The authors are thankful to Anonymous referee 1 for the general feedback and the valuable comments for improving the manuscript. Please find below the answers to the comments and changes in the manuscript text.

1)

(1) The abstract is relatively long and especially the first paragraph (until l.14) reads more like an introduction. It would be nice to shorten it a little, highlight more the importance and novelty of this study, and emphasize the key-findings.

(2) We modified the abstract, please find the new version at (3).

(3) 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 (maximum 26% during daytime). During daytime, no significant missing OH reactivity was reported at the site, neither inside, nor 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 rapidly 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.

2)

(1) Even though overall the text is easy to read, there are several flaws in formulations and sentence-structures. For example, in p.22050, l.11 the sentence probably ends after "troposphere" and similarly in l. 14 the sentence probably ends after the reference. Since I am not a native English speaker, I do not want to try and correct the English formulations. But I recommend to ask a native speaker to pre-review the text prior to the final publication.

(2) We thank both referees for this comment, therefore we will provide a revised final version of the manuscript which we hope will be better understood.

3)

(1) p.22050, l.10: Biogenic volatile organic compounds are globally the most abundant class of reactive organic compounds in the troposphere. Regionally, such as in urban environments, anthropogenically emitted compounds may dominate the atmospheric OH reactivity.

(2) We modified the text according to the suggestion of the referee.

(3) 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.

4)

(1) p. 22051, l. 16-17: The definition "low NOx" or "high NOx" can be misleading (see Wennberg 2013, "Let's abandon the "High NOx" and "low NOx" terminology").

(2) The text is modified.

(3) Isoprene dominant loss is the oxidation reaction with the OH radical, which involves the formation of six isomeric peroxyradicals which in unpolluted environments further react forming methyl vinyl ketone (MVK), methacrolein (MACR) and formaldehyde (HCHO) as primary products in the highest yields (Jenkin et al., 1998).

5)

(1) p.22053, l. 15: Please, replace "close" with "examine".

(2) We took into account the suggestion.

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

6)

(1) p.22053, l.19: I think it should be "determined" instead of "sampled".

(2) The text is modified.

(3) We determined the 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.

7)

(1) p.22054, l. 3-4: The closest city and town to the measurement site are Marseille and Manosque. Could you please include, how many inhabitants do live there? Also, I cannot see the cities in Figure 1. It would be nice to have their location pictured in Fig.1, especially since you refer to it in the text.

(2) Text and figure are modified according to the referee's comment.

(3)

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 (~ 1600000 inhabitants), and Manosque the closest town about 18 km south from the site (~ 22000 inhabitants) (Fig. 1).
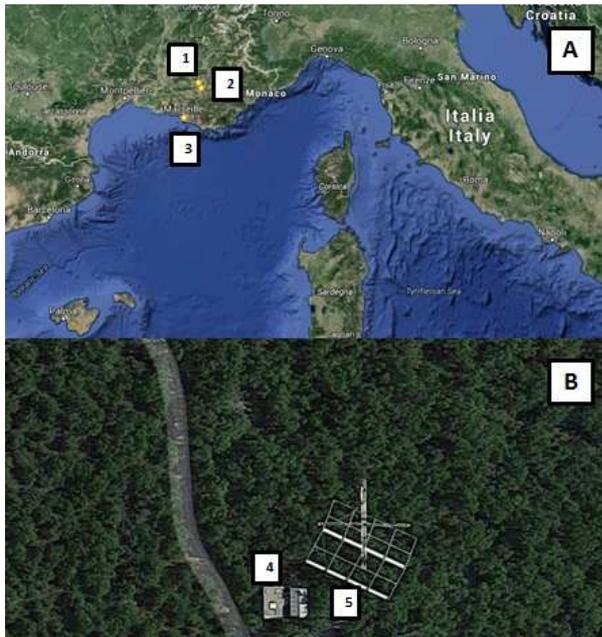

Figure 1. Site of Observatoire de Haute Provence (OHP) in the European map (panel A) and seen from above (panel B). Numbers refer to: (1) OHP field site, (2) town of Manosque, (3) city of Marseille, (4) room for instruments measuring trace gases, (5) movable trailer for measuring OH reactivity.

8)

(1) p.22054, l.16: You determined the leaf area index (LAI) during August 2010 as 2.4. Was it measured again afterwards in another year or another season? Is it not likely to change with time?

(2) No, unfortunately we do not have any more recent measurement of the leaf area index.

9)

(1) Section 2.1 Description of the field site: What was the dominant wind direction? Is the footprint of sampled air predominantly influenced by the oak forest?

(2) The dominant wind direction was north, therefore the sampled air was influenced predominantly by the oak forest. This information is included in the text.

10)

(1)

p.22055, l.7: I find the description of the set-up confusing. You have two PFA sampling lines on a mast. Are these two lines for the two instruments or for the two heights? Or do you have two lines at each height? How long were the lines? Did you have filters? Also, you write later (p.22055, l. 13) that you kept the lines heated, about 1 C above ambient temperature. So, did the line temperature vary according to the diel variation of ambient temperature? p.22055, l.21: The residence time in the lines for the CRM and PTR-MS instruments differed by about 10 seconds. Why did you not adjust these two flows to have the same residence time? Also, if you have individual lines for each instrument, did you test the two lines against each other? Can you rule out any line effect that would bias the CRM and PTR-MS observations for the comparison?

(2) We modified figure 1 to make the description of the sampling approach easier to follow. The two sampling lines are for two containers where the different instruments were placed (Fig 1, number 4 container A and number 5 container B). Sampling line directed to container A was ending with a manifold from where the instruments: PTR-MS, GC-FID, and HCHO analyser were sampling. Sampling line B was directed to a movable trailer where the instrument for measuring the OH reactivity was placed. This line was also ending with a manifold to split the line into sampling line to the zero air generator (for background pyrrole measurements) and sampling line to the reactor for ambient measurements of reactivity. Both manifolds ended with a sampling pump whose flow was adjusted in order to have about the same residence time in the two lines. We thought that a difference of 10 s was fine in this type of experiment to allow us to compare the measured and calculated reactivity. NOx, trace gases on cartridges for GC-MS analysis, and O3 were sampled through extra sampling lines. Therefore, the two lines are for the two containers. These lines had different lengths since the movable trailer (B) was closer to the mast compared to container A. Each line was jointed at 2 by a union connector, in a way that when sampling at 2 m was needed we simply had to disconnect the line at that point. Sampling line A was 30 m, while sampling line B was 18 m from the inlet to the manifold. We did not use any filter, only covered the lines to prevent rain entering inside and insect debris being sampled. The lines were heated above ambient temperature by using a thermocouple to prevent gases condensing inside the lines. The thermocouple heats up the lines by about 1 degree C and follows the diel variation of ambient temperature. Unfortunately we did not test the sampling lines against each other, therefore we cannot completely rule out any line effect that would affect our comparison. However, the two lines were used before only for measuring fluxes of isoprene and other biogenic VOC in the same forest and were both conditioned with the ambient air before the measurement campaign started. These different information will be provided in the text.

11)

(1) p.22055, l.18: C2 and C3 describe concentration levels detected during the CRM measurements and were not explained before. The CRM technique is later explained in section 2.3. Please, remove the CRM

specific terminology from this paragraph, or reorder the paragraphs, or explain it carefully e.g. as zero air and ambient measurements.

(2) This comment is taken into account.

(3) Sampling line B was used for OH reactivity measurements, here a manifold separated the main flow into two flows for measuring zero and ambient reactivity.

12)

(1) p.22055, l.25: At what height exactly did you install the extra line for sampling tubes for offline GC-MS analysis?

(2) At 2 m.

(3) In this case we used an independent extra line that was placed along the mast at 2 m from the ground.

13)

(1) p.22055, l.29: Why was the monoterpene concentration measured by the PTR-MS only every 5 minutes? Similar to comment 11), the PTR-MS technique and details about the instrumental field campaign set-up are presented later in Section 2.4.1. Hence, at this point it needs more explanation or it should be removed from the paragraph.

(2) We used a dwell time of 10 s for m/z 81 and m/z 137. We set the measurements to run full scans between m/z 21 and m/z 138, using different dwell times depending on the mass considered. A complete scan took about 5 minutes, therefore we have a data point of m/z 137 every 5 minutes. We removed this detail about the PTR-MS from this section.

14)

(1) p.22056, l.1-4: What height did the NOx and ozone (O3) instruments sample from?

(2) Both sampling lines were at about 4.3 m high. This detail is added in the text.

15)

(1) p.22056, l.13: Please, exchange "to take up" with "to react with".

(2) ok.

16)

(1) p.22056, l. 22: How did you produce the zero air? Did you adjust the humidity during zero air (C2) measurements to the ambient humidity? Since the OH is generated inside the glass reactor of the CRM, its levels depend on the humidity of the sample. If during the comparison C2 (zero air+OH+pyrrole) and

C3 (ambient air+OH+pyrrole) do not have the same humidity, the OH levels inside the reactor will be different. Hence, the total OH reactivity is under- or overestimated.

(2) This comment is right. Indeed, humidity differences between C2 and C3 levels during a CRM experiment affect the concentration of OH produced inside the reactor. In our case, we split the ambient air into two flows: a flow directed to a zero air generator and a flow directed to the reactor. Therefore, the flow entering inside the zero air generator has the same relative humidity of the flow of ambient air entering the reactor. Additionally, OH is produced inside the reactor by photolysis of the water vapour from a humidified, controlled flow of nitrogen. In proportion with the other flows entering the reactor, nitrogen alone makes the half of the total flow. We saw in some cases that small differences in humidity arise even when using a zero air generator to produce zero air. For such cases a correction for humidity differences is considered on the C2 level. During this field campaign such correction had an impact on the measurements below 10%.

17)

(1) p.22057, l.5: Was the total OH reactivity obtained as average every 10 minutes? What was the time resolution of the raw values?

(2) Raw values of OH reactivity are obtained every 10 minutes which correspond to differences between C3 (5 minutes) and C2 (5 minutes). Averages within the C2 level before and after every C3 are also considered to minimize differences between background reactivities. Depending on the settings used to perform the measurements we have between 5-10 points of m/z 68 during each stage of C3. A few points for each stage are discarded due to valve switching effects (usually the first and last point are discarded), whereas the remaining points are averaged to obtain a value of C3.

18)

(1) p.22057, l.9: Generally it would be more accurate to write "OH reactivity". There are other oxidants such as O3 or nitrate radicals (NO3) that react with most of the atmospheric constituents as well.

(2) This is right. The comment is considered.

19)

(1) p.22057, l.12: You write that propane represents a proxy of an unknown air mass. Why is that? I would think that the average reaction rate with OH of an air mass depends on its origin. A biogenic air mass might contain more reactive compounds (such as isoprene, monoterpenes) than an anthropogenic air mass (for which carbon monoxide (CO) or nitrogen dioxide (NO2) dominate).

(2) We wrote this comment because propane reacts with OH with a constant of reaction on the order of 10^{-12} molecules/cm^3*s, which is an averaged order of magnitude when a number of different reactive molecules are considered. However, the statement is not precise since as Anonymous Referee is pointing out, this strictly depends on the origin of the air masses. For this reason this statement is removed from the text.

20)

(1) p.22057, l.15-21: The correction described in this paragraph differs from previously published CRM studies (e.g. Sinha et al. 2008). Therefore, it would be good to include the graph that is described here either in the manuscript directly, or as supplementary information.

(2) A graph describing this correction is included in the supplementary information.

21)

(1) p. 22057, l. 20-21: How large were these two corrections relative to the measured total OH reactivity? It would be interesting to learn about the relative impact of these corrections.

(2) Both corrections used for processing the data decreased the values of the raw reactivity. The correction for humidity differences led to a 13% decrease of the original values, while the correction for kinetics led to a 47% decrease. Generally, the correction for humidity has a small weight, if some measures for minimizing the differences in humidity between C2 and C3 are considered, as in the case of using a zero air generator to produce zero air, for instance. The weight of the kinetics correction depends on the experimental conditions adopted in the reactor. Specifically, when operating in a window of pyrrole/OH within 1-3 the agreement within reactivity measured and reactivity injected during a calibration with a certified test gas responds better, hence smaller corrections are needed. For our specific case, we encountered a larger correction factor for the kinetics regime in this field work, due to a lower concentration of OH formed inside the reactor, hence a larger pyrrole/OH ratio.

22)

(1) p.22057, l. 23-26: Here you talk about the calibration of the PTR-MS instrument that was used for pyrrole detection. The instrument was calibrated in dry and wet conditions. You should briefly explain why this is necessary, and refer to Sinha et al. (2010) who pointed out that the PTR-MS sensitivity to pyrrole depends strongly on humidity.

(2) Yes, this is added in the text.

(3) 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). 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).

23)

(1) p. 22058, l. 11: This is not a sentence.

(2) it is corrected.

(3) with i being any measured compound listed in Table 1.

24)

(1) p.22058, l.23 and p.22059, l.18-24: The PTR-MS was calibrated with a standard gas mixture containing several volatile organic compounds. Particularly, m/z 71 was calibrated with crotonaldehyde. The atmospheric signal, however, was identified as isoprene products including methacrolein (MACR), methyl vinyl ketone (MVK) and isoprene hydroperoxides (ISOPOOH). First, I wonder if the PTR-MS sensitivity would be different for these compounds. Then, I think this section could be improved by explaining at first that m/z 71 typically was assigned to the sum of MVK and MACR, and only recently the mentioned interference of ISOPOOH was discovered. Could you please modify this part in the text?

(2) The calibration with crotonaldehyde instead of methacrolein and methyl vinyl ketone is performed due to logistical reasons and similarities of the molecules. First, it is easier to have and transport a certified gas standard of crotonaldehyde compared to MACR and MVK. Secondly, the molecules have similar chemical properties and the same mass, so it is often used crotonaldehyde for calibrating m/z 71 (see also the article of Kalogridis et al., 2014). However, we think that MACR MVK and ISOPOOH might have among them slightly different sensitivities. As far as we know, there are no studies available in literature about this, and it would be something interesting to know. Yes, the part related to the ISOPOOH is modified in the text.

(3) 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 NOx 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: methylvinyl ketone (MVK)+methacrolein (MACR)+isoprene hydroperoxides (ISOPOOH).

25)

(1) p.22059, l.2: The PTR-MS sensitivity depends on humidity for most of the compounds in the standard gas mixture used for calibration. Were the calibrations performed in dry or in wet conditions? Did you try to match typical ambient humidity levels?

(2) The calibrations of the PTR-MS were performed at ambient humidity levels, since the certified gas standard is diluted in cleaned ambient air.

26)

(1) Could you please check the acronyms used in the entire manuscript? Generally, I found that sometimes they were not introduced properly or differ from how they are used later. For example: p.22058, l.13 "PTR-QMS" is later "PTR-MS" (p.22059, l.14). Or: "MEK" (p.22059, l.25) is not defined when first mentioned as methyl ethyl ketone. Similar later for formaldehyde: "HCHO" (p.22060, l.19).

(2) Ok.

27)

(1) p.22060, l.6: Losses are typically enhanced by stainless steel tubing and Nafion dryers. Did you test your set-up for losses?

(2) Yes. Some tests were performed to check losses due to stainless steel tubing and the Nafion dryer. Specifically, no losses were observed for VOCs, except for a small contamination occurred for isobutene (10 pptv) due to the Nafion dryer (see also the article of Bonsang et al., 2008).

28)

(1) p.22062, l.3: The samples for GC-MS offline analysis were stored at 4C and analyzed within a month in the laboratory. Did you test if there are any losses of your compounds of interest during this procedure? How large do you estimate such losses?

(2) Unfortunately, we have not conducted any specific test for demonstrating if this procedure can lead to any losses of the compounds of interest for our study. However, ozone was removed from the tubes prior to the sampling procedure by using MnO_2-coated copper nets, according to the procedure reported in Larsen et al., 1997. Larsen and coauthors highlighted that for mixing ratios of ozone larger than 8 ppbv, losses are generally reported for more reactive monoterpenes as limonene for instance, a compound also measured in our study. This information is added in the text.

29)

(1) p.22062, l.12: It is really unfortunate that CO was not measured during the field campaign. I would think that usually atmospheric CO levels are quite variable and dependent on transport processes and regional pollution. Since you had to use the average of springtime measurements, could you as well report how variable the atmospheric CO levels were in spring 2012? Did you include this variability in the uncertainty of the total OH reactivity calculation?

(2) Yes, this information is added in the text and in the calculation of the uncertainty for the OH reactivity calculated. CO concentration was variable of 16 ppbv within the period 23/05/2012 to 18/06/2012 which corresponds to a mean value of OH reactivity of 1.02 ±0.09 s-1.

30)

(1) Section 3.1 Trace gases profiles and atmospheric regime: I do not understand the meaning of this title. Do you mean diel profiles? Vertical profiles? And what do you mean with atmospheric regime?

(2) The title of this section is probably too unclear, therefore it is adjusted to "trace gases mixing ratios" and we thank the referee for pointing this out.

31)

(1) p. 22063, l.11: ": : :isoprene covariates perfectly with PAR" Could you please provide the correlation coefficient?

(2) Isoprene mixing ratio does not covariate perfectly with PAR, due to the fact that the two parameters are not measured exactly at the same height and place, hence the perfectly is removed from the text.

32)

(1) p.22063, l. 13-15: To be precise, you could add the exact hour of the day when the peaks occur. If you do so, I think that isoprene above the canopy would peak at about 20 CEST (Fig. 2). This is after sunset. Can you explain why isoprene has its maximum that late in the day above the canopy?

(2) Yes, the maximum peak of isoprene concentration occurred at 20 CEST above the canopy. This is driven by the profile of isoprene concentration which was slightly shifted on 08/06/2014. Indeed if the daily median and not the daily mean is considered the concentration of isoprene would have a peak at 15 (CEST) in the early afternoon. We think that this peak of concentration of isoprene so late in the day is a result of the higher temperature of ambient air in the late afternoon occurred on 08/06/2014 (the profile of temperature is reported in Fig.6).

33)

(1) p.22064, l.8 and 10: You present the daily maximum inside the canopy for methanol and isoprene as 14 ppbv and 23 ppbv. Are these values averages?

(2) No. These numbers represents the maximum values of the daily maximum peaks reported during the days of the campaign we measured inside the canopy.

34)

(1) p.22064, l.12: What are 24h statistics? I am not familiar with this terminology.

(2) This terminology was used to allow an easier comparison with the table presented in the previous article where concentrations and fluxes in the same forest were measured (Kalogridis et al., 2014). It would mean that the values reported herein are obtained when all data points, measured during daytime and nighttime, are considered. The term is changed in the text.

35)

(1) p.22064, l.21: Please, add ": : :with ethane being the most abundant: : :"

(2) Yes.

36)

(1) p.22065, l.19-28: Could you make clear which height was sampled from at which day? So, during 11 June 2014 the instrument measured from 2m. You describe the temporal variation of total OH reactivity with two maxima during daytime. If you look at it differently, it could be a slight drop around noon. Could it be that at noon, when light intensity and temperature levels are at their maximum, the oaks favor photorespiration and tend to close their stomata? This would reduce the direct emission of reactive species at midday. Interestingly, the shape of total OH reactivity during daytime above the

canopy differs slightly from within the canopy. It follows less the diurnal cycle of light and temperature, but gradually increases during the daytime to reach peak levels at about 21 CEST. Could you comment on that?

(2) Yes. At 2 m (inside the canopy): 31/05/2014, 01/06/2014, 02/06/2014, 03/06/2014, 04/06/2014, 05/06/2014, 06/06/2014, 11/06/2014, 12/06/2014.

At 10 m (above the canopy): 29/05/2014, 30/05/2014, 07/06/2014, 08/06/2014.

Therefore, the OH reactivity on 11/06/2014 was measured at 2 m, inside the forest. Its profile covariates with isoprene concentration and it could be speculated that the drop in OH reactivity reported around noon on this day is a result of reduced direct emission of reactive species due to enhanced levels of light intensity and temperature. This effect could actually be possible, but not directly associated to isoprene, neither due to maximum levels of temperature and PAR. Indeed, as the figure below shows, the OH reactivity profile follows well the one of the concentration of isoprene, which is depending on light and temperature. However, light and temperature maximums are slightly shifted after the mentioned drop. Nicely, isoprene does not show the same first peak of reactivity (10.30 CEST), whilst oxygenated molecules might be more the possible cause of it. Therefore it looks like that a drop in concentration might happen for the oxygenated molecules, rather than for isoprene. However, isoprene is also the dominant species emitted by this type of oak, therefore if this effect is associated to the oak leaves then we would see a clearer drop in isoprene concentration as well. In conclusion, we do not think we have enough elements from our study to point out this physiological effect.
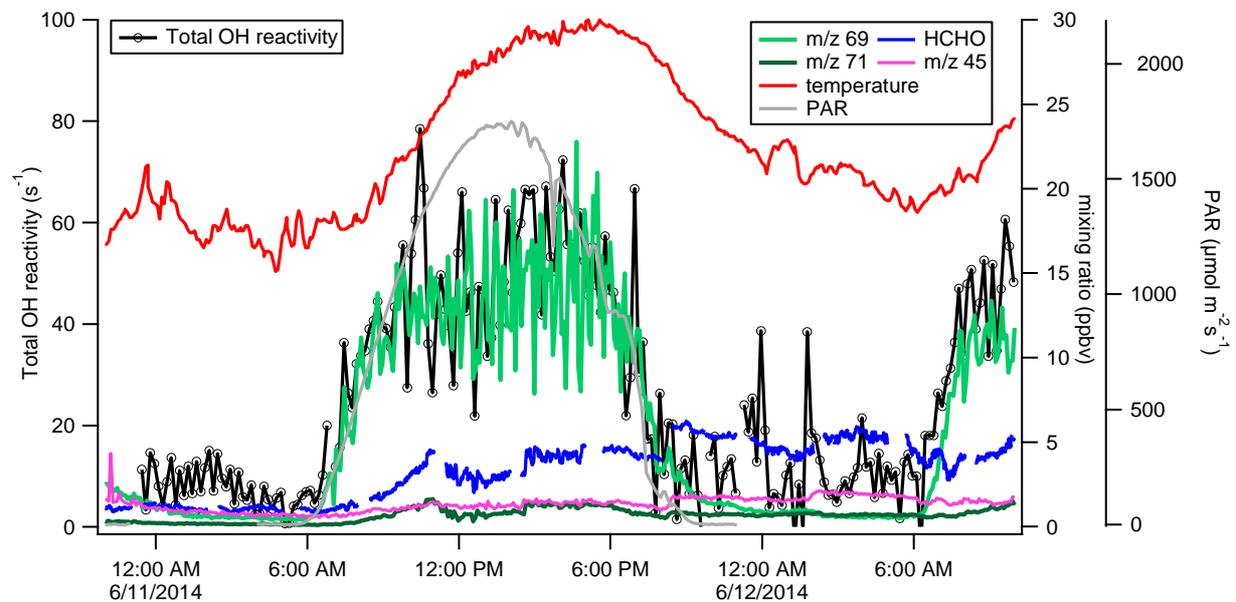
37)

(1) p.22066, l.22: How did you estimate 25% uncertainty for the calculated total OH reactivity? This value seems very small with respect to the high uncertainty every single reaction rate constant has. Additionally, the CO level was assumed to be constant which probably further increases the uncertainty of this value. It would be interesting to add a small paragraph about the uncertainty of the calculated OH reactivity to the experimental section.

(2) The error on the calculated value of OH reactivity is estimated by considering the propagation of the 1 sigma uncertainty on the rate constant of reaction between OH and the measured compound and the 1 sigma uncertainty associated to the concentration of the measured compound. The variability on CO adds very little to the overall uncertainty, being the mean reactivity of CO estimated to $1 \ s^{-1}$ with a variability of about 8%. More explanations on how the error is calculated are added to the text.

38)

(1) p.22067, l.3-p.22068, l.6: This is a very interesting paragraph. But it is written in a way that is difficult to understand. Could you please simplify and be more specific with the presentation. For example l.13-14: Why do you assume equal OH reactivity above and within the canopy? And l.16: I am not familiar with the expression "9 point percentage". p.22067, l. 15: Please, write correctly 30_C and 32_C. p.22068, l.3: Erase "definitely".

(2) We thank Anonymous referee 1 for pointing out these difficulties. This part is rephrased and the suggestions indicated are taken into account.

39)

(1) p.22068, l.25: You write that isoprene concentrations flattered much faster than its oxidation products. As reason you refer to its higher reaction rate. Most probably, it is as well the close proximity to the source, that causes the high variability. As a measure for short term you could provide the relative standard deviation (see e.g. Noelscher et al. 2012, ACP).

(2) The relative standard deviation is provided in the text.

40)

(1) p.22069, l.2: You state that ISOP.OXs/isoprene anticovariate with ozone as can be seen in Figures 9 and 10. I can see in Figure 9 that the increase of ISOP.OXs/isoprene falls together with the decrease in ozone. However, I cannot see such a behaviour in Figure 10. Therefore, I think it is too strong to talk about an anticorrelation. Can you provide a correlation coefficient of ISOP.OXs/isoprene with ozone to prove an anticorrelation?

(2) We thank the referee for this comment, indeed the term anticorrelation is too strong for these profiles and for this reason it is removed from the text.

41)

(1) p.22069, l.2 and Figures 9 and 10: Ozone levels are relatively high (about 50 ppb) for a forested environment. Do you have any explanation for such high ambient ozone mixing ratios?

(2) These high values do not derive to any process occurring in the forest, and are usually registered in this specific forest due to the proximity of urban sites as Marseille, and closer, Manosque.

42)

(1) p.22069, l.9 and following paragraphs: In order to explain the missing reactivity that was observed during two nights, you point to nighttime chemistry or lateron to surface oxidation reactions. Could you please also discuss the effect of boundary layer dynamics such as dilution or enhanced deposition during nighttime? What about humidity dependent emissions from the soil or microbial communities on leaves?

(2) Yes these effects are better discussed in the text.

43)

(1) p.22071, l.1: I do not think that forest environments may be called "perfect laboratories". The experiment examining the total OH reactivity in air within or above a forest is not a controlled study. Often even laboratory work is by far not perfect as the technical set-up, instrumental limitations, or other unknowns bias the scientific results.

(2) This is also modified in the text.

44)

(1) Table 3 presents mean mixing ratios of the PTR-MS detected compounds. If you additionally include the standard deviation or standard error, you could emphasize the variability of the total OH reactivity.

(2) yes the standard deviation is added in Table 3.

45)

(1) Figure 1 shows the measurement site. Could you please point to the cities mentioned in the text? And could you also show where the instruments and the inlet set-up are located in the oak forest?

(2) Yes, Figure 1 is modified.

46)

(1) Figure 2: The diel mean (?) profiles of isoprene, isoprene oxidation products, formaldehyde, PAR and temperature are presented for inside and above the canopy. At which height was the temperature measured?

(2) Yes, figure 2 represents the diel mean profiles. The temperature was measured by two sensors, one placed at 2 m (used for the left panel, inside the canopy) and the other one placed at 6.15 m (used for the right panel, above the canopy). This information is added in the figure's caption.

47)

(1) For several figures, please make sure that the labels or description text is not moved into axes or figure elements (such as in Figure 3, 7 and 8).

(2) Yes, the figures are adjusted.

48)

(1) It would be nice to point out at which height the presented data was measured. Similarly as in Figure 2, could you please add a box with "inside/above canopy" to the Figures 5, 6, 7, 8, 9, and 10?

(2) Yes. The figures are modified for this.

The authors would like to thank Anonymous referee 2 for her/his valuable comments to the manuscript. Please find below the answers to the comments and changes in the manuscript text.

1)

(1) Though, the paper is well structured, I agree with the comments of Reviewer 1, that at times there are serious language issues which tend to obscure the scientific meaning/clarity of the discussion. Thus the senior authors should help revise the submission or english language editing should be undertaken for the revsied version. The full list would be very big so I shall point out just a few where the choice of the words is not correct.

e.g. 1: Page 220068; Line 15 and at other places in the MS :words like scatter and flattered ....."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)." The authors probably mean the trace becomes flat??

"24 h statistics", "9 point percentage", "breakdown of reactivity " for pie charts..

(2) We are thankful to both referees for pointing out these language issues in the manuscript. We modified some parts of the text and a revision from a native English speaker of the final version will be done as well.

2)

(1) Qualitative conjectures should be avoided:.... ...e.g.Page 22063; Line 11: "co-variated perfectly with PAR...." In such cases, the correlation coefficient should be mentioned...

(2) This is right. We have included more information/removed some comments from the text.

3)

(1) Why do the authors have such high uncertainty for the CRM OH reactivity measurements (35 %) when other CRM systems typically do a better job and the authors' own previous work (e.g. Dolgorouky et al.,2012) had less uncertainty? If it is due to specific conditions encountered in the present deployment , then the same should be discussed.

(2) Yes, 35% uncertainty on the measured reactivity is a higher value than the one of the previous instrument used in our laboratory and higher than the stated uncertainties on other CRM instruments constructed in other laboratories. This number accounts also for the uncertainties on the correction factors needed to process the raw data sets of reactivity. Specifically, it includes the uncertainty on the rate coefficient of the reaction of pyrrole with OH, uncertainty on the flow rates of all gases flowing inside and outside the reactor, uncertainties on the correction factor for kinetics (which represents the largest source of error and its investigation is currently ongoing) and uncertainties on pyrrole concentration from the certified standard and pyrrole sensitivity to the PTR-MS. We also used a certified standard of pyrrole with a larger error associated to its concentration compared to the pyrrole cylinder used in the study of Dolgorouky et al.,2012. More information can be found in Zannoni et al., 2015 and the whole calculations are provided in the supplement of the article of Michoud et al., 2015.

4)

(1) How did the authors produce the C2 stage zero ? Did they try humidifying botlled zero air or was it using a catalytic scrubber? How was the humidity regulated for the reactivity measurements? These are important points to clarify because as seen in Fig 5 and Fig 6, the ambient RH covers quite a range (25% RH duirng daytime to ~ 60% RH at night), and ensuring the humidity is ok between C2 and C3 stages is no longer trivial.

(2) We produced the C2 stage zero by sampling ambient air through a zero air generator, which provided clean air at the same level of humidity of ambient air. Though, small differences in m/z 37/m/z 19 (here considered as tracer for absolute humidity) were noticeable between the stages C2 and C3 and a correction for humidity was applied to the data set of OH reactivity. Such correction had an impact of about 13% on the raw data of reactivity.

5)

(1)

The authors should discuss the magnitude of the pseudo first order correction for the measured OH reactivity values. Generally, the direction in which this correction works is to bring down the measured OH reactivity value, especially if an unreactive molecule like propane is used for inferring the correction. However in the present study, as isoprene and pyrrole both have similar reactivity with OH radicals (rate coefficients are of the order of 10-10 cm3 molecule-1 s-1), I am a little concerned that the correction

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applied to account for the pseudo first order effect could have caused underestimation of the measured OH reactivity, which could affect the conclusions about not having much missing OH reactivity.

 (2) In our study the correction for deviation from pseudo first order kinetics was estimated by testing the response of our instrument, on the field, to two specific ambient reactive tracers: isoprene, a key species in this forest environment, and propane which is less reactive to OH than isoprene and in the present study can better represent other atmospheric reactive gases sampled at the site. Additionally, tests are conducted at different pyrrole/OH ratios in order to cover the different OH fields and kinetics occurring inside the reactor during the campaign. The results from these tests will be available in the supplementary material. The magnitude of this correction impacted the data set of reactivity by decreasing the values by 47%. This magnitude is higher than those encountered in other field experiments with the same instrument due, to our opinion, to less OH radicals produced inside the reactor due to less intensity of the UV lamp we used for this campaign.

6)

(1) The high ozone concentrations (60-70 ppb!) and its time series seem to be at variance with the finding that not much photochemistry occurs within the forest and lack of transport of anthropogenically influenced air masses to the site (which the authors state to be the case based on the benzene and acetonitrile measurements). As the author seem to have NOx measurements and OH reactivity measurements, it may benefit the discussion if they discuss the photochemical regime for ozone formation in the forest based on the ratio of NOx OH reactivity/VOC OH reactivity (see for e.g. Sinha et al., 2012," Constraints on instantaneous ozone production regimes and rates..." Atmos Chem Phys).

(2) Ozone is continuously monitored at the field site and in the surrounding area (as Manosque, Marseille) by the regional air quality network. Such high levels reported in this study are usually observed at the site and in line with the levels observed at more polluted sites surrounding the area of OHP, suggesting that no specific photochemistry occurs within this forest and that this mixing ratio is rather the result of transported ozone.

We thank Anonymous referee for her/his suggestion in evaluating the photochemical regime in the forest. However, it falls a bit outside the main scope of this specific article which is comparing the measured and calculated reactivity to highlight any missing component in the forest.

7)

(1) What is the role of deposition of OVOCs and ozone to the forest and its implications if any for their conclusions? Some discussion on this would strengthen the MS further.

(2) Previous measurements in the same forest of OCS (carbonyl sulfide) and its observed analogy with ozone, suggested that the deposition flux of ozone in this forest was mostly the result of leaves uptake (Belviso et al., now in preparation). If this is the case, it can be speculated that ozone might lead to surface reactions forming the oxygenated molecules responsible for the missing reactivity observed

during nighttime. This could be possible since the downy oak is a broad-leaf tree species, which might enhance these processes. However, more studies at the leaf scale are needed to investigate whether this process is occurring. The discussion of the missing nighttime reactivity will be improved in the text considering also the comments of Anonymous referee 1.

8)

(1) Page 22058; At 2.2 mbar and 60 degree celsius, I think the Townsend ratio would be 135 Td and not 130 Td; Can the authors please check their calculation?

(2) Yes, it is checked and corrected in the manuscript.

9)

(1) Fragmentation of isoprene peroxides and their contribution to m/z 71 seems new. Can the authors cite some work and add more light on it? Unless the studies reporting the fragmentation used the same Td ratio in the drift tube, can one extrapolate those results for different Td conditions?

(2) It might be confusing in the manuscript but we did not separate the different components measured at m/z 71. However, since m/z 71 has been recently attributed also to ISOPOOH for unpolluted sites, we cannot neglect that we also measured these compounds at m/z 71. Since ISOPOOH have different vapor pressures and solubility compared to MVK and MACR these compounds have been separated and identified with the PTR-MS by using a water trap. As also suggested by Anonymous referee 1, we reworded this part of the manuscript to make clearer that we consider these compounds not because we separated them but because it was recently found that they also contribute to the m/z 71 (see point (3)). It is possible that these molecules can be measured at other Td conditions, their presence mostly depends on the level of NOx at the site of measurements.

(3) 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 NOx 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: methylvinyl ketone (MVK)+methacrolein (MACR)+isoprene hydroperoxides (ISOPOOH).

10)

(1) As the measurement site is a long term measurement site, where other routine measurements are performed, is there any information on the boundary layer dynamics between day and night at the site? van Stratum et al.,Atmos Chem Phys 2012 showed these to be significant for another Mediterranean site with pine trees and I wonder if that could explain the strange ozone profile.

(2) Unfortunately ozone is the only parameter which is continuously monitored at the site.

11)

(1) The authors may want to add some new OH reactivity measurements (average ~ 50 s-1)to Figure 11 from an environment where biogenic emissions are dominated by agro-foresty of high isoprene emitting trees such as poplar and eucalyptus and isoprene concentrations are as high as 3 ppb (Kumar and Sinha, Int. J. of Mass Spectrom., 374, 55-63, 2014. http://dx.doi.org/10.1016/j.ijms.2014.10.012).

(2) Yes. This is right, the results from these measurements are included in figure 11.

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

1

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, neither inside, nor 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

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 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~~makes up~~ 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 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 T~~the presence, position and number of ~~the~~ 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 $2 \ 10^6$ 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 from~~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).~~

The dominant loss of isoprene is the oxidation reaction with the OH radical, which involves the formation of six isomeric peroxyradicals which in unpolluted environments 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,

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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 the 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).,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 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 for infrom 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) all which will all influence BVOCs emissions in strength

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and pattern (Laothawornkitkul et al., 2009). Such findings highlight~~pose the attention on~~ the importance of conducting more, intense and long-term field studies in the Mediterranean region.

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 mg m^{-2} h^{-1}~~-~~) during summer 2010 (Baghi et al., 2012) and up to 9.7 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 examine the reactive carbon budget, and help assess the oxidative processes occurring through the canopy.

~~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 gas~~es~~ concentration~~s~~ 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.~~ 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, 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).~~

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 (~ 1600000 inhabitants), and Manosque the closest town about 18 km south from the site (~ 22000 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 11/07/2014) 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 due to~~for~~ its dominance in this forest it makes OHP a natural laboratory for focused studies on isoprene.

Our field work took place during 29/05/2014- 12/06/2014 , 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 m and 10 m), during 29/05/2014-12/06/2014. With an average canopy height of 5 m, air collection conducted at 2 m 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 seconds 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 minutes.

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.

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 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 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 (Figure 1, number 4), and to a movable trailer B (Figure 1, number 5), respectively. Both lines were ending 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 Hantzch analyser, which were all located in local A. On the other hand, sampling line B was used for measuring the 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 a similar residence time of the species sampled through lines A and B, which were respectively, 23 seconds and 13 seconds. The lines whole length was respectively 28 m 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, to prevent gases condensation. Measurements with this sampling set-up were performed sequentially on different days over the campaign period 29/05/2014- 12/06/2014 at two heights: 2 m and 10 m. With an average canopy height of 5 m, air collection conducted at 2 m 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 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.

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$_4$H$_5$N) and reactive molecules in ambient air to react with 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 isare 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:

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

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

10

Reactivity in ambient air is obtained every 10 minutes (calculated from 5 minutes on C2 and 5 minutes 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 qualified 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 ($k_{propane+OH}$=1.1 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 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 ratio 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) with 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 (see supplementary information). 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 pyrrole 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 only for only five days (three days inside the canopy and two days above the canopy) due to the time needed to

1 accurately test~~qualify~~ the performance of our instrument on the field, settings adjustment and tests

2 needed to process the raw data.

3 Our instrument performs measurements between the limit of detection, (LoD), of the instrument (3

4 s^{-1}, 3σ) up to 500 s^{-1} with an overall systematic uncertainty of 35% (1σ). More information on our

5 instrument can be found in Zannoni et al., 2015.

6 **2.4 Complementary measurements at the field site**

7 We measured the concentration of BVOCs emitted from the forest, their oxidation products and

8 main atmospheric constituents. Concentrations are used to calculate the OH reactivity at the site

9 with Eq. 2 and the species specific relative contribution.

10 $$R = \sum_i k_{i+OH} \cdot X_i \qquad\qquad (2)$$

11 with *i* being any measured compound listed in Table 1.~~With *i* any measured compound listed in~~

12 ~~Table 1.~~

13 The error on the calculated value of OH reactivity is estimated by considering the propagation of

14 the 1 σ uncertainty on the rate constant of reaction between OH and the measured compound and

15 the 1 σ uncertainty associated to the concentration of the measured compound.

16 2.4.1 Proton Transfer Reaction-Mass Spectrometer

17 We used a Proton Transfer Reaction- Mass Spectrometer (PTR-MS, High sensitivity quadrupole,

18 from Ionicon Analytik, Austria)~~We used a Proton Transfer Reaction Quadrupole Mass~~

19 ~~Spectrometer (PTR-QMS, Ionicon Analytik, Austria)~~ operated under standard conditions (p$_{drift}$=2.2

20 mbar, *E/N*=135~~0~~ Td (1 Td=10^{-17} Vcm^{-1}), T$_{inlet}$= 60°C) to record the concentrations of trace gases at

21 the site, (Lindinger and Jordan, 1998). We sampled the air masses in the scan mode, and inspected

22 all species with protonated mass from *m/z* 21 to *m/z* 138 with cycles of 5 minutes each. Sampling in

23 the scan mode procedure revealed to be a convenient way for analyzing unknown air parcels.

24 We calibrated the instrument using a gas calibration unit (GCU, Ionicon Analytik, Austria) with a

25 standard gas mixture (GCU, Ionicon Analytik, Austria) containing: methanol (*m/z* 33), acetonitrile

26 (*m/z* 42), acetaldehyde (*m/z* 45), acrolein (*m/z* 57), acetone (*m/z* 59), isoprene (*m/z* 69),

27 crotonaldehyde (*m/z* 71), methyl ethyl ketone (*m/z* 73), benzene (*m/z* 79), toluene (*m/z* 93), α-pinene

28 (*m/z* 137); see Table 2 for the list of compounds, their protonated mass, mean sensitivity from field

29 calibrations and masses LoD. Calibrations were run over the range 0-20 ppbv at the beginning and

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1 at the end of the field campaign, with no significant change in the detector sensitivity (differences

2 up to 10% and for most species within 5%) therefore we used a mean calibration factor for the

3 whole campaign.

4 Volume mixing ratios for the calibrated species were obtained following the procedure of Taipale et

5 al., 2008. Mixing ratios for the non-calibrated species were obtained from the transmission curve of

6 the instrument and the species specific transmission coefficient. Correlations within mixing ratios

7 obtained from calibration and transmission coefficients for calibrated species showed a good/fair

8 agreement (R^2 for *m/z* 33, *m/z* 45 and *m/z* 69 respectively 0.81, 0.86 and 0.43).

9 We used a Gas Chromatography-Flame Ionization Detector to cross validate the concentration

10 obtained for isoprene, which is the dominant compound at the site, usually measured at the

11 protonated *m/z* 69 with the PTR-MS but often prone to fragmentation in the drift tube (see section

12 2.4.2). All the measured species, except isoprene, were not cross validated, and their mass

13 identification was conducted based on the existing literature at similar sites, *e.g.* Kalogridis et al.,

14 (2014); Holzinger et al., (2002); Warneke et al., (2001). This is the case in particular for masses

15 *m/z* 71 and *m/z* 73. The former has usually been attributed to the sum of methyl vinyl ketone

16 (MVK) and methacrolein (MACR), the most abundant oxidation products of isoprene. Recent

17 studies have highlighted that another group of compounds, the isoprene hydroperoxides

18 (ISOPOOH), mostly originated from isoprene oxidation in unpolluted environments can also

19 fragment at *m/z* 71 in the PTR-MS (Liu et al., 2013 and Rivera-Rios et al., 2014). Since we did not

20 separate between these compounds, and conducted our field work in an unpolluted environment,

21 where the ISOPOOH might have been produced, we will refer hereinafter to *m/z* 71 as the sum of

22 the isoprene oxidation products ISOP.OXs: methyl vinyl ketone (MVK) + methacrolein (MACR) +

23 isoprene hydroperoxides (ISOPOOH). ~~Previous studies highlighted the presence of isoprene~~

24 ~~hydroperoxides (ISOPOOH) fragmenting at~~ *m/z* ~~71 in the PTR-MS, and representing a major yield~~

25 ~~from isoprene oxidation for low NOx environments, such as our case study (Liu et al., 2013 and~~

26 ~~Rivera Rios et al., 2014). Since we did not separate between these compounds, we will therefore~~

27 ~~refer hereinafter to~~ *m/z* ~~71 as the sum of the isoprene oxidation products ISOP.OXs: methyl vinyl~~

28 ~~ketone (MVK) + methacrolein (MACR) + isoprene hydroperoxides (ISOPOOH).~~ Mass-to-charge

29 73, here reported as methyl ethyl ketone (MEK) and calibrated as such, can have several

30 interferences. Among the possible interferences we speculate the presence of methylglyoxal, a

31 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., now in preparation.

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 minutes (10 minutes sampling followed by 20 minutes 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$_{GC\text{-}FID}$=0.86(isoprene$_{PTR\text{-}MS}$), R^2=0.93).

2.4.3 Formaldehyde analyzer

Formaldehyde (HCHO) 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., 2014). 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 min and 25 min and were performed every 12 h 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

14

1 121 zero measurements made during the campaign, which was consistent with the typical LoD

2 achieved (~ 30 pptv) with the same analyzer in the previous studies above cited.

3 To minimize the effects of temperature changes on the field (see details in Preunkert et al., (2013)),

4 the instrument was placed in a thermostated box at 24°C. A Teflon filter (47 mm diameter) was

5 placed on the sampling line between the manifold (see section 2.2) and the HCHO analyzer to

6 prevent large particles (*e.g.* plant debris) entering the instrument. A comparison conducted on the

7 field between line A (see section 2.2, including the Teflon filter) and a 3 m long PTFE line (OD

8 1/4") connected directly to the analyzer confirmed that no significant contamination or loss of

9 HCHO was present with this set up.

10 2.4.4 NO_x analyzer

11 Nitrogen oxides were measured with a commercial instrument (17i model, Thermo Scientific,

12 USA), based on chemiluminescence. Its calibration was performed after the field campaign, where a

13 LoD of 0.3 ppbv (2σ) and a precision of +/- 0.4 ppbv were estimated.

14 Nitrogen oxides were sampled at 15 m from the main sampling site, hence we assumed that their

15 concentration inside and above the canopy was not affected by any significant change.

16 2.4.5 GC-MS offline analysis

17 Adsorbing stainless steel sampling tubes ~~in stainless steel~~ with Tenax TA and Carbopack X as

18 sorbents were used to sample monoterpenes as α-pinene, β-pinene, β-myrcene and limonene for off-

19 line analysis with a Gas Chromatograph-Mass Spectrometer (GC-MS, 3800/2200 ion trap MS,

20 Varian, USA). Sampling was conducted at ambient temperature with an autosampler (Sypac V2,

21 Tera Environnement, France) every three hours, tubes were then stored at 4°C and analyzed within

22 one month in the laboratory. Ozone was removed from the tubes prior to the sampling procedure by

23 using MnO_2-coated copper nets, according to the procedure reported in Larsen et al., (1997).

24 Concentrations of individual monoterpenes were then used to infer their relative abundance from

25 the total monoterpenes concentration obtained with the PTR-MS and calculate their contribution to

26 the OH reactivity.

27 2.4.6 O_3, CH_4, CO

28 Ozone is constantly monitored at OHP from the regional Air quality network Air-Paca, France

29 (http://www.atmopaca.org/). The monitor is placed in a container located at a distance of a few

15

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 ppbv and 108 ± 16 ppbv 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 with discussion of the results discussing results inside the canopy and above the canopy respectively.

3   Results

3.1   Trace gases mixing ratio profiles and atmospheric regime

During the first campaign week of campaign we observed some peaks of contamination for about one hour every morning due to emissions from car exhausts 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 has similar profiles to PAR and temperature, 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 mean values peaks when temperature is highest in both cases: during the afternoon inside the canopy (2 PM, left panel) and, during the late afternoon above the canopy (8 PM, right panel). The latter peak measured so late above the canopy is driven by the enhanced ambient temperature measured on 8/06/2014 (represented in fig. 6). 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 8/6/2014, see Fig. 3.

16

1 Time series are reported in Fig. 3 for the whole campaign period, from 29/05/2014 to 12/06/2014,

2 with different colors indicating the~~and distinguished between~~ air masses sampled at 2 m (data

3 reported with the green line), and at 10 m (data reported with the blue line)~~, on different days~~. All

4 species show a progressive increase towards the end of the field campaign, when air temperature at

5 the site was higher compared to the first days of measurements~~s~~. Data collected between

6 07/06/2014-12/06/2014 above and inside the canopy can be directly compared, based on similar

7 conditions of temperature and solar radiation. Maximum values for isoprene inside and above the

8 canopy are close (maximum at 10 m is 19 ppbv, maximum at 2 m is 23 ppbv) and small differences

9 can be explained mainly on a dilution basis, a better mixing of air masses reached above the canopy

10 height due to the sparse canopy structure. Interestingly, high levels of *m/z* 71 and HCHO were

11 recorded during the nights between 07/06 and 08/06 and between 11/06 and 12/06. Such high

12 nighttime concentrations are also observed for other chemical species (see text below). Figure 4

13 illustrates time series for masses *m/z* 33, *m/z* 45, *m/z* 59, *m/z* 73 and *m/z* 137; identified respectively

14 as methanol, acetaldehyde, acetone, methyl ethyl ketone and sum of monoterpenes. Monoterpenes

15 are primary emitted biogenic compounds while the other species can have both primary and

16 secondary origins (Jacob et al., 2002; Jacob et al., 2005 and Millet et al., 2010). Methanol has a

17 daily maximum of 14 ppbv (inside the canopy), which makes it the second most abundant

18 compound measured at OHP after isoprene (daily max inside the canopy 23 ppbv), followed by

19 acetone, acetaldehyde, monoterpenes, ISOP.OXs, toluene and benzene, in order of abundance

20 (Table 3). Over 24 hours, ~~Based on a 24h statistics,~~ methanol is instead the first most abundant

21 compound at OHP, followed by isoprene, acetone and acetaldehyde. Both methanol and isoprene

22 have a diurnal profile, but methanol has a longer lifetime compared to isoprene (estimated to be 12

23 days and 1.4 hours respectively, see Atkinson and Arey, 2003) therefore over 24 hours the former

24 shows less variability in the atmosphere.

25 During the two nights mentioned above (08/06 and 12/06) the concentration of the oxygenated

26 compounds was higher compared to the other nights. More discussion on this behaviour is provided

27 in section 3.4.

28 Anthropogenic hydrocarbons mixing ratios in the fraction C2-C6 were individually below 1.5 ppbv,

29 with ethane being the most abundant (mean over the campaign= 0.9 ± 0.2 ppbv), followed by

30 acetylene, ethylene and iso-pentane. Anthropogenic tracers measured by PTR-MS showed the same

31 trend and confirmed the poor anthropogenic influence at this forested site: benzene maximum was

32 0.41 ppbv, the mean over 24 hours was 0.04 ppbv, toluene was maximum 0.69 ppbv and its mean

17

over 24 hours was 0.05 ppbv. ~~benzene maximum was 0.41 ppbv, with a 24h statistics mean of 0.04~~ ~~ppbv, toluene was maximum 0.69 ppbv and its mean over 24h was 0.05 ppbv.~~ Concentrations of NO and NO_2 were maximum 1.7 ppbv 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.

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 in~~at~~ different portions of the forest, with a distance between each other of ~~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-minute~~s~~ averaged values of total OH reactivity inside and above the canopy during 11-12/06/2014 and 7-8/06/2014, respectively, ~~–~~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 ± 19 s^{-1}. At 10 m it varied between the LoD and a maximum of 68 s^{-1} and was on average 24 ± 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 11/06/2014 OH reactivity started to increase at 6:00 AM (CEST) when the sun rose up and it reached a maximum around 10.30 AM, then again around 4:00 PM, associated to more intense solar radiation. It decreased after sunset, at 8:00 PM when also temperature and light reduced. Remarkably, the profile of OH reactivity resembled the one of isoprene concentration, except for the morning peak (10.30 AM) which could be possibly associated to 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

18

ambient temperature during the late afternoon on both sampling days. ~~Reactivity sampled at 10 m~~ ~~had also a diurnal profile.~~ On 7/06/2014 it started to increase at 6.30 AM, had its maximum around 6.30 PM and decreased at 9:30 PM. On 8/06/2014 it increased at 6:30 AM and reached its maximum at 2.15 PM.

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 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 ppbv and 180 ppbv. 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 ± 19 s^{-1} between 11-12/06/2014 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 11-12/06/2014 at 2 m and during 7-8/06/2014 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 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 large majority of tree species accounted 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 2 m high. At 10 m, it constituted from 24% during night to 74% during the day of the total reactivity (total means 6 s^{-1} and 20 s^{-1} respectively). The impact of isoprene on OH reactivity between the two heights of sampling differs only of 9%. If 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 to 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 less than this. 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%). 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 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.

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

20

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 ppbv 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 11-12/06/2014 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 11-12/06/2014 at 2 m and during 7-8/06/2014 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 s^{-1} and 20 s^{-1} respectively) at 10 m. Assuming the same OH reactivity

3.4 Nighttime missing reactivity

During the nights between 07/06/2014 and 08/06/2014 and between 11/06/2014 and 12/06/2014, the measured total OH reactivity and the calculated reactivity reported some discrepancies (Fig. 5 and 6). For the results above the canopy such discrepancy was visible around midnight, and significant differences were observed from 1 AM to 4.30 AM (Fig. 6). Inside the canopy, the signal of total OH reactivity started to scatter around 11.30 PM, then again at 2 AM and decreasedflattered back to the signal of calculated OH reactivity around 4.30 AM (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,

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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 (Fig. 3 and 4). Species profiles as reported in Fig. 3 show that on 07/06/2014 ISOP.OXs and HCHO started to increase during the day, around 1 PM, reached a maximum around 7.30 PM 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. Indeed, higher variability was observed on short time scale for isoprene compared to ISOP.OXs (0.9 and 0.5 respectively, relative standard deviation over the mean value during 07/06/2014). 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 (Fig. 9 and 10).Interestingly, ISOP.OXs/isoprene well anticovariated with ozone's decrease (Fig. 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 to noticeing that during the night between 07/06/2014 and 08/06/2014 the wind blew from the same direction with low speed, suggesting more stable meteorological conditions which could have favoured some nighttime chemistry (Fig. 10). Daytime air temperature onfor these two 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 Fig. 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. First, common anthropogenic tracers such as acetonitrile and benzene did not show any particularspecial increase during these events, supporting the idea that such nighttime higher concentrations of oxidized compounds in the atmosphere was associated to local drivers rather than transport. Secondly, we observed an increase inof atmospheric levels of some masses measured by the PTR-MS and not used before 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. According to the existing literature, tThese protonated masses can be identified as oxidation products resulting from the degradation of

23

1 isoprene ~~according to the existing literature~~ and associated respectively to: formic acid, acetic acid,

2 hydroxyacetone, 3-methylfuran and other unsaturated C5, methacrylic acid and isoprene

3 hydroperoxides (Warneke et al., 2001; Holzinger et al., 2002). We estimated roughly the

4 contribution of such species to the calculated OH reactivity and found out that only a small fraction

5 of the missing OH reactivity could be explained. Therefore there must be other unmeasured species

6 that were formed locally, very likely OVOCs that were present during those nights.

7 Gas phase chemistry during nighttime is usually initiated by ozone and the nitrate radical. The low

8 levels of NO_x observed at the site (nighttime NO was maximum 0.8 ppbv and on average 0.14 $\pm$

9 0.13 ppbv) indicate that nitrate chemistry is not a probable source of such oxidized compounds; on

10 the other hand ozone isoprene chemistry is slow and cannot explain alone their production in the

11 gas phase (isoprene lifetime with nitrate is 1.6 hours while with ozone is calculated to be 1.3 days

12 (Atkinson and Arey, 2003)). If the unmeasured OVOCs were not generated exclusively from

13 isoprene, neither had anthropogenic precursors, we speculate that the~~s~~e unmeasured OVOCs~~y~~ must

14 have been a combination of higher generation products derived from isoprene oxidation and

15 OVOCs resulting from reactive primary biogenic precursors, other than isoprene, and more reactive

16 towards ozone. We can expect that these biogenic precursors were larger molecules that could not

17 be measured by~~with~~ our means.

18 Holzinger et al., (2005) measured a whole class of oxidation products in a pine forest and suggested

19 that they must have formed from reactions of ozone with very reactive terpene-like compounds. He

20 estimated these compounds to be emitted approximately~~bout~~ 6-30 times more than~~the emission of~~

21 the observed monoterpenes above his forest. Karl et al., (2005) have identified the same

22 oxygenated compounds for different pine species and speculated their production at the leaf level,

23 rather than in the gas phase. Recent experiments on leaves of tobacco plants~~ations~~ have identified

24 the unsaturated semivolatile compounds undergoing ~~leaves~~ reactions on the leaves surface

25 (Jud~~Hansel~~ et al., ~~oral presentation EGU~~ 2015). Those compounds once deposited on the leaves

26 quickly undergo surface oxidation reactions with ozone releasing volatile products into the gas

27 phase. Oxidation reactions are favored by higher ambient RH, high ozone levels and can also occur

28 when leaves stomata are closed. Measuring the species initiating these surface reactions is

29 extremely difficult with the instruments we had on the field, therefore we do not have more clues to

30 support this hypothesis nor exclude it has occurred in the forest of OHP. Focused studies on the

31 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. 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 types of climatic zones to which the studied forests belong. The reader has to notice that not all the studies were carried out using 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 handside the intense temperature and solar radiation result in similar emission strength and reactivity, while on the other handside, 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 a better mixing of the air masses and a faster transport of the primary species to the atmosphere.

25

1 By comparison, the investigated mixed temperate forests and boreal forests produced lower OH

2 reactivity, which can also be attributed to the lower temperature and less intense solar radiation

3 leading to weaker emissions from the local canopies.

4

5 **4   Summary and conclusion**

6 During late spring 2014 at the downy oaks forest of the site Observatoire de Haute Provence we

7 found that the total OH reactivity was maximum 69 s^{-1} at 2 m (inside the canopy), and 68 s^{-1} at 10 m

8 (above the canopy). Interestingly, during daytime, at both heights the measured OH reactivity was

9 in good agreement, within the measurements uncertainties, with the calculated OH reactivity

10 obtained from the suite of measurements of trace gases concentration available during our field

11 experiment. Hence, we did not observe any missing OH reactivity neither inside nor above the

12 forest.

13 In addition, considered the homogeneity of the forest and strong reactivity of isoprene, we expected

14 isoprene to be the species contributing mostly to the OH reactivity, at least for measurements at 2 m

15 high. We found indeed that inside the canopy during daytime, isoprene contributed to the OH

16 reactivity at the 83%, followed by CO, NO_2 and HCHO. Above the canopy height, isoprene made

17 up 74%, followed by CO, NO_2, HCHO and MVK+MACR. Such results indicate that there was not a

18 significant difference in the speciation inside and above the canopy. During nighttime, when

19 isoprene emissions arrested and atmospheric concentrations were a few pptv, long lived species

20 such as CO and methane contributed to about 16-17% and 5% for both inside and above the canopy.

21 Still, even by night, isoprene accounted for the largest portion of OH reactivity.

22 The low levels of isoprene oxidation products observed during the day indicate that the intracanopy

23 oxidation is low, and almost all the isoprene emitted by the canopy is transported to the atmosphere,

24 which confirms the previous experimental work on isoprene fluxes conducted during spring 2012.

25 The fact that no missing OH reactivity was observed, especially above the canopy, additionally

26 corroborates the fact that any unmeasured compound, product of the oxidation of isoprene was

27 present.

28 During the nights between 07/06/2014-08/06/2014 and 11/06/2014-12/06/2014 from sampling

29 above and inside the canopy respectively, the total OH reactivity we measured was significantly

30 higher compared to the calculated OH reactivity. Such missing reactivity accounted for more than

31 50% and can be explained by locally produced unmeasured oxidation products. We speculate that

26

1 unmeasured OVOCs represent a mixture of species including higher generation products resulting
2 from isoprene oxidation and products of the reaction between reactive biogenic precursors and
3 ozone.

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

10 The Mediterranean region is rich in biodiversity, and biogenic activity is enhanced by its
11 characteristic climate. Out of 2 million km^2 of surface only about 100 thousands remain undisturbed
12 by human activity. We expect therefore that OH reactivity in the Mediterranean can vary much
13 depending on the type of vegetation, its extension and interaction with pollutants derived by human
14 activity. In addition, the Mediterranean is also a hotspot for climate change. This issue will certainly
15 impact the biogenic emissions strength and pattern which therefore will influence the total OH
16 reactivity. We would therefore pose the interest with our work to persecute studies of OH reactivity
17 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 (10m) (*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±0.72	5.35±0.53	4.44±0.42	2.80 – 13.51	5.47±0.11	5.72±0.41	4.81±0.20	7.87 – 11.16
45	Acetaldehyde	1.20±0.10	1.20±0.20	0.94±0.14	1.21 – 5.01	1.03±0.08	1.18±0.14	1±0.09	1.77 – 6.41
59	Acetone	2.39±0.73	2.37±0.64	2.20±0.15	2.33 – 10.03	2.08±0.17	2.04±0.25	2.06±0.13	2.02 – 7.12
69	Isoprene	2.54±1.78	3.54±1.53	0.47±0.17	1.17 – 22.77	2.26±1.66	2.80±1.45	0.42±0.15	5.11 – 19.02
71	ISOP.OXs	0.33±0.12	0.36±0.10	0.20±0.03	0.14 – 1.63	0.40±0.08	0.41±0.1	0.28±0.05	0.44 – 1.43
79	Benzene	0.04±0.02	0.04±0.01	0.03±0.01	0.12 – 0.36	0.07±0.01	0.11±0.01	0.07±0.01	0.14 – 0.41
93	Toluene	0.05±0.01	0.05±0.01	0.04±0.01	0.08 – 0.69	0.06±0.01	0.07±0.02	0.05±0.01	0.17 – 0.48
137	Monoterpenes	0.18±0.07	0.21±0.08	0.11±0.03	0.25 – 1.76	0.14±0.05	0.15±0.05	0.08±0.01	0.35 – 0.89

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

Figure 2. D~~iurnal profile~~ aily 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 +/- 1σ standard deviation. PAR data were collected at 6 m for both cases. Temperature data were collected at 2 m and at 6.15 m.
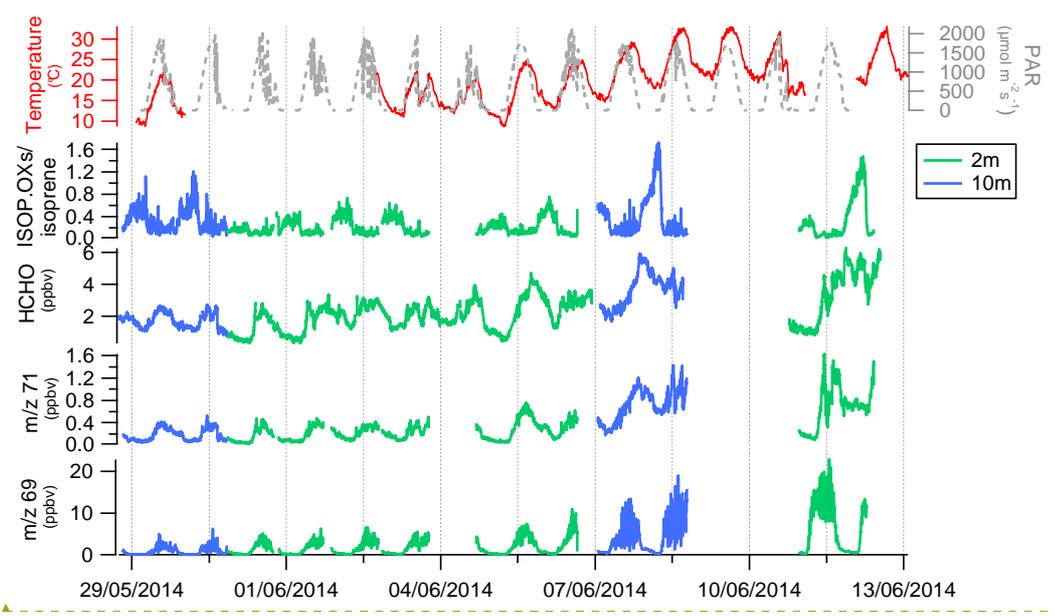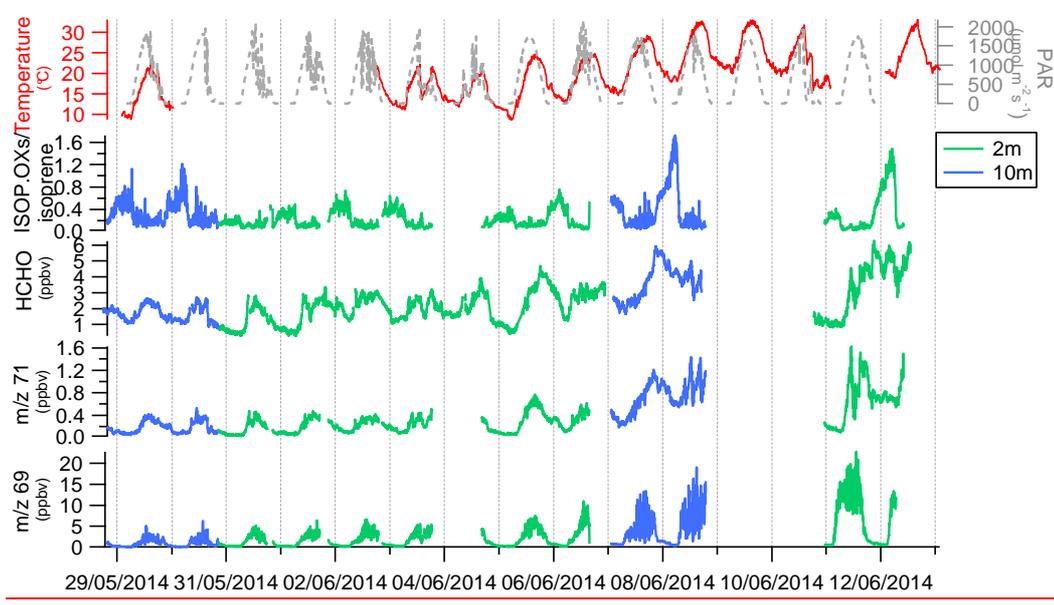
Figure 3. Time series of *m/z* 69 (isoprene), *m/z* 71 (ISOP.OXs=MVK+MACR+ISOPOOH), HCHO and ISOP.OXs/isoprene during the field campaign at OHP. Data were collected inside the canopy (2m, green line) and above the canopy (10m, blue line) on different days. Temperature and PAR measured at 6 m are reported as reference on the top panel.
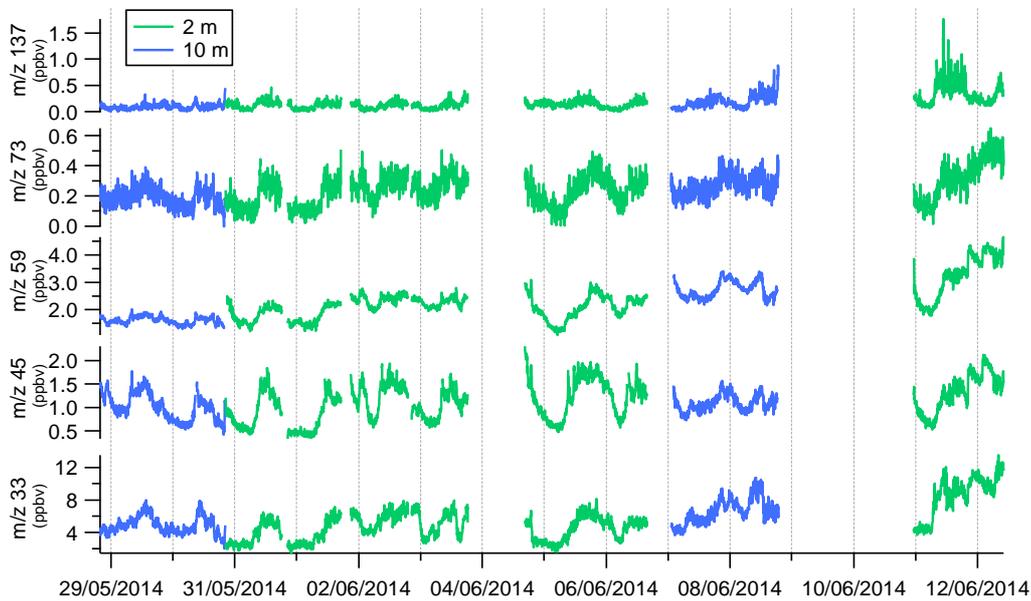
Figure 4. Time series of *m/z* 33 (methanol), *m/z* 45 (acetaldehyde), *m/z* 59 (acetone), *m/z* 73 (methyl ethyl ketone), *m/z* 137 (monoterpenes) inside (2 m, green line) and above (10 m, blue line) the canopy at OHP.
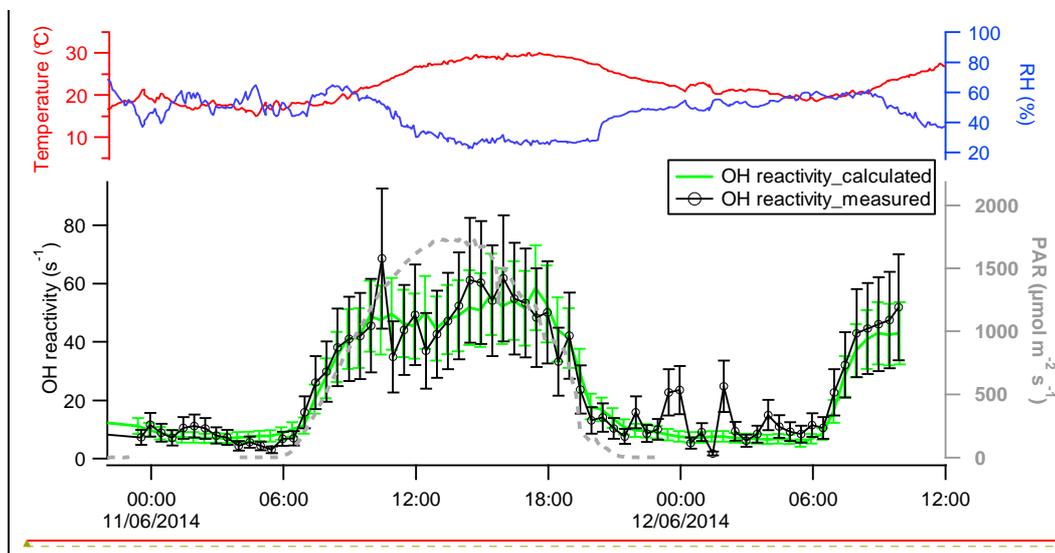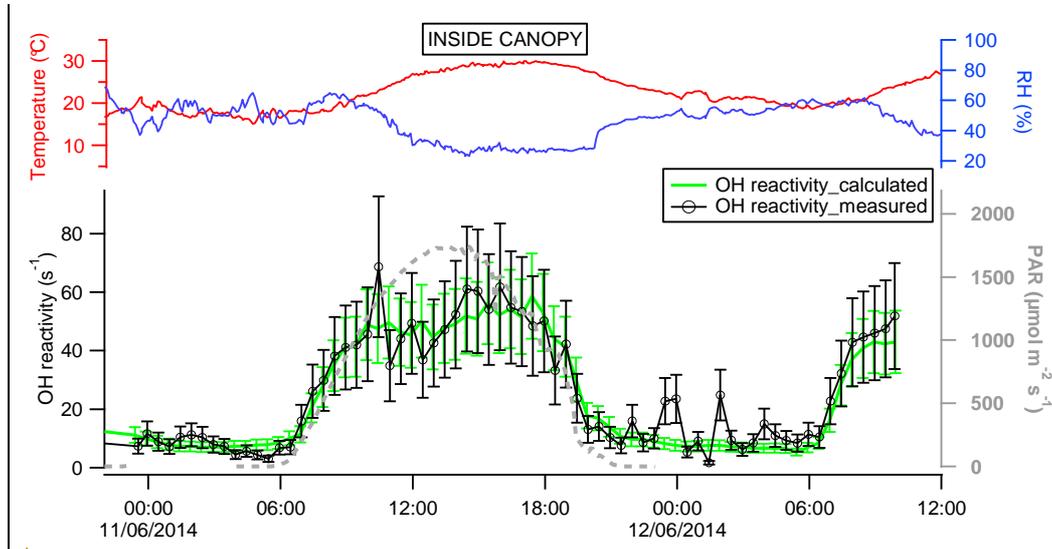
Figure 5. Total OH reactivity measured (black line and markers) with the Comparative Reactivity Method (CRM) and calculated OH reactivity from measured concentrations of trace gases (green line) on the left axes, Photosynthetical Active Radiation on the right axes (gray dashed line), temperature and 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.
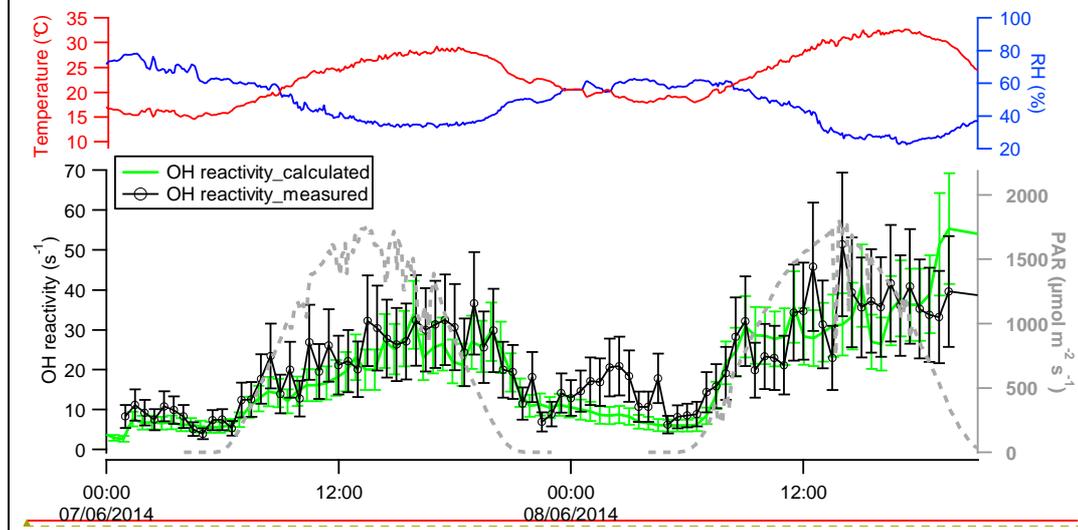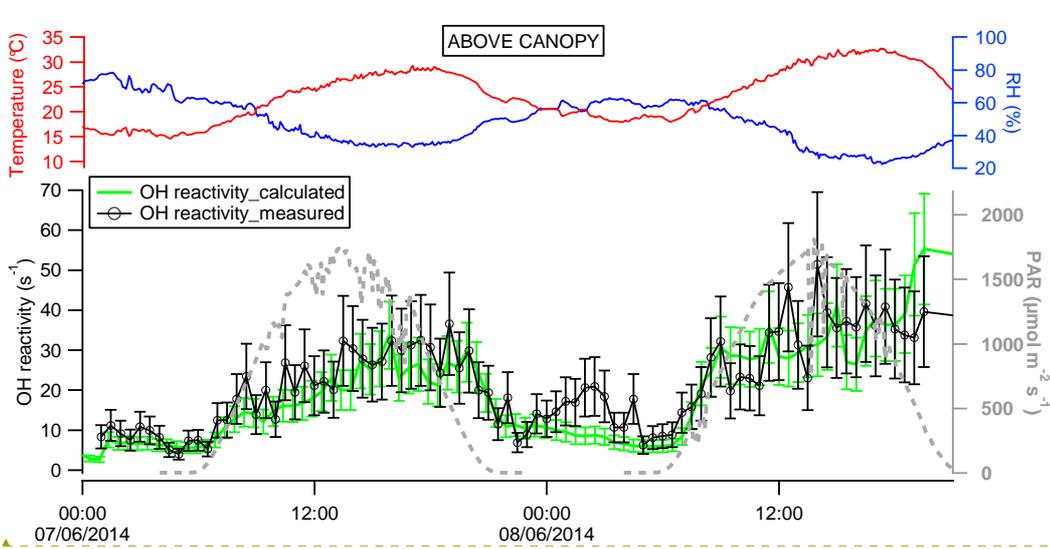
Figure 6. Total OH reactivity measured (black line and markers) and OH reactivity calculated (green line) above the canopy at 10 m height. Temperature (red line), RH (blue line) and PAR (gray dashed line) are reported for reference. Data points represent thirty minutes averages over the data collected. Uncertainties correspond to 35% and 25% for the measured and calculated reactivity respectively (1σ).
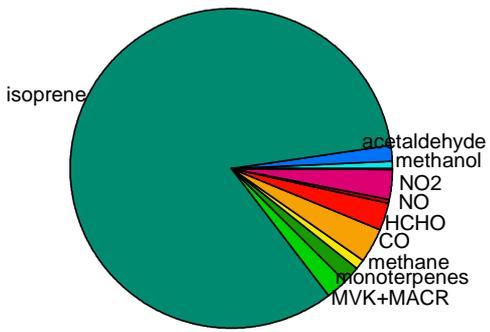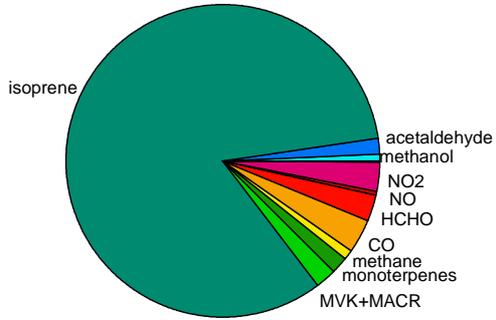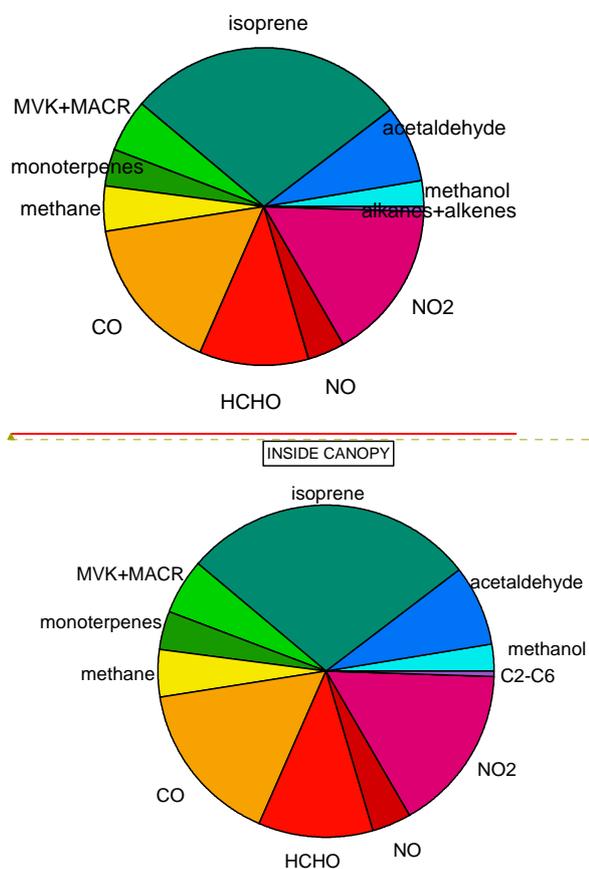
Figure 7. The components of~~total~~ OH reactivity ~~speciation~~ inside the canopy (2 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 11-12/06/2014. Total OH reactivity was 29 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. C2-C6 refer to alkanes and alkenes in the fraction C2-C6.

isoprene

acetaldehyde
methanol
alkanes+alkenes
NO2
NO
HCHO
CO
methane
monoterpenes
MVK+MACR

MVK+MACR
monoterpenes
methane

isoprene

acetaldehyde
methanol
others
alkanes+alkenes

NO2

CO

HCHO
NO

ABOVE CANOPY

isoprene

acetaldehyde
methanol
C2-C6
NO2
NO
HCHO
CO
methane
monoterpenes
MVK+MACR
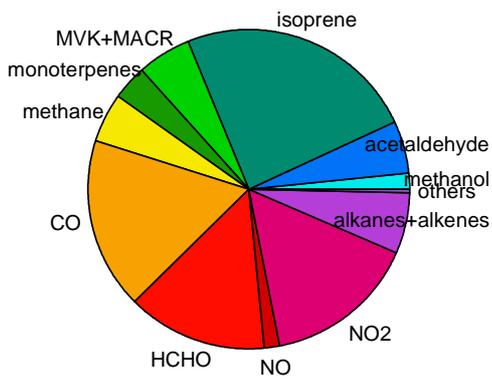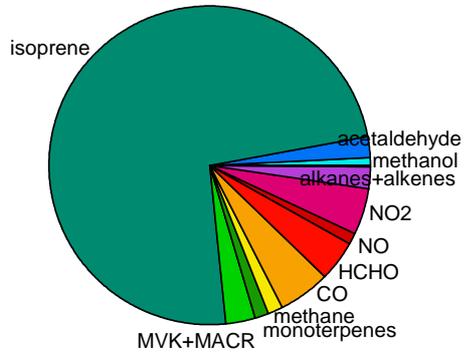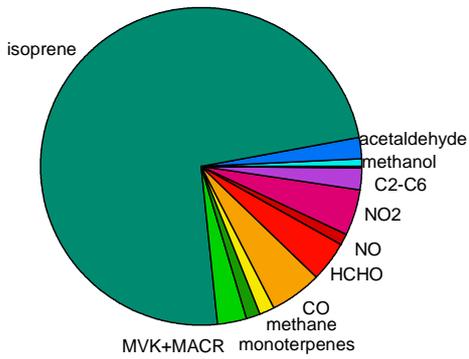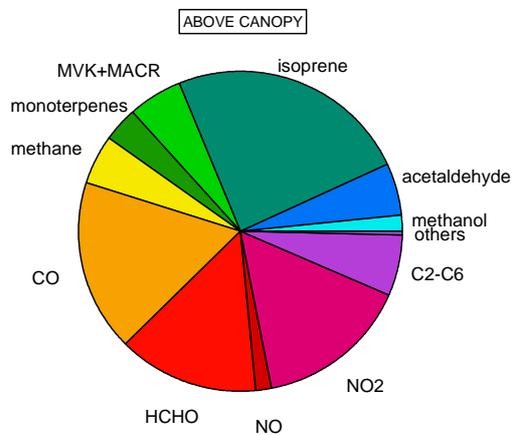
Figure 8. The components of~~total~~ OH reactivity ~~speciation~~ above the canopy (10 m height) during daytime (left pie chart) and during nighttime (right pie chart). Data refer to air masses sampled at OHP during 07-08/06/2014. Total OH reactivity was 20 s^{-1} (daytime mean value) and 6 s^{-1} (nighttime mean value). All compounds reported in Table 1 were used to calculate their relative contributions. C2-C6 refer to alkanes and alkenes in the fraction C2-C6. Others refer to the sum of the contributions of: acetonitrile, acetone, MEK, benzene and toluene.
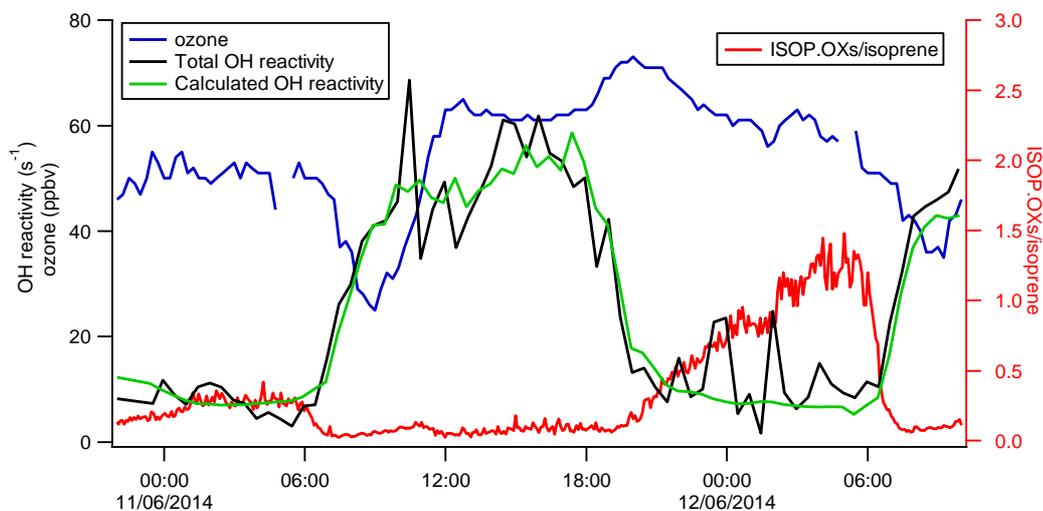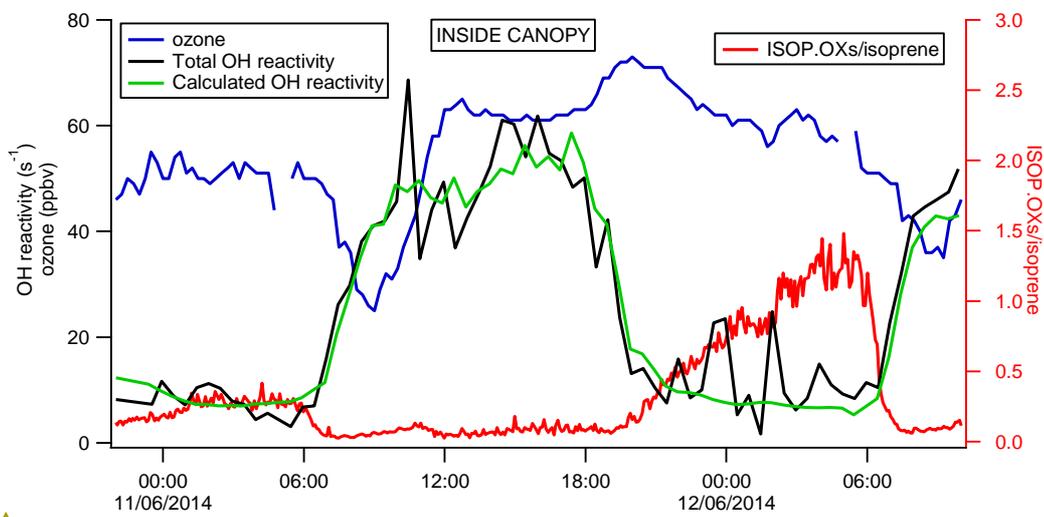
Figure 9. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 2 m height.
Ozone data were acquired a few hundred meters away from the sampling area.
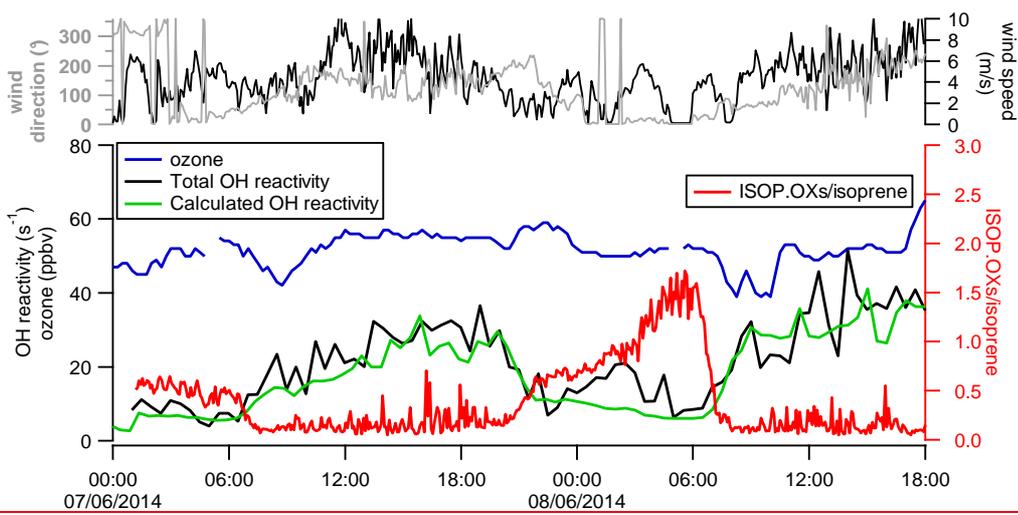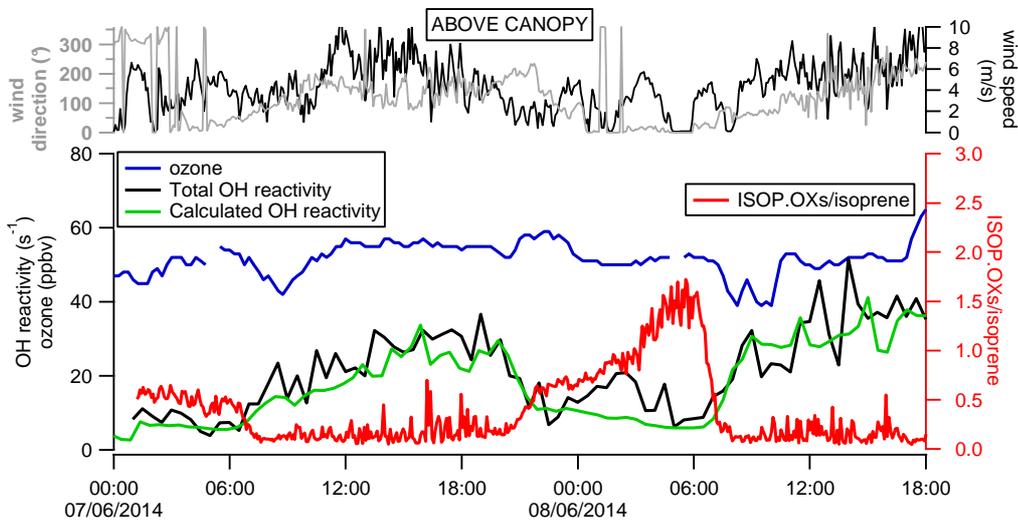
Figure 10. Total OH reactivity, calculated reactivity and ISOP.OXs/isoprene ratio at 10 m height. Ozone data were acquired a few hundred meters away from the sampling area. The upper panel shows wind direction and wind speed data.
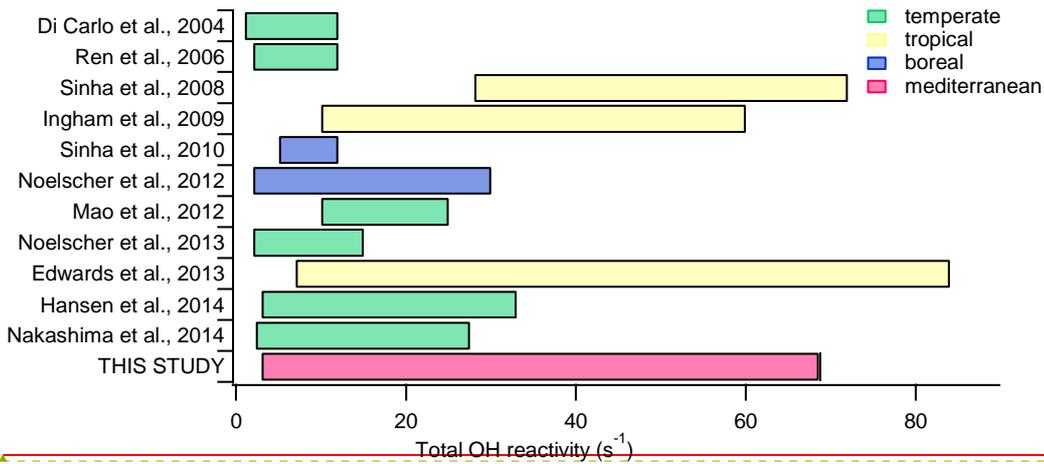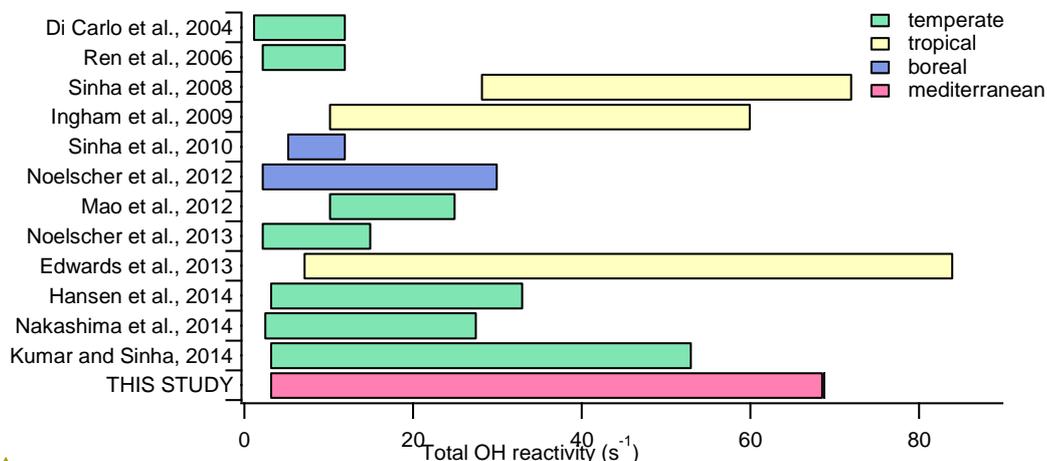
Figure 11. Total OH reactivity results from all the published experiments conducted worldwide at forested sites. Bars refer to the ranges observed between the minimum (often corresponding to the instrumental LoD) and the maximum values published. Studies were all conducted during spring-summer time. This study and those from Sinha and Noelscher adopted the Comparative Reactivity Method; while di Carlo, Ren, Mao, Ingham, Edwards and Hansen used a Total OH Loss Rate Measurement based on Laser Induced Fluorescence; Nakashima deployed a Laser Induced Fluorescence Pump and Probe Technique (see references for instrumental details).