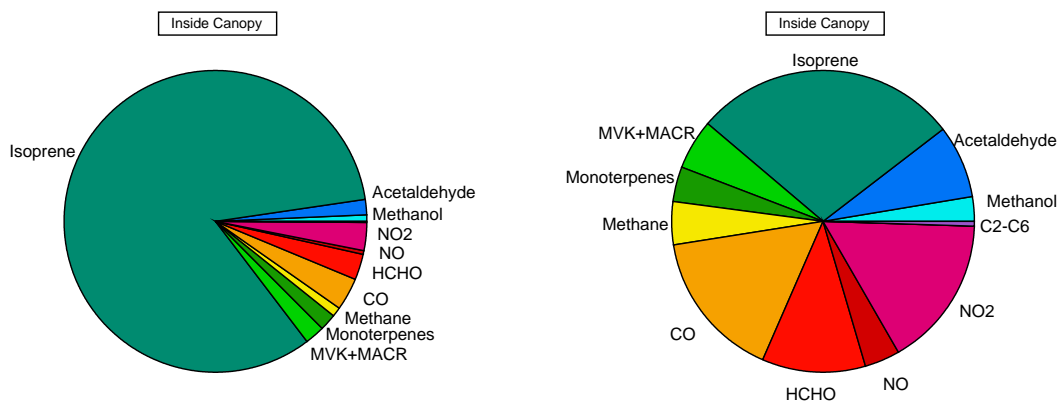


Figure 7. The components of OH reactivity inside the canopy (2 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 11–12 June 2014. Total OH reactivity was 29 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. C2–C6 refers to alkanes and alkenes in the fraction C2–C6.

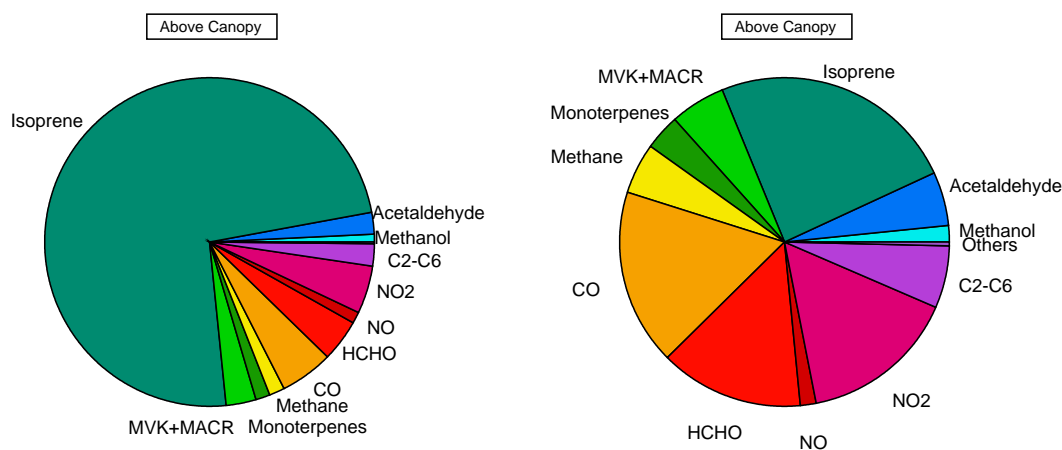


Figure 8. The components of OH reactivity above the canopy (10 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 7–8 June 2014. Total OH reactivity was 20 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. C2–C6 refers to alkanes and alkenes in the fraction C2–C6. Others refer to the sum of the contributions of: acetonitrile, acetone, MEK, benzene and toluene.

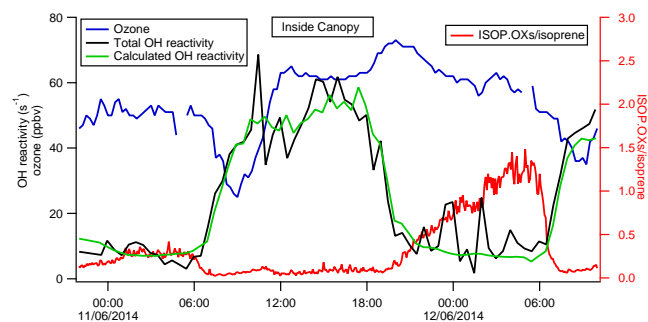


Figure 9. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 2 m height. Ozone data were acquired a few hundred meters away from the sampling area.

parable 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 (oxygenated volatile organic compounds) and ozone concentrations, and ISOP.OXs/isoprene ratio. It is striking 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 13:00, reached a maximum around 19:30 and then decreased during the night. While isoprene concentration is flatter much faster due to its higher reaction rate, its oxidation products reacted slower, which explains the higher

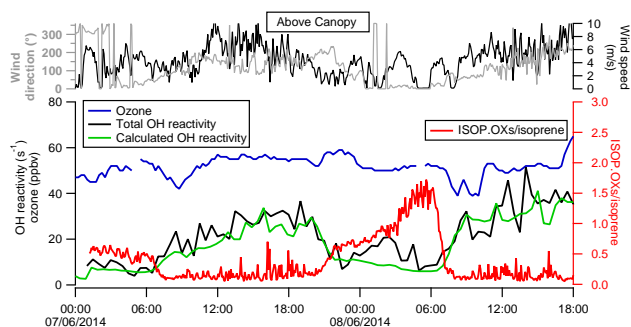


Figure 10. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 10 m height. Ozone data were acquired a few hundred meters away from the sampling area. The upper panel shows wind direction and wind speed data.

ISOP.OXs/isoprene ratio observed. Indeed, higher variability was observed on short timescale for isoprene compared to ISOP.OXs (0.9 and 0.5, respectively, relative standard deviation over the mean value during 7 June 2014). The ISOP.OXs/isoprene ratio had the same magnitude and trend for both missing reactivity events and reached a maximum during these two specific nights compared to the rest of the campaign period (Fig. 3). Interestingly, ISOP.OXs/isoprene increases when ozone decreases, especially for measurements at 10 m (Figs. 9 and 10). Profiles of other measured OVOCs (m/z 45, m/z 59, m/z 73; Fig. 4) show higher concentrations around midnight of both nights, suggesting an accumulation of oxygenated compounds and an intense nighttime chemistry. Indeed, meteorological parameters such as wind speed and wind direction for data collected at 10 m help to show that the wind blew from the same direction with low speed during the night between 7 and 8 June 2014, suggesting more stable meteorological conditions which could have favored nighttime chemistry (Fig. 10). Daytime air temperature on these 2 days was also the highest registered over the whole measurement campaign (Fig. 3). During nighttime, the atmospheric boundary layer is shallower, producing two main effects evident in Figs. 9 and 10: on one hand, it favors ozone deposition on leaves surface, which could be the main reason of the observed decrease of ozone concentration; on the other hand, it concentrates the atmospheric species present in ambient air, resulting in higher concentration of the compounds more stable in the atmosphere.

Several evidences make us believe that the production of OVOCs was linked to the oxidation of biogenic molecules. Firstly, common anthropogenic tracers such as acetonitrile and benzene did not show any particular increase during these events, supporting the idea that such nighttime higher concentrations of oxidized compounds in the atmosphere were associated with local drivers rather than transport. Secondly, we observed an increase in atmospheric levels of some masses measured by the PTR-MS and not used before to calculate the OH reactivity, such as m/z 47, m/z 61, m/z 75,

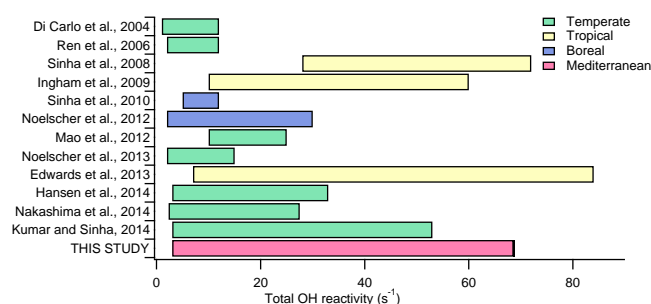


Figure 11. Total OH reactivity results from all the published experiments conducted worldwide at forested sites. Bars refer to the ranges observed between the minimum (often corresponding to the instrumental LoD) and the maximum values published. Studies were all conducted during spring/summertime. This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

m/z 83, m/z 87 and m/z 101. According to the existing literature, these protonated masses can be identified as oxidation products resulting from the degradation of isoprene and associated, respectively, with 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 probable source of such oxidized compounds; however, ozone isoprene chemistry is slow and cannot alone explain 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 neither generated exclusively from isoprene nor had anthropogenic precursors, we speculate that these unmeasured OVOCs 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 by our instrumentation.

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 approximately 6–30 times more than 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 plants have identified the unsaturated semivolatiles compounds undergoing reactions on the leaves surface (Jud et al., 2016). 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 and high ozone levels, and they 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, and therefore we do not have more clues to support this hypothesis or 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 to study the emissions from different plant species and their evolution due to natural factors such as light and air temperature in other forested sites exist to date. OH reactivity observations have been of great help over the years to elucidate the presence of unknown compounds and to eventually assess BVOCs oxidation patterns which had not before been 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 types of climatic zones to which the studied forests belong. The reader should note that not all the studies were carried out using the same method (see figure 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 also particularly homogeneous compared to other Mediterranean 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 hand the intense temperature and solar radiation result in similar emission strength and reactivity, while on the other hand biodiversity and canopy structure draw the major differences between the two sites. Indeed, the forest at OHP, besides being homogeneous, is shorter and sparser compared to tropical forests; such structure allows 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, the measured OH reactivity at both heights 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 either inside or above the forest.

In addition, considering the homogeneity of the forest and strong reactivity of isoprene, we expected isoprene to be the species contributing the most 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 83%, followed by CO, NO₂ and HCHO. Above the canopy height, isoprene made up to 74%, followed by CO, NO₂, 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 stopped 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 isoprene fluxes conducted during spring 2012. The fact that no missing OH reactivity was observed, especially above the canopy, additionally corroborates the fact that no significant unmeasured compound, the product of the oxidation of isoprene, was present.

During the nights between 7–8 and 11–12 June 2014 from sampling above and inside the canopy, respectively, the to-

tal 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 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 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 km² of surface only about 100 000 km² remains undisturbed by human activity. We expect, therefore, that OH reactivity in the Mediterranean can vary significantly depending on the type of vegetation and its extension and interaction with pollutants derived by human activity. In addition, the Mediterranean is a hotspot for climate change. This issue will certainly impact the biogenic emission strength and pattern, which will influence the total OH reactivity. With our work we would like to stimulate interest in studying the OH reactivity and BVOC levels at diverse biogenic sources in the Mediterranean area for extensive periods.

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