

**Publication: acp-2019-548**

**Title: Variability of OH reactivity in the Landes maritime Pine forest: Results from the LANDEX campaign 2017**

Dear Co-Editor,

Please find enclosed the revised version of the manuscript entitled “Variability of OH reactivity in the Landes maritime Pine forest: Results from the LANDEX campaign 2017”. The work presented, part of the LANDEX- 2017 campaign, aimed to characterize the variability of BVOCs and their OH reactivity inside and above the canopy of a maritime Pine forest, South of France, during July 2017. This version includes most of the suggestions made by the reviewers, as explained in the author’s response, which detailed point by point our answers to all reviewers comments.

Please note that, between the submission of the replies to the reviewers comments and the preparation of this new version, minor corrections were made, which only very slightly affected some of the values (most of the time, it only concerns the first digit after the decimal point) mentioned in the responses to referees comments or in the initial manuscript. It is important to note that, these corrections did not induce any change in the results interpretation and in the conclusion of this study. For clarity, a list of these minor changes is reported after the responses to the reviewers and before the revised manuscript.

As the manuscript has been significantly improved, thanks to all reviewers comments, we hope that it has now all the elements to be accepted in ACP.

We thank you for your consideration,

Kind Regards,

Sandy BSAIBES

- **Answers to RC1**

1- Abstract lines 29-30: Could you also add a comment or a value how big fraction was missing?

Revised version, page 1, lines 31- 32: Comparing the measured and the calculated OH reactivity highlighted an average missing OH reactivity of 22% and 33%, inside and above the canopy, respectively.

2- Page 6, lines 15-20: How about O<sub>3</sub>? Did you apply any O<sub>3</sub> correction? Have you detected any effect of O<sub>3</sub> in your CRM system?

- Based on previous experiments (Fuchs et al., 2017), no ozone dependency was seen for the LSCE-CRM. Therefore, no tests were performed to characterize the interference due to O<sub>3</sub> and no correction was applied to OH reactivity raw data.

This information has been added in the revised version of the manuscript as:

Revised version, page 6, lines 176- 179: In some CRM systems, corrections for potential NO<sub>2</sub> and/or O<sub>3</sub> artefacts are also considered (Michoud et al., 2015, Praplan et al., 2017). On one hand, NO<sub>2</sub> is subject to photolysis leading to NO, which can subsequently react with HO<sub>2</sub> yielding OH. On the other hand, O<sub>3</sub> can also be photolyzed in the reactor, producing O(<sup>1</sup>D), which reacts further with H<sub>2</sub>O, yielding two OH radicals.

And page 8, lines 228 -232: NO mixing ratios were lower than 0.5 ppbv (corresponding to the detection limit of the NO<sub>x</sub> monitor deployed during LANDEX) most of the time for the measurement time periods used in this study, and no correction was applied for the spurious formation of OH from the HO<sub>2</sub>+NO reaction. Similarly, for NO<sub>2</sub>, no correction was applied due to the low ambient mixing ratio of 1.1 ± 0.8 ppbv. Regarding O<sub>3</sub>, no dependency was seen for LSCE-CRM, based on previous experiments (Fuchs et al., 2017). Therefore, no correction was applied. The correction (D) on the reactivity values due to the dilution was around 1.46 during the campaign.

3- Page 7, lines 27-28: Please, be more specific. What was the concentration range of isoprene and α-pinene?

Revised version, page 7, lines 221 - 223: To determine the correction factor for the deviation from pseudo-first order kinetics, injections of known concentrations of isoprene ( $k_{\text{isoprene}+\text{OH}} = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 1- 120 ppbv) and α-pinene ( $k_{\alpha\text{-pinene}+\text{OH}} = 5.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 3 -190 ppbv) (Atkinson, 1985) were performed before and after the field campaign since they represent the dominant species in this forest ecosystem.

4- Page 9, lines 28-29: (a) Copper tubing impregnated with KI is commonly used for the DNPH measurements of aldehydes and ketones, but is it suitable for monoterpenes? Did you test the recovery of terpenes?

- As presented in Mermet et al. 2019 (AMTD), several tests were performed on scrubbers recommended by ACTRIS (copper tubes coated with potassium iodide, glass filters impregnated with sodium thiosulfate, and copper screens coated with manganese dioxide) to characterize (1) O<sub>3</sub> removal efficiency, (2) losses of BVOCs in the absence of ozone, and (3) potential ozone-induced losses of BVOCs in the scrubber. Copper tubes coated with potassium iodide (KI) appeared as the best choice for BVOC measurements. In the absence of ozone, KI scrubbers exhibited BVOC losses lower than 5 % for most non-oxygenated species, whereas in the presence of ozone, losses were relatively higher but remained lower than 15% (lower than 5 % for α- and β-pinene). The only two notable exceptions

were the most reactive compounds, i.e.  $\alpha$ -terpinene and  $\beta$ -caryophyllene, whose losses were approximately 20 % and 40 %, respectively. These two species represent only a minor fraction (3 % maximum) of the total sum of compounds measured with GC-BVOC2 inside the canopy, compared to maxima of 42- 43 % for  $\alpha$  and  $\beta$ -pinene.

(b) What about particle filter? Do you see losses of terpenes in them?

- No tests were made on the particle filters. ACTRIS 2014 measurement guidelines were followed. High flow rates were set in the sampling lines: 1 L min<sup>-1</sup> for GC instruments and 10 L min<sup>-1</sup> for the PTR-MS. The contact time between ambient BVOCs and the particle filters is extremely short and we don't expect significant losses.

(c) Maybe you could provide some reference on an earlier study where they have been tested.

- ACTRIS. 2014. "WP4- NA4: Trace Gases Networking: Volatile Organic Carbon and Nitrogen Oxides Deliverable D4.9: Final SOPs for VOCs Measurements." ACTRIS.

This information has been added in the revised version of the manuscript as:

Revised version Page 10, lines 304- 311: Measurements of VOCs (Table 3) were performed at different locations (Fig. 1) by a proton transfer reaction-mass spectrometer (PTR-MS) and four on-line gas chromatographic (GC) instruments. Ozone scrubbers (Copper tube impregnated with KI) and particle filters were added to the inlets of all GC sampling lines. Losses of BVOCs in these ozone scrubbers were investigated under similar sampling conditions in the absence and presence of O<sub>3</sub> (Mermet et al., 2019, AMTD). The scrubbers exhibited less than 5 % losses for most non-oxygenated BVOCs, whereas in the presence of ozone, losses were relatively higher for some BVOCs, but remained lower than 15 % (lower than 5 % for  $\alpha$ - and  $\beta$ -pinene). High flow rates were applied in the sampling lines: 1 L min<sup>-1</sup> for GC instruments and 10 L min<sup>-1</sup> for the PTR-MS, therefore, the contact time between ambient BVOCs and the particle filters was extremely short and no significant losses are expected.

- 5- Page 10, line 2 and 14: You used Carbotrap B and C for collecting terpenes. I am worried that they are not very good for mono- and sesquiterpenes and you may have some losses of them? Did you do some recovery tests? Have you detected any losses or isomerization while testing those? I would recommend for example Tenax TA cold trap for mono- and sesquiterpenes.
- Carbotrap C in GC-BVOC1 is already set by the manufacturer. Carbotrap B has been selected among the possible adsorbent as listed in the ACTRIS guidelines (ACTRIS, 2014). The method has been optimized in terms of temperature of the thermodesorption, the column, the sampling volume and sampling line including a scrubber. Results are shown in the Mermet et al. AMTD, 2019. Based on a reference mixture composed of 14 monoterpenes, tests resulted in a good separation for most of the compounds. Apart sabinene and terpinene, a good recovery has been obtained between the experimental response coefficient compared to the theoretical ones (determined from the Equivalent carbon number for FID). As a consequence, the calculated uncertainties are significantly higher for these 2 compounds, for which some isomerization or thermodegradation could occur. Indeed, Tenax TA is another well characterized adsorbent but thermodegradation of monoterpenes may also occur as reported by Coeur et al. (1997).

This information has been added in the revised version of the manuscript as:

Revised version page 11, lines 333- 335: The method has been optimized in terms of temperature of the thermodesorption, the column, the sampling volume and sampling line including a scrubber. More details about the optimization and the tests performed can be found in Mermet et al. AMTD, 2019.

6- Page 10, line 12: In some of the MARKES Unity systems b-pinene and some other monoterpenes are isomerized and concentrations of some monoterpenes, for example p-cymene, are increasing over the time. Did you detect low response for b-pinene or for some other monoterpenes or increase of p-cymene?

- p-cymene response observed was elevated comparing to other monoterpenes. For some monoterpenes a low response was observed. It is the case of sabinene, terpinolene, 2-carene for example, but not for the most abundant monoterpenes such as b-pinene, a-pinene, limonene or myrcene (Mermet et al., 2019). While isomerization may be an issue for measuring some monoterpenes with this instrument, the most abundant contributors to the OH reactivity are well measured and this issue does not impact the conclusions of this study. The method could be optimized by using another desorption system.

To take into account, the question of the reviewer, in the revised manuscript we refer the reader to the paper of Mermet et al. which gives all the results concerning the optimization and the tests which have been performed.

This has been added to the revised version of the paper page 11, lines 334- 336: Tests showed a low response for some compounds (i.e. sabinene, terpinolene, ...), however, the most abundant compounds, were well measured. More details about the optimization and the tests performed can be found in Mermet et al. (2019, AMTD).

7- Section 3.3.: Was the mean missing fraction higher inside or above canopy? I would guess there are more reaction products above the canopy.

- Section 3.3 aims to present a comparison between measured and calculated OH reactivity whereas missing reactivity (as absolute and relative fractions) is discussed in section 3.5. The mean relative missing fraction was around 48 % above the canopy and 38 % inside the canopy, when comparing the measured OH reactivity with the calculated one from PTR-MS data, which was measuring at both heights. However, it should be reminded that, measurements were not performed simultaneously above and inside the canopy, except for a short period from mid-day of the 17th, July to mid-day of the 18th, July.

This information is mentioned in the text:

Revised version page 28, lines 748- 749: When comparing measurements of OH reactivity with calculations based on PTR-MS data (see Table 3), an average of 38% ( $7.3 \text{ s}^{-1}$ ) and 48% ( $6.0 \text{ s}^{-1}$ ), remained unexplained inside and above the canopy, respectively.

8- Page 26, line 12: Is the typical B-value (0.057) for the monoterpene emissions or for the reactivity? Often B-value 0.09 is used for the monoterpene emissions.

- The  $\beta$  value is normally used for monoterpenes emissions from vegetation. When applied on missing OH reactivity data, it can be used to indicate if the missing OH reactivity is linked to primary emissions that are temperature-dependent like monoterpenes. When the measured ROH was compared to the calculated one from PTR-MS data, a  $\beta$  of 0.09 was obtained when the missing ROH was fitted in the equation used to describe the temperature dependency of monoterpenes emissions. This  $\beta$  was in the range of  $\beta$ -values normally seen for monoterpenes emissions. However, following the remark of reviewer 3, we have decided to examine the missing reactivity by taking into account in the calculated reactivity all the measured compounds available at the 6 m height. In this case, the missing was also fitted in the exponential relation, but the  $\beta$  value was higher (0.17), which indicates that the missing fraction is not only linked to primary

emissions but is also due to secondary oxidation products (Mao et al., 2012, Hansen et al. 2014, Kaiser et al., 2016).

Revised version, page 29, lines 775- 789: As reported in Di Carlo et al. (2004), the missing OH reactivity was fitted with an equation usually used to describe temperature dependent emissions of monoterpenes (Guenther et al., 1993):  $E(T) = E(293) \exp(\beta(T-293))$ , where  $E(T)$  and  $E(293)$  represent the emission rate at a given temperature  $T$  and at 293 K, respectively. In this equation,  $E(T)$  was substituted to MROH( $T$ ) and  $E(293)$  by MROH (293) with MROH representing the missing OH reactivity (Hansen et al., 2014). The value of  $\beta$  determined from the fit of the data for the 6 m height (day-time), is around 0.17, higher than the values attributed to monoterpenes emissions from vegetation (0.057 to 0.144 K<sup>-1</sup>). Higher  $\beta$ -values were also obtained by Mao et al. (2012), Hansen et al. (2014) and Kaiser et al. (2016), were they suggested that daytime missing reactivity is mostly linked to secondary oxidation products. However, the use of  $\beta$  factor must be made with caution, as the missing OH reactivity can be influenced by processes that do not affect BVOCs emissions (i.e. the boundary layer height and the vertical mixing). Furthermore, we cannot exclude the possibility of light and temperature dependent emissions. Indeed, Kaiser et al. (2016) also investigated the temperature dependency of day-time missing OH reactivity in an isoprene-dominated forest, reporting that part of the missing emissions could be characterized by a light and temperature dependence, knowing that temperature increases with increasing solar radiation. Regarding above canopy, most measurements were performed during cool days. Thus, it was not possible to analyze the temperature dependence of above canopy day-time missing OH reactivity.

9- Page 31, 14-15: I think that also for monoterpenes reactions with ozone can be very significant. Do you have any idea of OH radical concentrations at the site? It would be nice to know how much lower the lifetimes of VOCs were during the day and how important ozone reactions were. Sometimes ozone reactions can be very important also during the day.

Based on the referee's comment, calculations of  $\alpha$ -pinene lifetime (one of the major compounds) towards OH and O<sub>3</sub> were made.

Information has been added in the new version of the paper, page 26, lines 723- 734:

The concentration of OH was  $4.2 \times 10^6$  molecules cm<sup>-3</sup> on average during day-time with a maximum of  $4.3 \times 10^7$  molecules cm<sup>-3</sup> and around  $1.5 \times 10^6$  molecules cm<sup>-3</sup> on average during night-time (data available between the 13th and the 19th, July). However, a potential artefact on OH radical's measurements leading to a possible overestimation of OH radical's concentrations, could not be ruled out. Regarding ozone, its mixing ratio showed a diurnal cycle with maximum values during the day (max  $\approx$  60 ppbv, mean  $\approx$  29 ppbv), that were similar within and above the canopy due to efficient mixing, and lower levels during nights, with an average of 18 ppbv inside canopy, while levels higher by 1 - 9 ppbv on average, above the canopy. Considering OH and O<sub>3</sub> average mixing ratios, the  $\alpha$ -pinene lifetime was estimated to be 1.2 hours and 4 hours, respectively, during the day, and 3.6 hours and 5.8 hours, respectively, during the night. At maximum OH and O<sub>3</sub> mixing ratios during day-time, the  $\alpha$ -pinene lifetime was reduced to 7.4 min and 2 hours, respectively. Thus, OH chemistry remained dominant compared to ozonolysis of main emitted compounds on this site (i.e.  $\alpha$ -pinene). An article on the reactivity of monoterpenes with OH, ozone and nitrate for this campaign is in preparation (Mermet et al., in preparation).

#### Technical comments:

10- Table 1: Please, add an explanation to K' max

- Revised version (Table 1): ROH max (s<sup>-1</sup>) instead of K' max (s<sup>-1</sup>).

11- Page 10, line 13: You mention B-caryophyllene here, but it is not included into table 2. It should be removed from the text.

- B-caryophyllene was added in Table 3 of the revised paper.

12- You have lots of time series plots, but they are a bit hard to follow and it would be also nice to get some quick and easy to look at average plots or tables (for example mean reactivity and mean missing reactivity during night and day, inside and above canopy and during cold and warm nights).

- A table has been added in the revised version of the paper, page 28:

**Table 4. Summary of the measured OH reactivity and the missing OH reactivity inside and above the canopy, during the day and the night, taking into account only PTR-MS data or all the data available at each height for OH reactivity calculations. These averages are calculated for the periods when CRM, PTR-MS and others instruments data are available.**

	Mean Measured OH reactivity (s <sup>-1</sup> )	Mean missing OH reactivity with PTRQi-ToFMS (s <sup>-1</sup> )	Missing ROH considering PTRQi-ToFMS data + other measurements (s <sup>-1</sup> )
<b>Inside</b>			
Day	18.4	7.0	4.1
Night	21.4	9.0	5.6
Stable cool nights	20.5	5.7	2.1
Stable warm nights	41.6	10.9	6.9
Unstable cool nights	7.9	4.5	<LOD
Unstable warmnights	13.5	6.8	3.6
<b>Above</b>			
Day	10.4	5.0	3.1
Night	15.5	7.5	5.6
Stable cool nights	14.8	7.5	5.7
Stable warm nights	-----	-----	-----
Unstable warmnights	20.5	7.1	5.2
Unstable cool nights	-----	-----	-----

- A more detailed table has been added in the supplementary material: Table S9

13- Page 28, line 16: ')' is missing.

- Corrected.

14- Page 28, line 21: Should this be 'This compound showed a diurnal cycle similar to that of isoprene (Fig 4.c) and was not used to calculate . . . ?'

- Indeed.

Revised version, page 30, lines 810- 811: This compound showed a diurnal cycle similar to that of isoprene (Fig 5.c) and was not used to calculate the OH reactivity.

15- Page 29, line 5: What is '(S9)'?

- S9 is supplementary material 9.

16- Page 31, lines 8-10: I did not understand this sentence 'Complementary measurements performed inside (O<sub>3</sub>, NO<sub>x</sub>) and above the canopy (OVOCs, NMHCs, O<sub>3</sub>, NO<sub>x</sub> and butanol), explained with methane and carbon monoxide, part of the missing OH reactivity, that remained significant for warm days and stable/ warm nights.'

This part of the conclusion was modified: An investigation of the missing OH reactivity indicated averages of 6.0 and 7.3 s<sup>-1</sup> inside and above the canopy, respectively, over the whole campaign. However, it showed some diurnal variability at both heights. During day-time, higher missing OH reactivity was observed on warmer days inside and above the canopy. Plotted against temperature, inside canopy missing OH reactivity showed a dependency on temperature. The analysis suggested that the missing OH reactivity may be due to unmeasured primary emitted compounds and oxidation products. In this context, OH reactivity measurements from a *Pinus pinaster* Aiton branch enclosure, could be of great interest to verify the contribution of unaccounted/unmeasured BVOCs emissions to OH reactivity as done by Kim et al. (2011), for red oak and white pine branch enclosures. Furthermore, higher levels of isoprene oxidation products on warmer days also suggest that the missing reactivity could be due to the formation of unmeasured oxidation products. Regarding the night-time period, the highest missing OH reactivity was found inside canopy for the 4th-5th, July night. This night was characterized by higher levels of isoprene and its oxidation products, compared to the night of the 6th-7th, July with similar atmospheric conditions. Air masses backward trajectories showed a continental origin for this night, suggesting that species, emitted by the largely spread Landes forest, could have been imported to the site and accumulated due to the stable nocturnal boundary layer. These species, unmeasured by the deployed analytical instruments and hence not considered in OH reactivity calculations, could explain the higher missing OH fraction for the 4th-5th, July night. Finally, the investigation of sesquiterpenes and monoterpenes oxidation products (nopinone and pinonaldehyde) measured by PTR-MS highlighted their small contribution in terms of OH reactivity. They only explained a small fraction of the observed missing OH reactivity inside and above canopy during night.

## References:

- Mermet, K., Sauvage, S., Dusanter, S., Salameh, T., Léonardis, T., Flaud, P.-M., Perraudin, É., Villenave, É., and Locoge, N.: Optimization of a gas chromatographic unit for measuring BVOCs in ambient air, *Atmos. Meas. Tech. Discuss.*, <https://doi.org/10.5194/amt-2019-224>, in review, 2019
- ACTRIS, 2014. WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides Deliverable D4.9: Final SOPs for VOCs measurements. ACTRIS.
- Coeur, C., Jacob, V., Denis, I., Foster, P., 1997. Decomposition of  $\alpha$ -pinene and sabinene on solid sorbents, tenax TA and carboxen. *J. Chromatogr. A* 786, 185–187. [https://doi.org/10.1016/S0021-9673\(97\)00562-1](https://doi.org/10.1016/S0021-9673(97)00562-1)
- Atmospheric Reactivity of Biogenic Volatile Organic Compounds in a Maritime Pine Forest during the LANDEX Field Campaign Kenneth Mermet, Emilie Perraudin, Sébastien Dusanter, Stéphane Sauvage, Thierry Léonardis, Pierre-Marie Flaud, Sandy Bsaïbes, Julien Kammer, Vincent Michoud, Aline Gratien, Manuela Cirtog, Mohamad Al Ajami, François Truong, Sébastien Batut, Christophe Hecquet, Jean-François Doussin, Coralie Schoemaeker, Valérie Gros, Nadine Locoge and Eric Villenave, in preparation.

- **Answers to RC2:**

1- The characterization experiments for the CRM are described, but it remains unclear, how large corrections were. The authors should consider give some numbers, how big corrections were for typical chemical conditions of this campaign. A discussion about consequences for the accuracy of measurements would be beneficial.

Revised version, page 8, lines 237 - 240: Table 2 reports a summary of the corrections resulting from our tests and their impact on measurements. As shown in table 2, the application of (F), for the deviation from pseudo-first order kinetics, induces the largest correction, with an absolute increase of  $10.02 \text{ s}^{-1}$  on average. Furthermore, this factor (F) has the largest relative uncertainty, with  $\pm 36 \text{ %}$ , against  $\pm 2 \text{ %}$  for the humidity correction factor.

Correction	Correction factor	Mean absolute change in OH reactivity ( $\text{s}^{-1}$ )
Humidity changes between C2 and C3	$-89.18 \pm 2.16$	+ 2.4
Not operating the CRM under pseudo first order conditions	$F = (-0.52 \pm 0.20) \times (\text{pyrrole-to-OH}) + (3.38 \pm 0.60)$	+ 10.0
Dilution	$D = 1.46$	+ 2.8

2- The authors mention that one of the conclusions from previous campaigns were that potential loss of reactive VOCs could be a problem in CRM instruments. Did they quantitatively test this for example when they did the characterization experiment for the deviation from a pseudo-first order reaction system?

- In order to minimize potential losses of reactive VOCs in the CRM sampling system, heated ( $\approx 50 \text{ }^{\circ}\text{C}$ ) sulfurnert lines were used. Indeed, Kim et al. (2009), showed that losses of  $\beta$ -caryophyllene are negligible in heated lines with temperatures above  $20 \text{ }^{\circ}\text{C}$ . More details are also mentioned in the answer to comment 3.

Information has been added in the revised version of the manuscript as:

Page 7, line 199- 201: Ambient air was sampled through two 1/8" OD sulfurnert lines, collocated on a mast close to the trailer (see Fig. 1(a)). The lines lengths were 8 m for the measurements performed inside the canopy and 12 m for those performed above. These lines were heated up to  $50 \text{ }^{\circ}\text{C}$  as it was shown that losses of highly reactive molecules ( $\beta$ -caryophyllene) were negligible for temperature above  $20 \text{ }^{\circ}\text{C}$  (Kim et al., 2009).

3- Similarly, did the authors test, if VOCs were quantitatively transmitted through inlet lines for the GC and PTR-MS analysis? How often were filters in inlet lines exchanged and did they authors test, if the transmission of VOC through filters decreased with time?

- For GC instruments, VOCs were sampled through sulfurnert sampling lines, similar to those used in the CRM sampling system, heated up to  $50 \text{ }^{\circ}\text{C}$ , with a flow rate of, at least,  $1 \text{ L min}^{-1}$ , ensuring a short residence time of less than 8 s. Materials used are recommended by ACTRIS guidelines (ACTRIS 2014). Regarding the PTR-MS, the sampling lines were made of PFA (1/4"-OD) and were heated at  $50 \text{ }^{\circ}\text{C}$ . All lines were 15-m long and the flow rates were adjusted to  $10 \text{ L min}^{-1}$  to reduce the residence time below 2-s. Filters were also made of PFA and were changed every 2-weeks. No tests were performed to check the transmission of VOCs. However, Kim et al. (2009)

tested losses of  $\beta$ -caryophyllene (a sticky sesquiterpene) in a 40-m long Teflon tube (1/4"-OD) flushed at 25 L min<sup>-1</sup>. These operating conditions lead to a residence time similar to that observed during LANDEX for our PTR-MS sampling system. The authors varied the line temperature from zero to 40 °C using a temperature controlled environmental chamber and showed that losses of  $\beta$ -caryophyllene are negligible above 20 °C. The PTR-MS lines being heated to 50 °C in this study, no losses are expected for VOCs reported in this study.

This information has been added in the revised version of the manuscript as:

Page 12, lines 356- 359: Sulfinert material chosen for all GCs sampling lines and used in LSCE-CRM sampling system, is recommended by ACTRIS 2014. High flows were set in the lines (residence time of less than 8 s), that were heated up to 50 °C to minimize the losses of potential reactive species. Filters and scrubbers were changed twice for the GC-BVOC1 and one time for the other GC instruments.

Page 12, lines 364- 366: The lines (PFA, 1/4" OD) were heated at 50 °C and constantly flushed at 10 L min<sup>-1</sup> using an additional pump and rotameters. Indeed, Kim et al. (2009) tested losses of  $\beta$ -caryophyllene in similar operating conditions. Authors varied the temperature from zero to 40 °C showing that losses of  $\beta$ -caryophyllene are negligible above 20 °C. The residence time was lower than 2s.

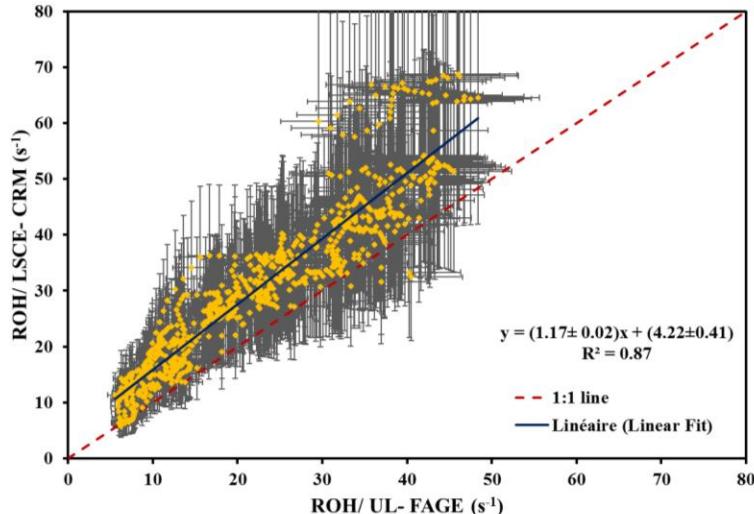
- 4- The authors should mention early in the paper, how they deal with contributions of NO<sub>2</sub> / NO to the OH reactivity.

Revised version page 16, lines 469- 474: A large range of NMHCs and OVOCs were measured at the 12 m height only by GC-NMHC and GC-OVOC (Table 3). Butanol (from SMPS exhausts) was also checked and found to be negligible at 12 m and highly and rapidly variable at 6 m (short peaks). NO and NO<sub>2</sub> were only measured at the 6 m height. Mean NO mixing ratio was below the LOD for the measurement period and NO<sub>2</sub> was around  $1.1 \pm 0.8$  ppbv on average. Thus, it was chosen not to take these species into account in the OH reactivity calculations, since they are not available at both levels. However, sensitivity tests were performed, in order to compute the relative contribution of butanol, OVOCs and NMHCs to OH reactivity (See section 3.5 and Fig. S5 and S6).

- 5- Page 14 Point 3). It would be useful to give some numbers for the estimate of OH reactivity from species only measured at 12m height in the main text.
- This paragraph (point 3, page 16 of the revised paper) describes the methodology used. No results were included. The contribution of species only measured at 12m to OH reactivity is mentioned on page 28 of the revised version, when investigating the missing OH reactivity.

6- Figure 3: In a correlation plot, error bars of measurements are needed. Did the regression procedure take into account errors of the measurements?

Errors bars were added as shown in Fig. 3, page 18 of the revised version. Errors of the measurements were not taken into account in the regression procedure.



**Figure 1.** Measured reactivity by LSCE-CRM instrument as function of the measured reactivity by UL-FAGE when both instruments were measuring at the same location within the canopy (data resampled with a time resolution of 1 min). Errors bars represent the overall systematic uncertainty ( $1\sigma$ ) that is around 15 % and 35 % for LP-LIF and the CRM, respectively.

7- P17 L19: How is the “higher vertical mixing leading to similar concentrations” quantified? The yellow frame (15 to 17 July) shows also large differences in monoterpene concentrations at different heights.

- In this part, we are discussing measurements performed by both instruments at the same height, but at two different locations. This comparison includes a first period of measurements between the 13th and the 15th (green frame) and a second period between the 17th and 18th of July (dashed green-yellow frame). During this second period, a higher vertical mixing is due to a higher  $u^*$ , that was around  $0.3 \text{ m s}^{-1}$ , higher to what was observed for stable nights ( $u^* \approx 0.1 \text{ m s}^{-1}$ ). The measurement period between the 15th and 17th of July corresponds to CRM and UL-FAGE measuring at two different heights.

Revised version, page 19, lines 547- 550: Similar trends in OH reactivity are seen between the two datasets, even if the first period was associated with a clear vertical stratification (Fig. 4, green frame), leading to higher concentrations of monoterpenes within the canopy, whereas the second period was characterized by a higher vertical mixing ( $\text{mean } u^* \approx 0.3 \text{ m s}^{-1}$ ), leading to similar concentrations of monoterpenes at the two heights (Fig. 4, dashed green-yellow frame).

8- P17 L21: (a) Which data are used for the linear regression discussed in this section?

The data used for the regression with a slope of 1.22 and an intercept of -0.69 correspond to the period when LSCE-CRM and UL-FAGE measured at the same height but different horizontal locations (17th and 18th of July, dashed green-yellow frame in Fig. 4).

(b) It does not sound likely that inhomogeneities of air masses result in a change in the intercept, but would increase the scatter of data in the correlation.

Revised version, page 18: From the 13th to 15th midday of July (1st period) and from the 17th midday to 18th midday (2nd period), the two instruments were sampling at the same height but from different horizontal locations within the canopy (with sequential within/above canopy measurements for CRM during the second period). The horizontal distance between the two inlets was around 10 m as shown in Fig. 1. .... At the same height but different horizontal locations, the linear regression of LSCE- CRM data plotted against UL-FAGE data (not shown) indicates a good agreement with a slope of  $1.22 \pm 0.01$ , an intercept of  $-0.69 \pm 0.17$  and a correlation coefficient of 0.85 (1st and 2nd period). Compared to the results at the same location (vertical and horizontal), the slope and the correlation coefficient are in the same range. Only the intercept differs significantly ( $-0.69 \pm 0.17$  compared to  $4.22 \pm 0.41$ ). This change could be related to air mass inhomogeneities which could be systematically less reactive at one location compared to the other one. From these observations, we can conclude that reactivity measurements performed at different horizontal locations are consistent and that inhomogeneities in ambient air can lead to differences on the order of several  $\text{s}^{-1}$ .

9- P18 L6: The reference Lou et al 2010 is not appropriate, because measurements in that paper were done in a mixed environment.

- The reference “Lou et al, 2010” was mentioned for the review part of it, in the introduction, where they put a table summarizing OH reactivity values in various environments. Instead, we now mention the review of “Yang et al, 2016” and “Dusanter and Stevens, 2017”.

10- P18 L20 / P20 L22: The authors may want to mention already here that it is well known that plant emissions are increasing with increasing temperature.

Revised version page 20, lines 596- 598: Another important parameter to consider is ambient temperature, which is known to enhance BVOCs emissions during the day when stomata are open, and which also plays a role for night-time emissions due to permeation, even though stomata are closed in the dark (Simon et al., 1994).

11- Section 3.3/3.5.: (a) The discussion would benefit, if the accuracy of calculated OH reactivity were taken into account (maybe also shown in Fig. 5).

- The accuracy of calculated OH reactivity cannot be determined in a simple way and are rarely reported in previous studies. It depends on random (precision) and systematic (calibration) errors on trace gas measurements and errors on reported rate constants. Propagating the different types of errors (when known) is not straightforward. However, we can estimate it to be around 22-24%, as reported in Hansen et al. (2015). These values were obtained under similar experimental conditions than those used in the Landex campaign, assuming that errors on rate constants are independent from each other and that errors on measured VOC concentrations are characterized by an independent random error of 5 % and a similar systematic error of 10 % for each VOC. This estimation has now been included in the revised version.

Revised version, page 23, lines 661- 662: Figure 6 shows that there is a good co-variation of the measured total OH reactivity by the CRM instrument with the values calculated from the PTR-MS data (22- 24% (2 $\sigma$ )).

(b) Is there an estimate of OH reactivity from oxidation products not taken into account here (for example from oxidation products like MVK/MACR)?

As mentioned in page 14, lines 415- 420 (revised version): “Since measurements from the PTR-MS instrument cover the whole campaign and were performed at the same heights than OH reactivity measurements, these measurements, including methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein + methylvinylketone + fragment ISOPOOH (MACR+MVK+ISOPOOH), methylethylketone (MEK) and the sum of monoterpenes (MTs), were selected to calculate the OH reactivity and to evaluate the potential missing OH reactivity at both levels”. Oxidation products of isoprene were already taken into account in OH reactivity calculations. Regarding MTs oxidation products, their contribution to OH reactivity remains low (around  $0.2 \text{ s}^{-1}$  on average and a maximum of  $1.2 \text{ s}^{-1}$  together). However, and as reported in table 3 (new version), fragmentation was not corrected for and reported concentrations are likely lower limits.

The answer could be found in the new version of the paper:

Page 30, lines 826- 829: Checking monoterpenes’ oxidation products variabilities (nopinone and pinonaldehyde), both nights exhibited higher concentration levels of these species, however their contribution to OH reactivity remained relatively low, and did not exceed  $1 \text{ s}^{-1}$ , on average for both nights, keeping in mind that this is a lower limit of their contribution (since the reported measurements do not account for potential fragmentation in the PTR-MS).

(c) Is there any estimate, if transportation from other sources could have been impacted the location?

We found some difference when checking air mass backward trajectories which suggested an explanation for the higher missing OH reactivity inside canopy for the 4th-5th, July night.

The answer could be found in the revised version of the paper:

Page 30, line 832- Page 31, line 839, line: When looking at air masses backward trajectories (Fig. 10), the 4th-5th night was characterized by an air mass originally coming from the ocean, which spent at least 48 hours above the continent before reaching the site. This could have led to the enrichment of the air mass with species emitted by the widely spread Landes forests and their oxidation products. Thus, the significant missing OH reactivity observed during the mentioned night is likely related to unconsidered compounds of biogenic origin characterized by a similar behavior to that of isoprene, acetic acid and MVK+MACR+ISOPOOH, which accumulated in the stable nocturnal boundary layer. In contrast, air masses spent approximately 12-18 hours above the continent during the 6th-7th of July, with more time above the ocean. Marine air masses are generally known to be clean, with relatively low levels of reactive species.

12- Section 3.4.: Would the authors expect a difference in the distribution of OH reactants? Was there any attempt to estimate how much of the emissions were oxidized inside the canopy?

- MVK+MACR+ISOPOOH/ isoprene had generally higher values during the day and were higher above the canopy, which suggests a difference in the distribution of OH reactants. Another paper on BVOCs reactivity with atmospheric oxidants (ozone, OH radical and nitrate) is in preparation. In this paper, differences of BVOCs consumption were observed between inside and above the canopy, which conducted to different distribution of co-reactants linked to difference of oxidants concentrations and/or BVOCs concentrations between both levels (Mermet et al., in preparation).

13- P29: Sesquiterpene oxidation products are likely not measured. Could the authors still estimate how much reactivity would be expected, if the difference between in and above canopy was due to oxidation?

It is mentioned in the revised version of the paper, page 31, line 870- page 32, line 879: Plotting the ratio SQT(above)/MTs(above) with the ratio SQT(inside)/MTs(inside) shows a good linear correlation with a slope of 0.72 and an R2 of 0.5. Knowing that sesquiterpenes are highly reactive with ozone (Ciccioli et al., 2002), which can dominate the chemistry during dark hours, this observation suggests that a larger fraction of these species ( $\approx 30\%$ ) could be consumed by ozonolysis above canopy, leading to the formation of unidentified secondary compounds. However, sesquiterpenes were present at relatively low concentrations (max of 0.25 ppbv and 0.12 ppbv, inside and above canopy, respectively). Assuming that all sesquiterpenes are  $\beta$ -caryophyllene and considering that 30 % are transformed into first generation oxidation products through ozonolysis reactions, the maximum mixing ratio of these products would be around 0.07 ppbv each assuming a yield of 1. However, it was reported by Winterhalter et al. (2009) that oxidation products of  $\beta$ -caryophyllene were much less reactive (100 times) than their precursor. Thus, the contribution of sesquiterpenes night-time oxidation products to the missing OH reactivity is likely negligible.

14- Figures in the main text and supplementary material: Font sizes are very small. It would be easier for the reader, if they were larger. The position of legend below the x-axis label is unusual. Errors bars of measurements would be helpful to judge differences, if quantities are compared.

- All the suggestions of formatting have been taken into account.

**Technical:** The authors should follow the style of the journal for example how figures are referenced, dates are given and SI units should be used.

- These points have been corrected.

## References:

- ACTRIS. 2014. "WP4- NA4: Trace Gases Networking: Volatile Organic Carbon and Nitrogen Oxides Deliverable D4.9: Final SOPs for VOCs Measurements." ACTRIS.
- S. Kim, T. Karl, D. Helmig, R. Daly, R. Rasmussen, and A. Guenther, Atmos. Meas. Tech., 2, 99–112, <https://doi.org/10.5194/amt-2-99-2009>, 2009.
- Yang, Y., Shao, M., Wang, X., Nölscher, A. C., Kessel, S., Guenther, A. and Williams, J.: Towards a quantitative understanding of total OH reactivity: A review, Atmos. Environ., 134(2), 147–161, doi:10.1016/j.atmosenv.2016.03.010, 2016.
- S. Dusanter and P. Stevens, Recent Advances in the Chemistry of OH and HO<sub>2</sub> Radicals in the Atmosphere: Field and Laboratory Measurements, Advances in Atmospheric Chemistry, pp. 493–579 (2017).
- K. Mermet, E. Perraquin, S. Dusanter, S. Sauvage, T. Léonardis, P.-M. Flaud, S. Bsaïbes, J. Kammer, V. Michoud, A. Gratien, M. Cirtog, M. Al Ajami, F. Truong, S. Batut, C. Hecquet, J.-F. Doussin, C. Schoemaecker, V. Gros, N. Locoge and E. Villenave, Atmospheric Reactivity of Biogenic Volatile Organic Compounds in a Maritime Pine Forest during the LANDEX Field Campaign, in preparation. - Winterhalter, R., Herrmann, F., Kanawati, B., Nguyen, T. L., Peeters, J., Vereecken, L. and Moortgat, G. K.: The gas-phase ozonolysis of  $\beta$ -caryophyllene (C<sub>15</sub>H<sub>24</sub>). Part I: An experimental study, Phys. Chem. Chem. Phys., 11(21), 4152–4172, doi:10.1039/b817824k, 2009.

- **Answers to RC3:**

- 1- The conclusion of this study is obviously hand waving as they conclude that the origin of mixing OH reactivity is either uncharacterized emission or oxidation products. Those are basically the nature of all VOCs in the atmosphere anyway. A deeper discussion may be utilizing a box model is recommended to narrow down the source of missing OH reactivity.
- We thank the referee for his/her suggestion. Indeed, running the model would definitely provide more insights into the origin of the missing OH reactivity, however the use of a box model is out of the scope of this paper and would require much more time (to prepare the data files, to constrain the model, to run the model and to interpret the results). Nevertheless, this idea has been added in the perspectives. Please note that section 3.5 on the investigation of missing OH reactivity was restructured, in order to make the discussion about the origins of missing OH reactivity more clear.
- 2- It is not entirely clear whether ambient VOC samples and OH reactivity samples were collected with the same sampling tubes. Please clarify this point as it is very important to evaluate potential imparity.
- VOC measured with the PTR-QiTofMS and used for OH reactivity calculations were sampled through 1/4"-OD PFA lines, heated at 50 °C and constantly flushed at 10 L min<sup>-1</sup> (page 12, lines 363- 364, revised version of the paper). For OH reactivity measurements, samples were collected through 1/8"-OD sulfonert lines, heated up to 50 °C with a sampling flow rate of 1- 1.2 L min<sup>-1</sup> (page 7, lines 199- 205). As mentioned in the answer to referee 2, comments 2 and 3, all lines were heated up to 50 °C, so no losses of VOCs are expected.
- 3- As the oxidation product of CO is HO<sub>2</sub>, it is more likely susceptible to interference from OH recycling during the calibration process with high CO concentrations. What CO levels do you use for calibration? Could you provide at least simple discussion that was not the case in your calibration process?
- It was initially mentioned in the text: “The measurements with CO do not correspond to a calibration procedure as the UL-FAGE instrument provides directly OH reactivity from a mono-exponential fit of the OH decay measured. It is a systematic procedure to check that the instrument provides consistent reactivity values. For that, a mixture of humid dry air with different concentrations of CO (from  $4 \times 10^{13}$  to  $3.7 \times 10^{14}$  cm<sup>-3</sup>, corresponding to OH reactivity from 10 to 90 s<sup>-1</sup>) are injected in the photolysis cell. In absence of NO, HO<sub>2</sub> is not recycled in OH and does not interfere with the OH measurement”.

This is clarified in the revised version of the text, page 9, lines 276- 282: In order to check the consistency of the OH reactivity measurements, the well-known (CO + OH) reaction rate constant was measured. Different CO concentrations, from  $4 \times 10^{13}$  to  $3.7 \times 10^{14}$  cm<sup>-3</sup> in humid zero air are injected in the photolysis cell, allowing to measure reactivities ranging from 10 to 90 s<sup>-1</sup> and to determine (using a linear regression:  $R^2 = 0.97$ ) a rate constant of  $k_{CO + OH} = (2.45 \pm 0.11) \times 10^{13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in good agreement with the reference value of  $2.31 \times 10^{13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson et al., 2006) at room temperature. Under these conditions (absence of NO), HO<sub>2</sub> formed by the reaction of CO+OH is not recycled in OH and does not interfere with the measurements of OH.

- 4- It appears that the trace gas OH reactivity such as CO, NOx, O<sub>3</sub> and SO<sub>2</sub> is not considered in the calculated OH reactivity assessments. Considering the rural location, this may not be a substantial factor, but it still requires to be included.
- NOx measurements were only performed at 6 m height. They were not included in the initial OH reactivity calculation, as indicated in page 16, point 3 (revised version), however their contribution to OH reactivity was estimated and discussed in page 28, lines 750- 753, together with O<sub>3</sub> calculated OH reactivity and CO estimated OH reactivity. No SO<sub>2</sub> measurements were performed on site but are expected to be very low.
- 5- Page 13 Line 12: Further quantitative discussion on the impacts from MT to the isoprene mass. What species would be susceptible for the fragment and how prevalent it can be?
- Two papers were cited in the text in which *m/z* 69 was found as a product ion of monoterpenes fragmentation. Tani et al., 2013, reported that the relative abundance of *m/z* 69 from myrcene fragmentation was 3.1 % for a E/N ratio of 120- 122 Td, while Kari et al., 2018 showed that *m/z* 69 contributes between 3.8 and 4.7 % to the total corrected cps of  $\beta$ -myrcene, depending on E/N (range: 80- 130 Td). Other monoterpenes that can fragment at *m/z* 69 are monoterpene alcohols linalool and cineole (Tani et al., 2013).
- 6- It is well known that PTR sees higher MT then the sum of speciated MT quantified by GC. Add this discussion whether that was the case during the observational period. This may give us some insight on the missing OH reactivity.
- The PTR-MS indeed measured higher MT mixing ratios than the sum of speciated MTs quantified by GC in our study. Comparisons were done at both levels. Graphs and respective discussions are presented in the supplementary material 2 “Consistency between GC and PTR-MS for monoterpene measurements”.

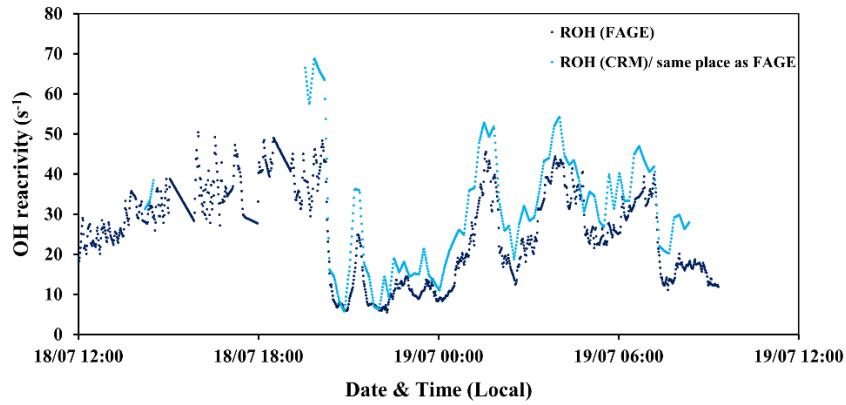
This information is mentioned in the text: Page 15, point 1 (revised version).

- 7- Page 14 Line 3: Further quantitative discussion is required. It is not clear how the 4 % value has been drawn.

In order to determine the interference level of MT on isoprene measurements by PTR-MS, correlations between isoprene concentrations measured with the GC-NMHC and with the PTR-MS have been performed for different %. The agreement observed between the corrected isoprene concentrations from PTR-MS and the isoprene concentrations measured by GC was then evaluated. It was found that subtracting 4 % of the monoterpenes concentration was leading to the best agreement between the 2 instruments for isoprene. This approach assumes that the fragmentation level of monoterpenes does not change over the whole campaign.

- 8- Figure 2: (a) it is extremely confusing what I should look up to for the comparison. It would be better separate into figures describing in the different periods. I would recommend to present an intercomparison figure first so that readers can get a sense on the potential bias from the instrumentation.
- We thank the referee for the suggestion. It was taken into account.

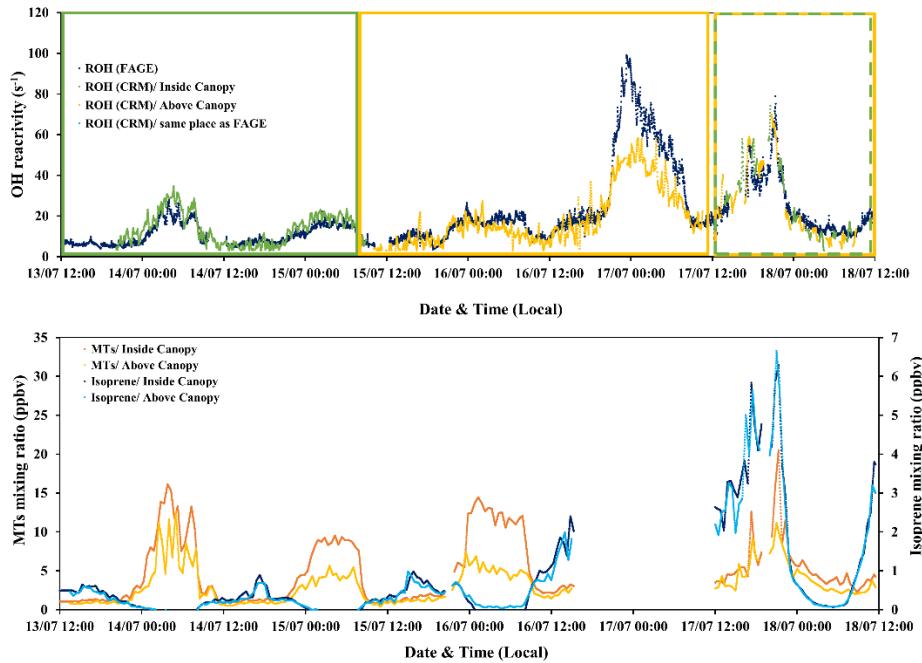
Revised version, page 17: Figure 2.



**Figure 2.** Time series of total OH reactivity measured by UL-FAGE (dark blue) and LSCE-CRM (light blue) instruments from the 18<sup>th</sup> to 19<sup>th</sup> of July 2017, at the same location inside canopy.

(b) Also, please make it clear which MT species are consisting the total MT presented in the figure.

Revised version of the legend of Fig. 4(b): ...The lower graph (b) shows the sum of monoterpenes (MTs) and isoprene measured with the PTR-MS, in the field for the same period. Dark blue and light blue dots correspond to isoprene concentrations at 6 and 12 m height, respectively. Orange and yellow dots represent monoterpenes concentrations at 6 and 12 m height, respectively.



**Figure 4.** (a) Time series of total OH reactivity measured by UL-FAGE and LSCE-CRM instruments from the 13th to 18<sup>th</sup> of July 2017 (upper graph). Dark blue symbols represent the measured reactivity by UL-FAGE, green, yellow and blue symbols represent the measured reactivity by LSCE-CRM inside canopy, above canopy and inside canopy at the same location as the UL-FAGE instrument, respectively. The lower graph (b) shows the sum of monoterpenes (MTs) and isoprene measured with the PTR-MS, in the field for the same period. Dark blue and light blue dots correspond to isoprene concentrations at 6 and 12 m height, respectively. Orange and yellow dots represent monoterpenes concentrations at 6 and 12 m height, respectively.

9- Figure 3: If you take a diurnal average and adjust the intercept, then do two diurnal variations agree better? It seems CRM has  $4 \text{ s}^{-1}$  offset but the text description says otherwise. Please make them consistent! In addition, even without the intercept, there are  $\sim 20 \text{ %}$  differences in the relationship. Please discuss the potential reasons!

- Regarding the slope, the 20 % difference is within the uncertainty of the instruments.
- Concerning the offset, the text has been clarified (Revised version):

Page 17, line 515- page 18, line 524: When OH reactivity measurements from LSCE-CRM are plotted versus OH reactivity measurements from UL- FAGE (Fig. 3), the linear regression exhibits a slope of  $1.17 \pm 0.02$ , an intercept of  $4.2 \pm 0.4 \text{ s}^{-1}$  and a  $R^2$  of 0.87. This high intercept is statistically significant at  $3\sigma$  and can partly be due to an overestimation of the UL-FAGE zero that is subtracted to the measured ambient OH reactivity. This issue is related to the quality of zero air used for zeroing the instrument. Indeed, previous comparisons have shown that using zero air of better quality (99.999%) may result in a zero of about  $2 \text{ s}^{-1}$  lower (Hansen et al., 2015). An intercomparison of OH reactivity instruments made in the SAPHIR chamber (Fuchs et al., 2017) has also shown a positive bias of  $1 \text{ s}^{-1}$  for the UL-FAGE instrument when high grade zero air was flushed in the chamber. A maximum overestimation of the UL-FAGE zero by  $3 \text{ s}^{-1}$  is possible for this study leading to an underestimation of the ambient OH reactivity by  $3 \text{ s}^{-1}$ . Finally, we cannot exclude a potential offset in LSCE-CRM measurements, that could be related to a possible desorption of “sticky” compounds from the Teflon pump.

10- A more description on  $u^*$  is required: how you measured them and justify the classifications.

- The turbulence was characterized using a 3D sonic anemometer (R3, Gill instruments), localized at 15 m above ground level (Kammer et al., 2018).

The information has been added in the text:

Revised version, page 13, lines 382- 384: Meteorological parameters such as temperature, relative humidity, global radiation, vertical turbulence, wind speed and wind direction were monitored using sensors already available at the ICOS measurement site. More details can be found in Kammer et al., 2018.

- Classification criteria for stable, unstable and stable/unstable nights can be found in Kammer et al., 2018, studying new particle formation episodes at the same site. In their study, the authors reported that, when NPF episodes started,  $u^*$  was always lower than  $0.5 \text{ m s}^{-1}$ . This may be explained by the fact that nocturnal stratification led to precursor concentration increase, favoring nocturnal gas to particle conversion. Whereas, during day-time,  $u^*$  was typically higher than  $0.5 \text{ m s}^{-1}$ . In our study, mean  $u^*$  was considered and the classification was done based on graphical observations.

11- Page 20 line 12: Have you seen the described extreme weather events during the observations? If you have not, then this discussion is irrelevant.

- Indeed, this extreme weather was observed between the 18th and the 19th, July. It was clarified in the text:

Revised version, page 22, lines 624- 627: However, it is worth noting that during this night, an intense wind, rain and thunders occurred, which could have led to the observed bursts of BVOCs (Nakashima et al., 2013), leading to distinct peaks of BVOCs and total OH reactivity and thus relatively high total OH reactivity compared to other nights from the same class.

12- The stable nocturnal boundary layer could cause accumulation of long-lived oxidation products of VOCs instead of vertical mixing. Therefore, the speculation for the MT emission attributing missing OH reactivity is not conclusive. The authors need to substantiate argument.

- Yes, the reviewer is right and the accumulation of oxidation products could explain part of the missing reactivity since a higher missing OH reactivity was observed during the night of the 4th-5th, July when continental air masses imported emissions from forests and their oxidation products. The measured species showed higher levels during this stable night, a condition that could be favorable for their accumulation, as well as other unmeasured long-lived oxidation products. The information has been added in the revised version:

Page 30, line 830- 31, line 842:

Interestingly, isoprene, acetic acid and MVK+ MACR+ISOPPOOH exhibited higher concentration levels during the night of the 4th- 5th, July, which was not the case for the 6th-7th, July night. Indeed, these species marked relatively high nocturnal/ inside canopy levels. When looking at air masses backward trajectories (Fig. 10), the 4th-5th night was characterized by an air mass originally coming from the ocean, which spent at least 48 hours above the continent before reaching the site. This could have led to the enrichment of the air mass with species emitted by the widely spread Landes forests and their oxidation products. Thus, the significant missing OH reactivity observed during the mentioned night is likely related to unconsidered compounds of biogenic origin characterized by a similar behavior to that of isoprene, acetic acid and MVK+MACR+ISOPPOOH, which accumulated in the stable nocturnal boundary layer. In contrast, air masses spent approximately 12-18 hours above the continent during the 6th-7th of July, with more time above the ocean. Marine air masses are generally known to be clean, with relatively low levels of reactive species. Even though, the night of the 5th-6th, July shows similar air mass backward trajectories to the night of the 4th-5th, the higher turbulence during this night prevents the accumulation of reactive species (including long-lived oxidation products) due to a higher boundary layer height, lowering the reactivity and the missing OH reactivity (Fig. 10).

## List of the minor changes made since the author's response (5<sup>th</sup> October, 2019)

- Regarding CRM and FAGE instruments data, considered in the comparison of these instruments measurements at two different locations inside canopy, we found that a short period (30 minutes) was missing from the data set. It was corrected, which changes the mean measured OH reactivity by the CRM from 19.1 to 19.2 s<sup>-1</sup> (section 3.3).
  - Section 3.1.2.:
 

Submitted version: CRM vs. FAGE resulted in a linear regression with a slope of 1.22, an intercept of -0.69 and a correlation coefficient of 0.85.

Revised version: CRM vs. FAGE resulted in a linear regression with a slope of 1.26, an intercept of -1.17 and a correlation coefficient of 0.87.
- Regarding the contributions of individual compounds to calculated OH reactivity (section 3.4), we made sure that the whole measurement period was considered and that the period between the 16<sup>th</sup> July at 15h and the 17<sup>th</sup> July at 12h (due to an electrical failure as mentioned in section 3.3) was excluded. Slight corrections are shown in the following table.

	Submitted version	Revised version
Inside canopy/ Day-time contribution	65% MTs, 27% Isoprene 3% MVK+ MACR	68% MTs, 25% Isoprene 2% MVK+ MACR
Inside Canopy/Night-time contribution	91% MTs, 5% Isoprene 2% OVOCs	92% MTs, 4% Isoprene 1% OVOCs
Above canopy/ Day-time contribution	63% MTs and 29% isoprene 2% OVOCs	65% MTs and 27% isoprene 3% OVOCs
Above canopy/ Night-time contribution	88% MTs 7% isoprene	89% MTs 6% isoprene

This period from the 16th (15h) to the 17th (12h) was also excluded from data presented in Fig. 8, as well as from the correlation between SQT<sub>above</sub>/MT<sub>sabove</sub> and SQT<sub>inside</sub>/MT<sub>sinside</sub> in section 3.5 (night-time missing OH reactivity), which corrects the slope from 0.72 (with R<sup>2</sup> of 0.5) to 0.73 (with R<sup>2</sup> of 0.6).

- Averages of measured and calculated OH reactivity, summarized in table 4 (presented in the revised version based on the suggestion made by referee 1, section 3.5), were revised (in red are the values in the response to the referee and in black the values in the revised version).

	Mean Measured OH reactivity (s <sup>-1</sup> )	Mean missing OH reactivity with PTRQi-ToFMS (s <sup>-1</sup> )	Missing ROH considering PTRQi-ToFMS data + other measurements (s <sup>-1</sup> )
<b>Inside</b>	<b>19.0/</b> 19.1	<b>7.3/</b> 7.2	<b>4.3/</b> 4.2
Day	<b>18.4/</b> 16.8	<b>7.0/</b> 7.3	<b>4.1/</b> 4.7
Night	<b>21.4/</b> 22.0	<b>9.0/</b> 7.1	<b>5.6/</b> 3.6
Stable cool nights	<b>20.5/</b> 20.5	<b>5.7/</b> 5.5	<b>2.1/</b> < LOD
Stable warm nights	<b>41.6/</b> 41.6	<b>10.9/</b> 10.7	<b>6.9/</b> 6.7
Unstable cool nights	<b>7.9/</b> 7.9	<b>4.5/</b> 4.5	<b>&lt;LOD/</b> <LOD
Unstable warmnights	<b>13.5/</b> 13.5	<b>6.8/</b> 6.8	<b>3.6/</b> 3.6
<b>Above</b>	<b>12.6/</b> 12.8	<b>6.0/</b> 6.1	<b>4.2/</b> 4.3
Day	<b>10.4/</b> 10.7	<b>5.0/</b> 5.1	<b>3.1/</b> 3.3
Night	<b>15.5/</b> 15.5	<b>7.5/</b> 7.5	<b>5.6/</b> 5.6
Stable cool nights	<b>14.8/</b> 14.8	<b>7.5/</b> 7.5	<b>5.7/</b> 5.7
Stable warm nights	<b>---</b> / ---	<b>---</b> / ---	<b>---</b> / ---
Unstable cool nights	<b>---</b> / ---	<b>---</b> / ---	<b>---</b> / ---
Unstable warmnights	<b>20.5/</b> 20.5	<b>7.1/</b> 7.1	<b>5.2/</b> 5.2

This correction affects also the values mentioned in the response to the referees (based on this Table), that were added to the revised version of the manuscript (page 28, section 3.5):

- Line 749: 7.2 instead of 7.3 s<sup>-1</sup>, and 6.1 s<sup>-1</sup> instead of 6.0 s<sup>-1</sup>
- Line 753: 4.2 s<sup>-1</sup> instead of 4.3 s<sup>-1</sup>
- Line 763: 4.3 s<sup>-1</sup> instead of 4.2 s<sup>-1</sup>
- Page 29, line 773: 7.5 s<sup>-1</sup> instead of 7.6 s<sup>-1</sup>
- Table in supplementary material 9 (revised version).

In addition, for consistency only averaged contributions of NMHCs and OVOCs corresponding to the common measurements periods are presented in the revised text.

- Lines 754- 758 (revised version): 0.48 s<sup>-1</sup> on average, (0.43 s<sup>-1</sup> from NMHCs and 0.05 s<sup>-1</sup> from OVOCs measured by GC) of the missing OH reactivity between the 10<sup>th</sup> and the 12<sup>th</sup> July. However, after the 14<sup>th</sup> of July, the GC measuring OVOC stopped working, but NMHCs alone account for 0.5 s<sup>-1</sup> of missing OH reactivity on average.

Instead of (page 28, lines 5- 8, submitted version): 0.45 s<sup>-1</sup> on average, (0.34 s<sup>-1</sup> from NMHCs and 0.11 s<sup>-1</sup> from OVOCs measured by GC) of the missing OH reactivity between the 10<sup>th</sup> and the 12<sup>th</sup> July. However, after the 14<sup>th</sup> of July, the GC measuring OVOC stopped working, but NMHCs alone account for 0.6 s<sup>-1</sup> of missing OH reactivity on average.

- Since standard OH reactivity experiments were conducted at pyrrole-to-OH ratios ranging between 1.7 and 4, for consistency, CRM data points with pyrrole-to-OH ratio > 4 were excluded from the calculation of the average increase in OH reactivity due to the different corrections (Answer to RC2, comment 1). Hence, the increase due to humidity correction is now 2.2 s<sup>-1</sup> instead of 2.4 s<sup>-1</sup>, the increase due to the correction for the deviation from pseudo-first order kinetics is now 10.4 s<sup>-1</sup> instead of 10.0 s<sup>-1</sup> and the increase due to the correction for dilution is now 2.6 s<sup>-1</sup> instead of 2.8 s<sup>-1</sup> (Table 2, revised version).

- The contribution of acetic acid to OH reactivity was corrected:  
Submitted version, page 29, line 2: Maximum OH reactivity was on average  $0.8 \text{ s}^{-1}$  for warm days, 3.8 times higher than for cool days (inside canopy measurements).  
Revised version, page 30, line 811: Maximum OH reactivity was on average  $0.07 \text{ s}^{-1}$  for warm days, 4 times higher than for cool days (inside canopy measurements).

# Variability of OH reactivity in the Landes maritime Pine forest: Results from the LANDEX campaign 2017

Sandy Bsaibes<sup>1</sup>, Mohamad Al Ajami<sup>2</sup>, Kenneth Mermet<sup>3,4,5</sup>, François Truong<sup>1</sup>, Sébastien Batut<sup>2</sup>, Christophe Hecquet<sup>2</sup>, Sébastien Dusanter<sup>3</sup>, Thierry Léornadis<sup>3</sup>, Stéphane Sauvage<sup>3</sup>, Julien Kammer<sup>1,4</sup>,  
5 Pierre-Marie Flaud<sup>4,5</sup>, Emilie Perraudin<sup>4,5</sup>, Eric Villenave<sup>4,5</sup>, Nadine Locoge<sup>3</sup>, Valérie Gros<sup>1</sup>, Coralie Schoemaeker<sup>2</sup>

<sup>1</sup> Laboratoire des Sciences du Climat et de l'Environnement, LSCE, UMR CNRS-CEA-UVSQ, 91191 Gif-sur-Yvette, France

<sup>2</sup> Laboratoire PhysicoChimie des Processus de Combustion et de l'Atmosphère, PC2A, UMR 8522, 59655 Villeneuve  
10 d'Ascq, France

<sup>3</sup> IMT Lille Douai, Univ. Lille – SAGE - Département Sciences de l'Atmosphère et Génie de l'Environnement, F-59000 Lille, France

<sup>4</sup> Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence Cedex, France

<sup>5</sup> CNRS, EPOC, UMR 5805, F-33405 Talence Cedex, France

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*Correspondence to:* Sandy Bsaibes (sandy.bsaibes@gmail.com)

Valérie Gros (valerie.gros@lsce.ipsl.fr)

## Abstract.

Total OH reactivity measurements were conducted during the LANDEX intensive field campaign in a coniferous  
20 temperate forest located in the Landes area, south-western France, during July 2017. In order to investigate inter-canopy and intra-canopy variability, measurements were performed inside (6 m) and above the canopy level (12 m), as well as at two different locations within the canopy, using a Comparative Reactivity Method (CRM) and a Laser Photolysis -Laser Induced Fluorescence (LP-LIF) instrument. The two techniques were intercompared at the end of the campaign by performing measurements at the same location. Volatile organic compounds were also monitored at both levels with a proton transfer-  
25 time of flight mass spectrometer and online gas Chromatography instruments to evaluate their contribution to total OH reactivity, with monoterpenes being the main reactive species emitted in this *Pinus pinaster* Aiton dominated forest. Total OH reactivity varied diurnally, following the trend of BVOCs of which emissions and concentrations were dependent on meteorological parameters. Average OH reactivity was around **19.2 s<sup>-1</sup>** and **16.5 s<sup>-1</sup>**, inside and above the canopy, respectively. Highest levels of total OH reactivity were observed during nights with a low turbulence ( $u^* \leq 0.2$  m/s) leading  
30 to lower mixing of emitted species within the canopy and thus an important vertical stratification, characterized by a strong concentration gradient. Comparing the measured and the calculated OH reactivity highlighted an average missing OH reactivity of 22 % and 33 %, inside and above the canopy, respectively. A day/night variability was observed on missing OH reactivity at both heights. Investigations showed that during day-time, missing OH sinks could be due to primary emissions and secondary products linked to a temperature-enhanced photochemistry. Regarding night-time missing OH reactivity,

35 higher levels were seen for the stable and warm night of the 4<sup>th</sup>-5<sup>th</sup>, July, showing that these conditions could have been favorable for the accumulation of long-lived species (primary and secondary species) during the transport of the air mass from nearby forests.

## 1 Introduction

The hydroxyl radical OH is considered as the most important initiator of photochemical processes in the 40 troposphere during day-time, and the prevailing “detergent” from local to global scales. It controls the lifetime of most trace gases and contributes to the self-cleansing power or so-called “oxidation capacity” of the atmosphere.

Even though the main primary source for OH in the lower troposphere is the photolysis of ozone at short wavelengths, the 45 OH production and loss processes are numerous and difficult to quantify. Such losses involve several hundreds of chemical species and as many reactions to consider. In this respect, a direct measurement of total OH reactivity ( $\text{ROH}$ ) is of great interest to better understand the OH chemistry in the atmosphere and to investigate the budget of OH sinks in a particular environment.  $\text{ROH}$  is defined as the pseudo first-order loss rate (in  $\text{s}^{-1}$ ) of OH radicals, equivalent to the inverse of the OH lifetime. It is the sum of the reaction frequencies of all chemical species reacting with OH, as shown in Eq. (1):

$$\text{ROH} = \sum_{i=1}^n k_{\text{OH}+X_i} \cdot [X_i] \quad (1)$$

In this equation, a chemical reaction frequency for a species  $X_i$  with OH ( $\text{ROH}+X_i$ ) is the product of its rate-coefficient  $k_{\text{OH}}$  50 with its concentration  $[X_i]$ . The measured total OH reactivity can be compared with calculated values based on the sum of reaction frequencies as shown in Eq. (1) and for which the concentration of  $X_i$  has been measured at the same location. Any significant discrepancy between measured and calculated OH reactivity explicitly demonstrates missing OH sinks, commonly called missing OH reactivity, and points out that potentially important unmeasured reactive species and chemical processes associated with these species may affect our understanding of OH atmospheric chemistry.

55 Two approaches have been used to measure the total OH reactivity. The first approach derives OH reactivity from direct measurements of OH decay rates due to its reaction with trace species present in ambient air introduced in a reaction tube. OH can be generated and detected differently according to 3 types of techniques: The Flow Tube-Laser Induced Fluorescence (FT-LIF, (Hansen et al., 2014; Ingham et al., 2009; Kovacs and Brune, 2001)), the Laser Photolysis-Laser Induced Fluorescence (LP-LIF, (Sadanaga *et al.*, 2004; Parker *et al.*, 2011; Amédio, 2012; Stone et al., 2016; Fuchs *et al.*, 60 2017)) and the Flow Tube-Chemical Ionization Mass Spectrometry (FT-CIMS, (Muller et al., 2018)). The second approach is called the Comparative Reactivity Method (CRM) and it consists in an indirect quantification of OH losses from the concentration change of a reference molecule that competes with ambient reactive species to react with artificially produced OH. The reference substance, pyrrole, is measured with a Proton Transfer Reaction Mass Spectrometer (PTR-MS, (Sinha *et al.*, 2008; Dolgorouky *et al.*, 2012; Michoud *et al.*, 2015)) or with a Gas Chromatograph-Photo Ionization Detector (GC-PID, 65 (Nölscher et al., 2012)) or chemical ionization mass spectrometry (CIMS, (Sanchez et al., 2018)).

Both LP-LIF and CRM techniques were deployed in a Pine forest for this study, the instruments deployed are presented in more details below and a general description is provided here. In the LP-LIF method, OH is generated by laser pulsed photolysis of ozone in a reaction tube, at typically 266 nm, followed by the rapid reaction of O(<sup>1</sup>D) with ambient water vapor. OH radicals react with ambient reactive species in the reaction tube and the concentration of OH decreases after 70 the laser pulse. The air from the reaction tube is continuously pumped into a low-pressure detection cell where the OH decay is monitored by laser-induced fluorescence at a high time resolution (range of hundreds of  $\mu$ s) (Sadanaga *et al.*, 2004). Compared to flow-tube set-ups, lower flow rates of ambient air are needed in the LP-LIF technique (less than 10 L min<sup>-1</sup> compared to several tens of L min<sup>-1</sup>). In addition, the use of O<sub>3</sub> laser photolysis instead of continuous water photolysis by lamps at 185 nm for OH generation, the latter being commonly used in FT-LIF or CRM, limits the spurious formation of OH 75 from the reaction of HO<sub>2</sub> with ambient NO. However, in order to quantify wall loss reactions, an instrument zero has to be subtracted from all measurements, and a correction may have to be applied for the recycling of OH radicals in the presence of high NO levels (Stone *et al.*, 2016; Fuchs *et al.*, 2017).

In the Comparative Reactivity Method (CRM), ambient air, wet nitrogen and pyrrole are introduced into a glass reactor where OH radicals are produced by the photolysis of water vapor. The mathematical expression used to determine 80 the OH reactivity of the analyzed sample is derived in terms of the initial concentration of pyrrole (C1), the background concentration of pyrrole reacting alone with OH (C2) and the concentration of pyrrole after competition with air reactants (C3). The CRM exhibits several advantages compared to direct measurements techniques, like the commercial availability of PTR-MS and the need of a smaller sampling flow rate of ambient air (few hundreds of mL min<sup>-1</sup>), which broadens the application of the technique to branch and plant enclosure studies. On the other hand, this indirect method requires a raw 85 data processing with careful corrections for measurement artefacts related to humidity changes and secondary chemistry that can impact the pyrrole concentration (Sinha *et al.*, 2008; Michoud *et al.*, 2015).

A few inter-comparisons were reported in the literature for urban and remote areas (Hansen *et al.*, 2015; Zannoni *et al.*, 2015; Sanchez *et al.*, 2018) and chamber experiments (Fuchs *et al.*, 2017) aiming at reproducing ambient conditions observed in various environments. The latter, including a large number of OH reactivity instruments (FT-LIF, LP-LIF, 90 CRM) and conducted in the SAPHIR atmospheric simulation chamber, allowed to compare the performances of each technique. Results showed that OH reactivity can be accurately measured for a wide range of atmospherically relevant chemical conditions by all instruments. However, CRM instruments exhibited larger discrepancies to calculated OH reactivity compared to instruments directly probing OH radicals, and these differences were more important in the presence of terpenes and oxygenated organic compounds.

95 Over the past two decades, OH reactivity measurements were conducted in various environments at the ground level using the available techniques: urban and suburban areas, forest areas, marine areas (Yang *et al.*, 2016; Dusander and Stevens, 2017). A few aircraft measurements have also been carried out to complete ground-based observations (Brune *et al.*, 2010). Many studies highlighted the interest of investigating OH reactivity in forest areas exhibiting large concentrations of biogenic VOCs (BVOCs) since BVOC emissions exceed anthropogenic VOCs by a factor of 10 at the global scale (Guenther

100 et al., 1995). Results showed that our understanding of OH sinks in these environments was incomplete with observations of large missing OH reactivity ranging between 25 % and 80 %. Total OH reactivity appeared to be impacted by several factors such as the forest type and the dominant emitted species, the seasonality, the canopy level as well as specific atmospheric conditions (Hansen et al., 2014; Nölscher et al., 2013; Praplan et al., 2019; Sanchez et al., 2018; Zannoni et al., 2016).

105 Among these biogenic hydrocarbons, monoterpenes represent a large class of  $C_{10}H_{16}$  compounds, which are mainly emitted by conifers as well as broad-leaves trees. They can be oxidized by OH, ozone and the nitrate radical, leading to atmospheric lifetimes ranging between minutes and days (Atkinson and Arey, 2003). The oxidation of primary BVOCs can therefore contribute to the formation of tropospheric ozone and secondary organic aerosols from the local to the regional scales, with oxidation products of BVOCs having a potential impact at a larger scale. Regarding coniferous forests, an averaged OH reactivity of  $6.7 \text{ s}^{-1}$  was observed over a temperate Pine forest located in the southern part of the Rocky 110 Mountains in the USA during summer 2008 (Nakashima et al., 2013). Measured OH reactivity exhibited a diurnal variation with minima during day-time when MBO (2-methyl-3-buten-2-ol) was the main contributor, and maxima during night-time when the OH reactivity was dominated by monoterpenes. Approximately 30% of the measured OH reactivity remained unexplained and could be related to unmeasured or unknown oxidation products of primary emitted biogenic compounds. 115 Another campaign also carried out in a temperate coniferous forest, located in the Wakayama Forest Research Station in Japan during summer 2014 (Ramasamy et al., 2016), showed comparable results with an average total OH reactivity of  $7.1 \text{ s}^{-1}$ . OH reactivity varied diurnally with temperature and light, reaching a maximum at noon-time. Monoterpenes were the main drivers of the total OH reactivity in the considered ecosystem, accounting for 23.7 %, followed by isoprene (17.0 %) and acetaldehyde (14.5 %). The missing OH reactivity (29.5 % on average) was found to be linked to light and temperature dependent unmeasured primary and secondary species.

120 In the present study, we report on the measurement of total OH reactivity from a field experiment conducted in the Landes temperate forest, southwestern France. This work was part of the LANDEX project (LANDEX, i.e. the Landes Experiment: Formation and fate of secondary organic aerosols generated in the Landes forest) that aimed at characterizing secondary organic aerosol formation observed in this monoterpene-rich environment. The dominant tree species at the site is maritime pine, *Pinus pinaster* Aiton, which is known to be a strong emitter of  $\alpha$  and  $\beta$ -pinene, leading to a diurnal 125 concentration profile of monoterpenes characterized by maximum values at night and minimum values during daytime (Simon et al., 1994). Nocturnal new particle formation episodes (NPFs) were reported in this ecosystem, suggesting the contribution of BVOC oxidation to the nucleation and growth stages of particles (Kammer et al., 2018).

130 Measurements of OH reactivity and trace gases were performed at two heights to cover the inside and above canopy, and at two different locations inside the canopy to investigate the intra-canopy variability. Two different instruments were deployed: the CRM from LSCE (Laboratoire des Sciences du Climat et de l'Environnement) that measured inside and above the canopy and the LP-LIF from PC2A (Physicochimie des Processus de Combustion et de l'Atmosphère) that performed measurements inside the canopy. The deployment of two different instruments was a good opportunity to (i) compare measurements made with both methods in a real biogenic environment after the inter-comparison experiment performed in

the SAPHIR chamber and recent improvement of the CRM instrument, (ii) investigate the levels and diurnal variability of  
135 OH reactivity at two different heights, and (iii) investigate both the OH reactivity budget and the missing reactivity pattern using a large panel of concomitant trace gas measurements.

## 2 Experimental

### 2.1 Site description

The LANDEX intensive field campaign was conducted from the 3<sup>rd</sup> to the 19<sup>th</sup> of July 2017 at the Bilos field site in the  
140 Landes forest, south-western France. The vegetation on the site was dominated by maritime pines (*Pinus pinaster* Aiton) presenting an average height of 10 m. The climate is temperate with a maritime influence due to the proximity of the Atlantic Ocean. This site is part of the European ICOS (Integrated Carbon Observation System) Ecosystem infrastructure. A more detailed description of the site is available in Moreaux *et al.* (2011) and Kammer *et al.* (2018).

### 2.2 OH reactivity instruments

145 The LP-LIF instrument, referred here as UL (University of Lille)-FAGE (Fluorescence Assay by Gas Expansion), measured the OH reactivity in the canopy, whereas the CRM instrument, referred as LSCE-CRM, alternatively measured the OH reactivity at two heights (see Fig. 1(b)). Table 1 summarizes the performance of both instruments. The LP-LIF technique has a 3-fold better limit of detection than the CRM, however the CRM has a larger dynamic range since it can measure the OH reactivity up to 300 s<sup>-1</sup> without sample dilution. The overall systematic uncertainty ( $1\sigma$ ) is around 15 % and 35 % for the LP-  
150 LIF and the CRM, respectively. The LSCE-CRM and UL-FAGE characteristics are given in the following paragraphs.

**Table 1.** Performance of the two OH reactivity instruments deployed during the LANDEX campaign.

Instrument	LOD*(s <sup>-1</sup> ) (3 $\sigma$ )	ROH max (s <sup>-1</sup> )	Time resolution (s)	Uncertainty (1 $\sigma$ )
LSCE-CRM	3	300	600	35 %
UL-FAGE	0.9	150**	30-120	15 %

\* LOD: Limit of Detection; \*\* Without dilution

### 2.2.1 The Comparative Reactivity Method (CRM) and instrument performance

The total OH reactivity was measured during the whole campaign, inside and above the canopy, by the LSCE-CRM instrument. This technique, first described by Sinha *et al.* (2008), is based on measuring the concentration of a reagent compound (pyrrole) that reacts with OH under different operating conditions (i.e. steps) at the output of the sampling reactor by a PTR-MS instrument. The first step consists in introducing pyrrole with dry nitrogen and dry zero air to measure the C1 level, which corresponds to the pyrrole concentration in absence of OH. C1 accounts for potential photolysis due to photons emitted by the mercury lamp used to produce OH. During the second step, dry nitrogen and zero air are replaced by humid gases and a pyrrole concentration C2 is measured. C2 is lower than C1 because pyrrole reacts with OH. In the last step, zero air is replaced by ambient air, which leads to a competition between the reactions of OH with pyrrole and ambient trace gases. A C3 concentration, higher than C2, is measured. The difference between C3 and C2 depends on the amount and reactivity of reactive species present in ambient air and is used to determine the total OH reactivity from Eq. (2), where it is assumed that pyrrole reacts with OH following pseudo-first order reaction kinetics, i.e. [pyrrole] >> [OH]:

$$170 \quad R_{OH} = \frac{(C_3 - C_2)}{(C_1 - C_3)} \cdot kp \cdot C_1 \quad (2)$$

Where  $kp$  is the reaction rate constant of pyrrole with OH ( $1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1985)).

This technique requires multiple corrections to derive reliable measurements of total OH reactivity due to: (1) potential differences in relative humidity between C2 and C3, leading to different OH levels, (2) the spurious formation of OH in the sampling reactor when hydroperoxy radicals ( $\text{HO}_2$ ) react with nitrogen monoxide (NO), (3) not operating the instrument under pseudo-first order conditions, and (4) dilution of ambient air inside the reactor by the addition of  $\text{N}_2$  and pyrrole (Sinha *et al.*, 2008; Michoud *et al.*, 2015). **In some CRM systems, corrections for potential  $\text{NO}_2$  and/or  $\text{O}_3$  artefacts are also considered (Michoud *et al.*, 2015; Praplan *et al.*, 2017).** On one hand,  $\text{NO}_2$  is subject to photolysis leading to NO, which can subsequently react with  $\text{HO}_2$  yielding OH. On the other hand,  $\text{O}_3$  can also be photolyzed in the reactor, producing  $\text{O}(\text{^1D})$ , which reacts further with  $\text{H}_2\text{O}$ , yielding two OH radicals.

180 Intensive laboratory experiments as well as tests during the LANDEX field campaign were performed to characterize these corrections and assess the performances of the instrument over time. During the LANDEX field campaign, a slightly modified version of the CRM-LSCE instrument was used compared to the instrument previously deployed during the intercomparison experiment at the SAPHIR chamber (Fuchs *et al.*, 2017). Indeed, this last study showed that the OH reactivity measured by all CRM instruments was significantly lower than the reactivity measured by the other instruments in 185 the presence of monoterpenes and sesquiterpenes. A potential reason discussed for this discrepancy was the loss of terpenes in the inlet of the CRM instruments. The LSCE-CRM sampling system was built with  $\frac{1}{4}$ " OD non-heated PFA tubing and was relying on a Teflon pump to introduce the sample into the reactor. In order to measure the total OH reactivity in a monoterpenes-rich environment, several technical improvements were made on the previous version of the instrument

described by Zannoni *et al.* (2015). First, all the PFA sampling lines were replaced by 1/8" OD sulinert lines, continuously  
190 heated to around 50°C to prevent condensation and minimize sorption processes. Second, temperature sensors were placed at several locations inside the system to monitor potential variations; the dew point was measured in the flow out through the pump to monitor humidity fluctuations, and the pressure was also monitored to make sure that measurements were performed at atmospheric pressure. All the flows going in and out of the reactor, the temperature at various places, the humidity and the pressure in the reactor were recorded continuously to track potential variations.

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### **Ambient air sampling**

Ambient air was sampled through two 1/8" OD sulinert lines collocated on a mast close to the trailer (see Fig. 1(a)). The  
200 lines lengths were 8 m for the measurements performed inside the canopy and 12 m for those performed above. These lines were heated up to 50 °C as it was shown that losses of highly reactive molecules (i.e.  $\beta$ -caryophyllene) were negligible for temperatures above 20 °C (Kim *et al.*, 2009).

During sampling, the air flow was driven through one line by two pumps. The first one was a Teflon pump located upstream of the reactor and the other one was that from the Gas Calibration Unit (GCU) used to generate humid zero air from ambient air. Together, the two pumps allowed air sampling between 1 – 1.2 L min<sup>-1</sup>, with the excess going to an exhaust.

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### **CRM-LSCE system characterization**

Several tests were performed before, during and after the campaign to assess the performance of the instrument operated  
210 during the whole campaign. The PTR-MS was calibrated at the beginning and at the end of the field campaign showing a good stability under dry and wet conditions (slope of  $15.5 \pm 0.9$  (1 $\sigma$ )). Regular C1 measurements were made to check the stability of the initial pyrrole concentration all along the campaign. C1 was  $70.7 \pm 4.0$  (1 $\sigma$ ) ppbv.

Small differences in humidity observed between C2 and C3 were considered while processing the raw data. In order to  
215 assess this correction, experiments were performed to assess the variability of C2 on humidity by contrasting the change in C2 ( $\Delta$ C2) for various changes in the  $m/z$  37-to- $m/z$  19 ratio ( $\Delta$  [ $m/z$  37-to- $m/z$  19 ratios]),  $m/z$  37 and  $m/z$  19 being representative of  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  and  $\text{H}_3\text{O}^+$ , respectively, and their ratio being proportional to humidity. During this campaign, three humidity tests were performed by varying the humidity in ambient air samples. These tests were in good agreement and showed a linear relationship between  $\Delta$ C2 (ppbv) and  $\Delta$  ( $m/z$  37-to- $m/z$  19 ratio) with a slope of -89.18. The correction was applied as discussed in Michoud *et al.* (2015).

An important assumption to derive ROH from Eq. (2) is to operate the instrument under pseudo-first-order conditions (i.e.  
220 [pyrrole] >> [OH]), which is not the case with current CRM instruments. To determine the correction factor for the deviation from pseudo-first order kinetics, injections of known concentrations of isoprene ( $k_{\text{Isoprene+OH}} = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 1-

120 ppbv) and  $\alpha$ -pinene ( $k_{\alpha\text{-pinene+OH}} = 5.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , 3 -190 ppbv) (Atkinson, 1985) were performed before and after the field campaign since they represent the dominant species in this forest ecosystem.

225 The measured OH reactivity obtained from these tests were then compared to the expected OH reactivity, leading to a correction factor that is dependent on the pyrrole-to-OH ratio. Therefore, standard OH reactivity experiments were conducted at different pyrrole-to-OH ratios ranging from 1.7 to 4.0, which encompass the ratio observed most of the time during the campaign. These tests led to a correction factor ( $F$ ) =  $-0.52 \times (\text{pyrrole-to-OH}) + 3.38$ .

230 NO mixing ratios were lower than 0.5 ppbv (corresponding to the detection limit of the NO<sub>x</sub> monitor deployed during LANDEX) most of the time for the measurement time periods used in this study, and no correction was applied for the spurious formation of OH from the HO<sub>2</sub>+NO reaction. Similarly, for NO<sub>2</sub>, no correction was applied due to the low ambient mixing ratio of  $1.1 \pm 0.8$  ppbv. Regarding O<sub>3</sub>, no dependency was seen for LSCE-CRM, based on previous experiments (Fuchs et al., 2017). Therefore, no correction was applied. The correction ( $D$ ) on the reactivity values due to the dilution was around 1.46 during the campaign. Thus, the total OH reactivity may be expressed as:

$$\text{ROH}_{\text{final}} = \left[ \frac{(C_3 - C_2(\text{corrected}))}{(C_1 - C_3)} \cdot kp \cdot C_1 \right] \cdot F \cdot D \quad (3)$$

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Finally, overall uncertainties were estimated at 35 % ( $1\sigma$ ) for the measured OH reactivity by the CRM (Zannoni *et al.*, 2015). Table 2 reports a summary of the corrections resulting from our tests and their impact on measurements. As shown in Table 2, the application of ( $F$ ), for the deviation from pseudo-first order kinetics, induces the largest correction, with an absolute increase of  $10.4 \text{ s}^{-1}$  on average. Furthermore, this factor ( $F$ ) has the largest relative uncertainty, with  $\pm 36 \%$ , against  $\pm 2 \%$  for the humidity correction factor.

**Table 2.** Summary of corrections applied to raw reactivity data for LSCE-CRM. Correction coefficients are obtained from experiments performed before, during and after the field campaign.

Correction	Correction factor	Mean absolute change in OH reactivity ( $\text{s}^{-1}$ )
Humidity changes between C2 and C3	$-89.18 \pm 2.16$	$+ 2.2$
Not operating the CRM under pseudo first order conditions	$F = (-0.52 \pm 0.20) \times (\text{pyrrole-to-OH}) + (3.38 \pm 0.60)$	$+ 10.4$
Dilution	$D = 1.46$	$+ 2.6$

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250 **2.2.2 UL-FAGE reactivity instrument**

Total OH reactivity was measured at a different location inside canopy, from the 13<sup>th</sup> to the 19<sup>th</sup> of July, using LP-LIF instrument of the PC2A laboratory (UL-FAGE reactivity) which has already been used in several intercomparisons and field campaigns (Hansen *et al.*, 2015; Fuchs *et al.*, 2017). The reactivity instrument comprises three parts: the photolysis laser, the 255 photolysis cell (reaction tube) and the LIF cell based on FAGE technique. The photolysis laser is used to generate OH radicals within the photolysis cell by the photolysis of O<sub>3</sub> in the presence of water vapor. The photolysis laser is a YAG laser (Brilliant EaZy, QUANTEL) with a doubling and a quadrupling stage providing a radiation at 266 nm with a repetition rate of 1 Hz. The photolysis beam is aligned at the center of the photolysis cell and is expanded (diameter of 4 cm reaching the entrance of the cell) by two lenses (a concave one  $f=25$  mm and a convex with  $f=150$  mm) in order to increase the 260 photolysis volume and to limit the diffusion effect in the photolysis cell.

This photolysis cell is a stainless steel cylinder with an internal diameter of 5 cm and a length of 48 cm. It presents two 265 openings on the opposite sides, one as an entrance for the air samples and the second connected to a pressure monitor (Keller PAA-41) to measure the pressure inside the cell. Ambient or humid clean air (which is produced by passing a fraction of dry synthetic air, purity of 99.8 %, through a water bubbler, called zero air and used to determine the OH reactivity in the absence of reacting species) are injected through the first opening with a small flow of synthetic air (about 20 mL min<sup>-1</sup>) passing through an ozone generator (Scientech) to generate an ozone concentration of about 50 ppbv in the total flow. The ozone concentration is chosen to produce enough OH to have a good signal/noise ratio, but kept low enough to minimize the reactions involving O<sub>3</sub>.

The sampled mixture is continuously pumped into the FAGE cell (pressure=2.3 Torr) by a dry pump (Edwards, GX 600L) 270 and the LIF signal is collected by a CPM (Perkin Elmer MP1982), an acquisition card and a LabView program. The detection of the fluorescence is synchronized with the photolysis laser pulses by delay generators. The OH reactivity time resolution was at the minimum set to be 30 s, meaning that each OH decay was accumulated over 30 photolysis laser shots and fitted by a mono-exponential decay. The number of sets of 30 photolysis laser shots accumulated is determined according to the signal to noise ratio (S/N) obtained (typically 4). When the S/N is lower, a set of 30 OH decays is added to 275 the previous one and so on until reaching the criteria. As the reactivity and the humidity vary along the day, S/N varies as a function of the ambient species concentrations. In order to check the consistency of the OH reactivity measurements, the well-known (CO + OH) reaction rate constant was measured. Different CO concentrations, from  $4 \times 10^{13}$  to  $3.7 \times 10^{14}$  cm<sup>-3</sup> in humid zero air are injected in the photolysis cell, allowing to measure reactivities ranging from 10 to 90 s<sup>-1</sup> and to determine (using a linear regression:  $R^2 = 0.97$ ) a rate constant of  $k_{CO+OH} = (2.45 \pm 0.11) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in good 280 agreement with the reference value of  $2.31 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson *et al.*, 2006) at room temperature. Under these conditions (absence of NO), HO<sub>2</sub> formed by the reaction of CO+OH is not recycled in OH and does not interfere with the measurements of OH.

## Ambient air sampling

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Ambient air was sampled in the canopy at about 5 m through a PFA line (diameter = 1/2 inches), a PFA filter being installed at the entrance of the tube to minimize particle or dust sampling. In the photolysis cell, the gas flow was sampled at 7.5 L min<sup>-1</sup> and the pressure was approximately 740 Torr, i.e. lower than the atmospheric pressure due to the restriction of the flow through the Teflon sampling line. For the reactivity measurements in zero air, synthetic air from a cylinder was used and a 290 part of the flow (2 L min<sup>-1</sup>) passed through a bubbler filled with Milli-Q water to reach a water vapor concentration of about 3000 ppmv.

## ROH, zero analysis

295 In order to determine the OH reactivity in ambient air  $ROH_{ambient}$ , it is necessary to subtract the reactivity measured using "zero air"  $ROH_{zero}$ , which represents the OH losses not related to the gas phase reactions with the species of interest, present in the ambient air, but due to wall losses, diffusion, etc., to the reactivity measured.

$$ROH_{ambient} = ROH_{measured} - ROH_{zero} \quad (4)$$

300 Zero air tests were conducted twice a day (in the morning and at night) when the reactivity measurements took place. The average of all experiments performed with zero air leads to a mean value of  $ROH_{zero} = (4.0 \pm 0.5) \text{ s}^{-1}$ . This value was therefore chosen as  $k_{zero}$  for the whole campaign.

## 2.3 Ancillary Measurements and corresponding locations

305 Measurements of VOCs (Table 3) were performed at different locations (Fig. 1) by a proton transfer reaction-mass spectrometer (PTR-MS) and four on-line gas chromatographic (GC) instruments. Ozone scrubbers (Copper tube impregnated with KI) and particle filters were added to the inlets of all GC sampling lines. **Losses of BVOCs in these ozone scrubbers were investigated under similar sampling conditions in the absence and presence of O<sub>3</sub> (Mermet et al., 2019, AMTD).** The scrubbers exhibited less than 5 % losses for most non-oxygenated BVOCs, whereas in the presence of ozone, losses were relatively higher for some BVOCs, but remained lower than 15 % (lower than 5 % for  $\alpha$ - and  $\beta$ -pinene). High flow rates 310 were applied in the sampling lines: 1 L min<sup>-1</sup> for GC instruments and 10 L min<sup>-1</sup> for the PTR-MS, therefore, the contact time between ambient BVOCs and the particle filters was extremely short and no significant losses are expected.

GC-BVOC1 is a gas chromatograph coupled to a flame ionization detector (airmo VOC C6- C12, Chromatotec), used by LSCE to monitor high-carbon VOCs (C6- C12) at 12 m height with a time resolution of 30 min. Sampling was

undertaken for 10 min. The instrument sampled ambient air with a flow rate of  $60 \text{ mL min}^{-1}$ . Once injected, the sample  
315 passed through a capture tube containing the adsorbent Carbotrap C, for VOCs preconcentration at room temperature ; the capture tube is then heated up to  $380^\circ\text{C}$  and the sample is introduced into the separating column (MXT30CE, id = 0.28 mm, length = 30 m, film thickness = 1  $\mu\text{m}$ ), with hydrogen as the carrier gas. During the campaign, calibrations were performed with a certified standard containing a mixture of 16 VOCs (including 8 terpenes) at a concentration level of 2 ppbv (National Physical Laboratory, Teddington, Middlesex, UK). Three calibrations were performed 3 times (at the beginning, in the  
320 middle and at the end of the campaign). As they were showing reproducible results (within 5 % for all the terpenes except cineole), a mean response factor per VOC was used to calibrate the measurements. Note that limonene and cymene had close retention times which lead to overlapping peaks and for this reason, only the sum of both compounds has been reported. For further details, refer to Gros *et al.* (2011). The sampling was done using a 13-m long sulfonert heated line (1/8") connected to an external pump for continuous flushing.

325 GC-BVOC2 is an online thermodesorber system (Markes Unity 1) coupled to a GC-FID (Agilent). It was used to monitor 20 C5-C15 BVOCs, including isoprene,  $\alpha$ - and  $\beta$ -pinene, carenes and  $\beta$ -caryophyllene at the 6 m height with a time resolution of 90 min. Ambient air was sampled at a flow rate of  $20 \text{ mL min}^{-1}$  for 60 min through a sorbent trap (Carbotrap B) held at  $20^\circ\text{C}$  by a Peltier cooling system. The sample was thermally desorbed at  $325^\circ\text{C}$  and injected into a BPX5 columns (60 m  $\times$  0.25 mm  $\times$  1  $\mu\text{m}$ ) using helium as carrier gas (30 min). Calibrations were performed at the beginning, in the middle  
330 and at the end of the campaign with a certified standard mixture (NPL, Teddington, Middlesex, UK, 2014) containing 33 VOCs (including 4 BVOCs:  $\alpha$ - pinene,  $\beta$ -pinene, limonene and isoprene) at a concentration of 4 ppbv each. The sampling was done using a 10 m long sulfonert line (1/4") heated at  $55^\circ\text{C}$  and connected to an external pump to adjust the sampling flow rate at  $1 \text{ L min}^{-1}$ . The method has been optimized in terms of temperature of the thermodesorption, the column, the sampling volume and sampling line including a scrubber. Tests showed a low response for some compounds (i.e. sabinene,  
335 terpinolene, ...), however, the most abundant compounds, were well measured. More details about the optimization and the tests performed can be found in Mermet *et al.* (2019, AMTD).

GC-NMHC is an online GC equipped with two columns and a dual FID system (Perkin Elmer<sup>®</sup>) that was described in detail elsewhere (Badol *et al.*, 2004). It was used to monitor 65 C<sub>2</sub>-C<sub>14</sub> non-methane hydrocarbons (NMHC), including alkanes, alkenes, alkynes and aromatics, at the 12 m height with a time resolution of 90 min. Ambient air was sampled at a  
340 flow of  $15 \text{ mL min}^{-1}$  for 40 min through a Nafion membrane and through a sorbent trap (Carbotrap B and Carbosieve III) held at -30°C by a Peltier cooling system. The trap was thermodesorbed at 300°C and the sample was introduced in the GC system. The chromatographic separation was performed using two capillary columns with a switching facility. The first column used to separate C<sub>6</sub>-C<sub>14</sub> compounds was a CP-Sil 5 CB (50 m  $\times$  0.25 mm  $\times$  1  $\mu\text{m}$ ), while the second column for C<sub>2</sub>-C<sub>5</sub> compounds was a plot Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> (50 m  $\times$  0.32 mm  $\times$  5  $\mu\text{m}$ ). Helium was used as carrier gas. Calibrations were  
345 performed at the beginning, middle and end of the campaign with a certified standard mixture (National Physical Laboratory (NPL), Teddington, Middlesex, UK, 2016) containing 30 VOCs at a concentration level of 4 ppbv each. The sampling was

done using a 13 m long sulfinert line (1/4") heated at 55 °C and connected to an external pump for continuous flushing at 2 L min<sup>-1</sup>.

GC-OVOC is an online GC-FID (Perkin Elmer®) used to monitor 16 C<sub>3</sub>-C<sub>7</sub> oxygenated VOCs (OVOCs), including 350 aldehydes, ketones, alcohols, ethers, esters and six NMHCs (BVOCs and aromatics). A detailed description can be found in Roukos *et al.* (2009). The measurements were performed at the 12 m height with a time resolution of 90 min. Ambient air was sampled at a flow rate of 15 mL min<sup>-1</sup> for 40 min through a water trap (cold finger, -30 °C) and a quartz tube filled with Carbopack B and Carbopack X held at 12.5 °C. VOCs were thermally desorbed at 280 °C and injected into a CP-Lowox columns (30 m × 0.53 mm × 10 µm) using helium as carrier gas. Calibrations were performed 3 times during the campaign 355 using a standard mixture (Apel Riemer, 2016) containing 15 compounds. This mixture was diluted with humidified zero air (RH = 50 %) to reach VOC levels of 3-4 ppbv. The sampling was done with the same sampling system than the GC-NMHC. **Sulfinert material chosen for all GCs sampling lines and used in LSCE-CRM sampling system, is recommended by ACTRIS, 2014.** High flows were set in the lines (residence time of less than 8 s), that were heated up to 50 °C to minimize the losses of potential reactive species. Filters and scrubbers were changed twice for the GC-BVOC1 and one time for the 360 other GC instruments.

The PTR-MS (PTR-QiToFMS, IONICON Analytic GmbH) sequentially measured trace gases at 4 levels (L1=12 m, L2=10 m, L3=8 m, L4=6 m) with a cycle of 30 minutes (6 min at each level and 6 min of zero air). The drift tube was operated at a pressure of 3.8 mbar, a temperature of 70 °C and a E/N ratio of 131 Td. Four identical sampling lines of 15 meters were used to sample ambient air at each height. The lines (PFA, 1/4" OD) were heated at 50 °C and were constantly 365 flushed at 10 L min<sup>-1</sup> using an additional pump and rotameters. **Indeed, Kim et al. (2009) tested losses of β-caryophyllene in similar operating conditions. Authors varied the temperature from zero to 40 °C showing that losses of β -caryophyllene are negligible above 20 °C. The residence time was lower than 2 s.**

Teflon filters were used to filter particles at the entrance of the sampling lines. The PTR-MS drawn ambient air at a flow rate of 300 mL min<sup>-1</sup> from the different lines using Teflon solenoid valves and a 1.5-meter-long inlet (PEEK, 1/16" OD) heated at 370 60 °C. Zero air was generated using a Gas Calibration Unit (GCU, IONICON Analytic GmbH) containing a catalytic oven and connected to L1. Ion transmissions were calibrated over the 21-147 Da mass range every 3 days using the GCU unit and a certified calibration mixture provided by IONICON (15 compounds at approximately 1 ppmv, including methanol, acetaldehyde, acetone, aromatic compounds, chlorobenzenes, etc.). Measurements of methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein + methylvinylketone + fragment ISOPOOH, methylethylketone, sum of monoterpenes, sum 375 of sesquiterpenes, acetic acid, nopinone and pinonaldehyde, obtained from levels 1 and 4 corresponding to the levels where OH reactivity measurements were performed, are discussed in this article. Sesquiterpenes, acetic acid, nopinone and pinonaldehyde measurements were not corrected for fragmentation in the drift tube and we cannot rule out the detection of other isomers at these masses such as glycolaldehyde for acetic acid measurements.

Inorganic traces gases (O<sub>3</sub> and NOx) were measured by commercial analyzers deployed by IMT-Lille-Douai (L1 to 380 L4 for O<sub>3</sub>) and EPOC (L4 for NOx). The nitrate radical (NO<sub>3</sub>) was measured using an IBB-CEAS instrument (Incoherent

Broad Band Cavity Absorption Spectroscopy) developed by the LISA (Laboratoire Interdisciplinaire des Systèmes Atmosphériques) research group and deployed for the first time on site during the LANDEX field campaign. Meteorological parameters such as temperature, relative humidity, global radiation, vertical turbulence, wind speed and wind direction were monitored using sensors already available at the ICOS measurement site. [More details can be found in Kammer et al., 2018.](#)

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**Table 3.** Summary of supporting measurements performed inside and/or above the canopy .

Instrument	Resolution time (min)	Measured species
GC-BVOC1	30	$\alpha$ -pinene, $\beta$ -pinene, myrcene, $\Delta$ -carene, p-cimene, limonene + cymene, cineol
GC-BVOC2	90	$\alpha$ -pinene, $\beta$ -pinene, myrcene, limonene, camphene, sabinene, $\alpha$ -phellandrene, 3-carene, p-cymene, ocimene, 1,8-cineol(=eucalyptol), $\alpha$ - terpinene, $\gamma$ -terpinene, terpinolene isoprene <sup>§</sup> , nopinone <sup>§</sup> , linalool <sup>§</sup> , $\beta$ -caryophyllene <sup>§</sup>
		<i>§ These compounds were not considered in the calculation of the weighted k rate constant for the reaction of monoterpene with OH. Nopinone, linalool and <math>\beta</math>-caryophyllene had relatively low contributions to OH reactivity, that were around 0.02, 0.37 and 0.18 s<sup>-1</sup> on average, respectively. Maximum contributions did not exceed 2.2 s<sup>-1</sup> for linalool and 1.5 s<sup>-1</sup> for <math>\beta</math>-caryophyllene.</i>
GC-NMHC	90	ethane, ethylene, propane, propene, isobutane, butane, acetylene, trans-2-butene, cis-2-butene, isopentane, pentane, 1,3-butadiene, 2-methyl-butene + 1-pentene, cyclopentene or terpene, hexene, hexane, 2,4-dimethylpentane, benzene, 3,3-dimethylpentane, 2-methylhexane, isoctane, heptane, toluene, octane, ethylbenzene, m+p-xylenes, styrene, o-xylene, nonane, 4-ethyltoluene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,3-dichlorobenzene, undecane, isopropylbenzene, n-propylbenzene
GC-OVOC	90	furan, tert-amylmethylether, 2-butanone, ethanol, isopropanol, butanol+2-hexanone, benzaldehyde
PTR-MS	6 min every 30 min at each level	methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein+methylvinylketone+fragment ISOOPOOH, methylvinylketone, sum of monoterpene, sum of sesquiterpenes*, acetic acid*, #, nopinone*, pinonaldehyde*
		<i>*Fragmentation was not corrected for and reported concentrations are likely lower limits.</i>
		<i>#potential interferences from isomeric compounds such as glycolaldehyde</i>

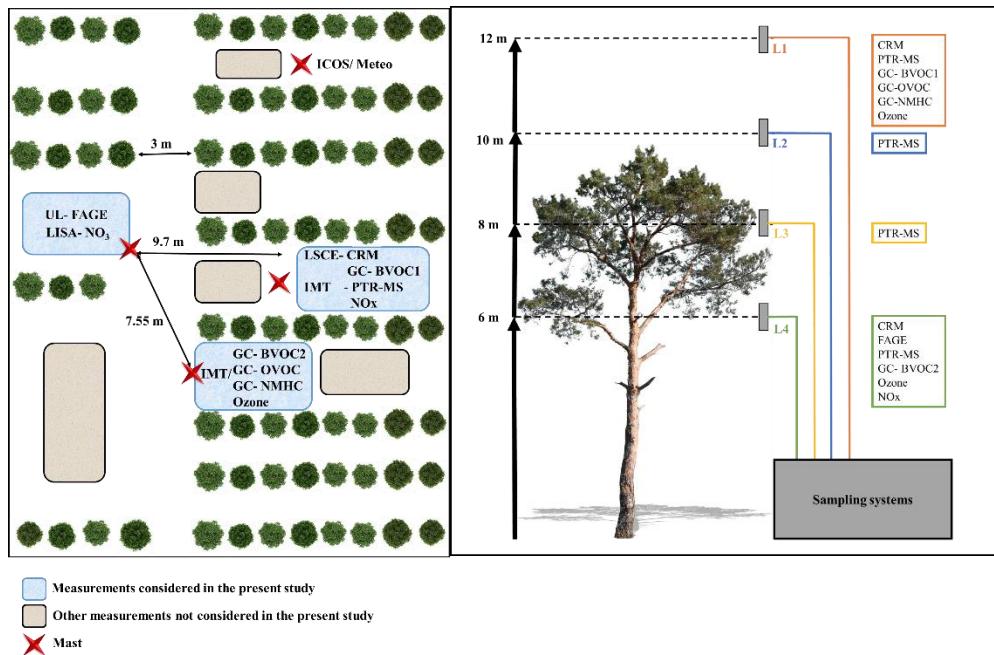
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**Figure 1.** Deployment of instruments at the measurement site. Left side (a) corresponds to the horizontal deployment, the right side (b) represents the different sampling levels with respect to the average trees' height.

## 2.4 OH reactivity calculation

As different instruments were available to quantify VOCs at different locations (Fig. 1 and Table 2), a selection of the data used to calculate the OH reactivity (Eq. (1)) was made, based on data availability for the different instruments (Table S1). Since measurements from the PTR-MS instrument covers the whole campaign and were performed at the same heights than OH reactivity measurements, these measurements, including methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein+methylvinylketone+fragment ISOPOOH, methylethylketone and the sum of monoterpenes, were selected to calculate the OH reactivity and to evaluate the potential missing OH reactivity at both levels. However, using only this set of data presents some limitations:

- 1) The PTR-MS only measures the sum of monoterpenes ( $m/z$  137+ $m/z$  81), while the detected monoterpenes are speciated by the GCs.
- 2) It was observed that isoprene measurements at  $m/z$  69 were disturbed by the fragmentation of some terpenic species (Kari et al., 2018; Tani, 2013), which led to a significant impact on the night-time measurements when isoprene was low.
- 3) Some NMHCs and OVOCs measured by GC at the 12 m height were not measured by the PTR-MS. This requires to assess the contribution of these additional species to the total OH reactivity for both heights.

430 To overcome these limitations, several tests were made to evaluate the reliability of the PTR-MS data to calculate the OH reactivity.

435 1) In order to use the sum of monoterpenes measured by the PTR-MS to calculate the total OH reactivity, it was necessary to determine a weighted rate constant for the reaction of monoterpenes with OH. After checking the consistency between the two GCs (BVOC1 and BVOC2, see supplementary material S2) and comparing the sum of monoterpenes measured by each GC to the PTR-MS measurements (simultaneous measurements at the same height - Fig. S2(b) and (c)), the weighted rate constant was calculated as the sum of the rate constants of each OH + monoterpene reaction multiplied by the average contribution of each specific monoterpene to the sum. The contribution of each monoterpene was calculated by dividing the concentration of the 8 speciated monoterpenes that were measured by both GCs ( $\alpha$ -pinene,  $\beta$ -pinene, myrcene,  $\Delta$ -carene, p-cimene, limonene + cymene, cineol), by their total concentration (Fig. S3(a)).

440 The weighted rate constant is defined as:

$$k_{OH,weighted} = \sum_i k_{OH+x_i} F_i \quad (5)$$

445 Where  $F_i$  represents the contribution of each individual species to the total concentration of monoterpenes, and  $k_{OH+x_i}$  the corresponding rate constant with OH. The reaction rate constant of the different trace species quantified in the field were taken from the literature (Atkinson et al., 2006). The OH reactivity of monoterpenes measured by PTR-FMS was calculated according to the following equation:

$$R_{OH-monoterpenes} = k_{OH,weighted} \times [MT] \quad (6)$$

where [MT] represents the sum of monoterpenes measured by PTR-MS.

450 The calculated OH reactivity inside and above the canopy (Fig. S3(b) and (e)) from (i) the use of the weighted OH reaction rate constant and the total concentration of monoterpenes measured by GC and (ii) the use of individual species and their associated rate constants are in relatively good agreement as shown by the scatter plots. A slope of 0.95,  $R^2=0.99$  has been obtained using the monoterpenes measured with the GC-BVOC1 at 12 m (Fig. S3(c)); a slope of 0.94,  $R^2=1.0$  using the same 8 compounds commonly monitored with GC-BVOC1 but measured at 6 m with GC-BVOC2 (Fig. S3(f)). When replacing the total concentration of monoterpenes measured by GCs by the PTR-MS measurements, slopes of 1.22 and 1.19 were obtained at 12 and 6 m heights, respectively (Fig. S3(d) and S3(g)). This increase in the slope values is likely due to an underestimation of the total monoterpene concentration by the GC instruments since these instruments only measured the most abundant monoterpenes present at the site. We cannot rule out a small overestimation of monoterpenes by the PTR-MS since fragments from other species such as sesquiterpenes could be detected at the monoterpene  $m/z$ . However, this

interference should be negligible due to the low concentration of ambient sesquiterpenes. These results are in agreement with the scatterplots comparing the sum of monoterpenes measured by GC and by PTR-MS (slopes of 1.29 and 1.10 at the 12 and 6 m heights, respectively, see Fig. S2(b) and S2(c)). Thus, the PTR-MS data was used to calculate the OH reactivity from monoterpenes for both heights, with a weighted reaction rate constant of  $76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at the 12 m height and  $77.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at the 6 m height.

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- 2) As mentioned above, some monoterpenes have been observed to fragment at  $m/z$  69.0704, which would result in an interference for isoprene measurements. In order to use the PTR-MS data for this species (only instrument measuring isoprene at 12 m), the contribution of monoterpenes to  $m/z$  69 has been estimated by comparing the GC-BVOC2 and PTR-MS measurements of isoprene performed at 6 m. This comparison showed that approximately 4 % of the monoterpenes concentration measured by PTR-MS had to be subtracted to that measured at  $m/z$  69.0704 to get a good agreement between the PTR-MS and GC-BVOC2 measurements of isoprene as shown in Fig. S4(a).

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- 3) A large range of NMHCs and OVOCs were measured at the 12 m height only by GC-NMHC and GC-OVOC (Table 3). Butanol (from SMPS exhausts) was also checked and found to be negligible at 12 m and highly and rapidly variable at 6 m (short peaks). NO and  $\text{NO}_2$  were only measured at the 6 m height. Mean NO mixing ratio was below the LOD for the measurement period and  $\text{NO}_2$  was around  $1.1 \pm 0.8 \text{ ppbv}$  on average. Thus, it was chosen not to take these species into account in the OH reactivity calculations. However, sensitivity tests were performed, in order to compute their relative contribution to OH reactivity (See sect. 3.5 and Fig. S5 and S6). Regarding methane and carbon monoxide, an estimation was made seen their relatively low  $k$  reaction rate coefficient with OH, taking mean concentration values of 2000 ppbv and 150 ppbv, respectively.

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The above limitations are summarized in Table S7 (supplementary material). Data used to calculate the OH reactivity has been resampled to 1 min, based on a linear interpolation (see Table 3 for the respective time resolution of the different instruments). This time base was chosen to be comparable to the time resolution of the UL-FAGE reactivity instrument, in order to keep the dynamics in OH reactivity variability.

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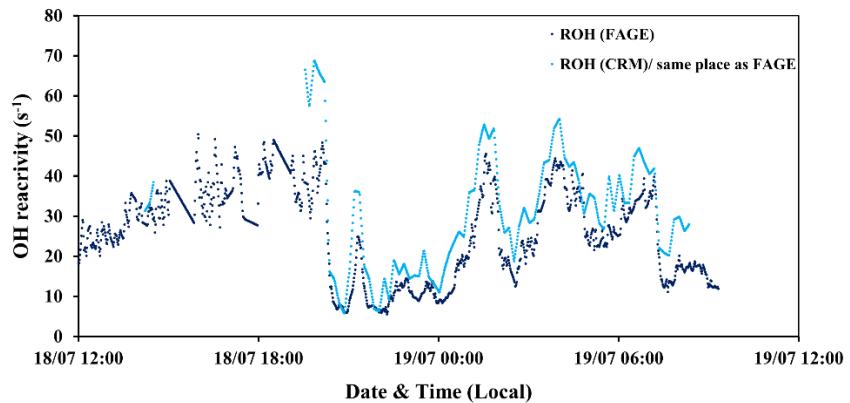
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### 3. Results

Measurements performed by both instruments at the same location were first compared to evaluate the agreement between the two techniques. The horizontal variability of total OH reactivity (same height) is also discussed. A second part of the result section is dedicated to a description of the total OH reactivity variability on the vertical scale with some 490 meteorological parameters. A comparison between measured and calculated OH reactivity for both the 6 and 12 m heights as well as a description of the BVOC contributions to the measured OH reactivity are then presented. Finally, we discuss the missing OH reactivity observed during this campaign and its possible origin.

#### 3.1.1 Inter-comparison of LSCE-CRM and UL-FAGE OH reactivity measurements at the same location

495 The direct comparison between LSCE-CRM and UL-FAGE reactivity instruments was done during the last two days of the campaign (Fig. 2). The sampling line of LSCE-CRM was moved to be collocated to the sampling line of UL-FAGE. Both instruments were measuring at the same location inside the canopy level, above the UL container at 5 m height. In this way the comparison between both instruments was made possible while minimizing the variabilities which could be related to the heterogeneity in ambient air. During this period, similar values were measured by both instruments, as shown 500 in Fig. 2, with total OH reactivity ranging between 5 and  $69 \text{ s}^{-1}$ . The lowest values were observed during day-time.



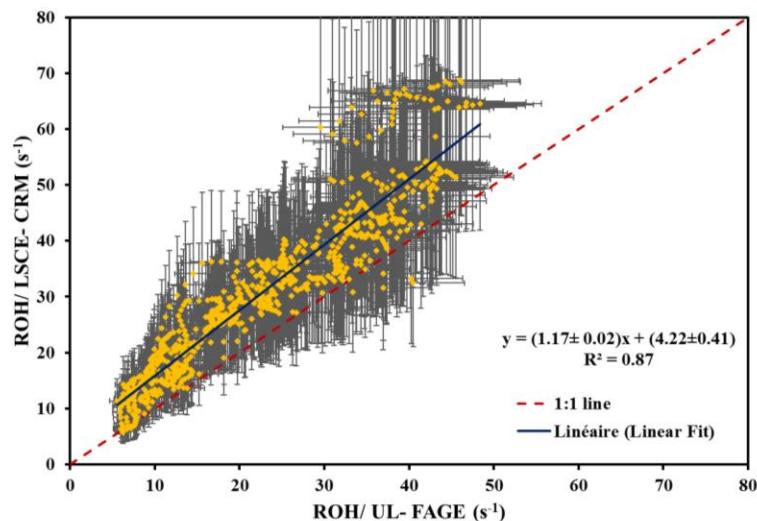
**Figure 2.** Time series of total OH reactivity measured by UL-FAGE (dark blue) and LSCE-CRM (light blue) instruments from the 18<sup>th</sup> to 19<sup>th</sup> of July 2017, at the same location inside canopy.

515 When OH reactivity measurements from LSCE-CRM are plotted versus OH reactivity measurements from UL-FAGE (Fig. 3), the linear regression exhibits a slope of  $1.17 \pm 0.02$ , an intercept of  $4.2 \pm 0.4 \text{ s}^{-1}$  and a R<sup>2</sup> of 0.87. This high intercept is statistically significant at  $3\sigma$  and can partly be due to an overestimation of the UL-FAGE zero that is subtracted

to the measured ambient OH reactivity. This issue is related to the quality of zero air used for zeroing the instrument. Indeed, previous comparisons have shown that using zero air of better quality (99.999%) may result in a zero of about  $2\text{ s}^{-1}$  lower (Hansen et al., 2015). An intercomparison of OH reactivity instruments made in the SAPHIR chamber (Fuchs et al., 2017) has also shown a positive bias of  $1\text{ s}^{-1}$  for the UL-FAGE instrument when high grade zero air was flushed in the chamber. A maximum overestimation of the UL-FAGE zero by  $3\text{ s}^{-1}$  is possible for this study leading to an underestimation of the ambient OH reactivity by  $3\text{ s}^{-1}$ . Finally, we cannot exclude a potential offset in LSCE-CRM measurements, that could be related to a possible desorption of “sticky” compounds from the Teflon pump. These results indicate that both instruments respond similarly (within 20 %) to changes in OH reactivity and the offset of  $4.2\text{ s}^{-1}$  has to be taken into account when OH reactivity measurements from LSCE-CRM and UL-FAGE are further compared for different locations and heights. It is worth noting that the higher points of OH reactivity observed in Fig. 3 correspond to the period from 19h30 to 20h (local time) of the 18<sup>th</sup>, July when the ambient relative humidity increased quickly by 20 % which was not seen on previous days and may have interfered with LSCE-CRM OH reactivity measurements.

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**Figure 3.** Measured reactivity by LSCE-CRM instrument as function of the measured reactivity by UL-FAGE when both instruments were measuring at the same location within the canopy (data resampled with a time resolution of 1 min). Errors bars represent the overall systematic uncertainty ( $1\sigma$ ) that is around 15 % and 35 % for LP-LIF and the CRM, respectively.

### 3.1.2 LSCE-CRM and UL-FAGE OH reactivity measurements at two different locations inside the canopy

From the 13th to 15th midday of July (1st period) and from the 17th midday to 18th midday (2nd period), the two instruments were sampling at the same height but from different horizontal locations within the canopy (with sequential within/above canopy measurements for CRM during the second period). The horizontal distance between the two inlets was

around 10 m as shown in Fig. 1. Similar trends in OH reactivity are seen between the two datasets, even if the first period was associated with a clear vertical stratification (Fig. 4, green frame), leading to higher concentrations of monoterpenes within the canopy, whereas the second period was characterized by a higher vertical mixing (mean  $u^* \approx 0.3 \text{ m s}^{-1}$ ), leading to similar concentrations of monoterpenes at the two heights (Fig. 4, dashed green-yellow frame). These observations are linked to the vertical turbulence which influences BVOC levels inside and above the canopy, resulting in a more or less important vertical stratification, as discussed in section 3.2.

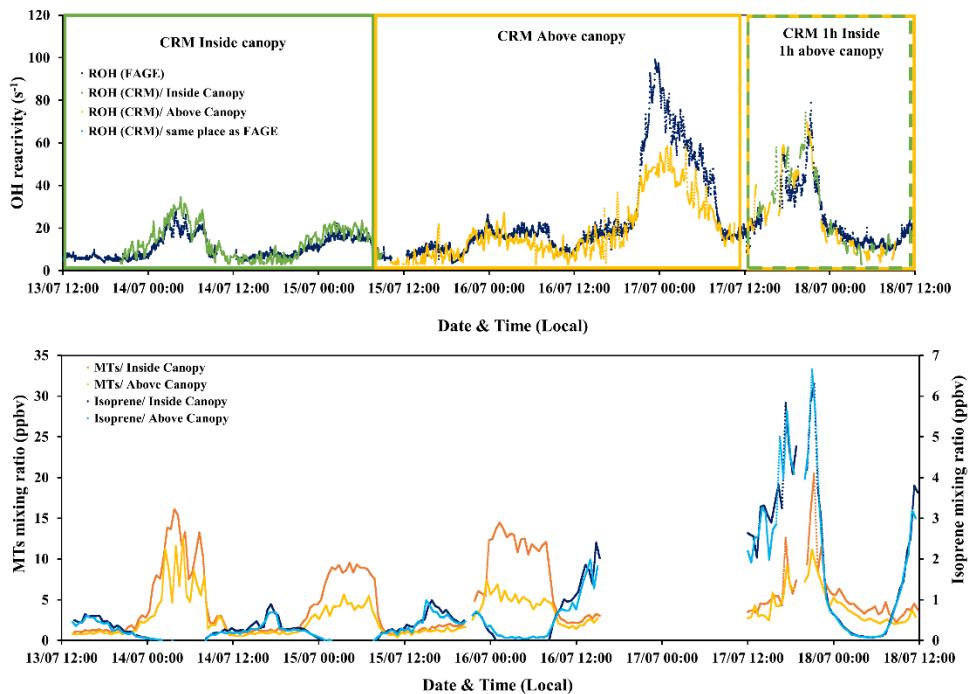
At the same height but different horizontal locations, the linear regression of LSCE- CRM data plotted against UL-FAGE data (not shown) indicates a good agreement with a slope of  $1.26 \pm 0.01$ , an intercept of  $-1.17 \pm 0.17$  and a correlation coefficient of 0.87 (1st and 2nd period). Compared to the results at the same location (vertical and horizontal), the slope and the correlation coefficient are in the same range. Only the intercept differs significantly ( $-1.17 \pm 0.17$  compared to  $4.22 \pm 0.41$ ). This change could be related to air mass inhomogeneities which could be systematically less reactive at one location compared to the other one. From these observations, we can conclude that reactivity measurements performed at different horizontal locations are consistent and that inhomogeneities in ambient air can lead to differences on the order of several  $\text{s}^{-1}$ .

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**Figure 4.** (a) Time series of total OH reactivity measured by UL-FAGE and LSCE-CRM instruments from the 13th to 18<sup>th</sup> of July 2017 (upper graph). Dark blue symbols represent the measured reactivity by UL-FAGE, green, yellow and blue symbols represent the measured reactivity by LSCE-CRM inside canopy, above canopy and inside canopy at the same location as the UL-FAGE instrument, respectively. The lower graph (b) shows the sum of monoterpenes (MTs) and isoprene measured with the PTR-MS, in the field for the same period. Dark blue and light blue dots correspond to isoprene concentrations at 6 and 12 m height, respectively. Orange and yellow dots represent monoterpenes concentrations at 6 and 12 m height, respectively.

### 3.2 Measured OH reactivity and meteorological parameters

Figures 5(a) and 5(b) show the variability of total OH reactivity measured inside and above the canopy by LSCE-CRM and UL-FAGE, together with global radiation, temperature and friction velocity. Considering the whole campaign, the measured OH reactivity at both heights shows a diurnal trend ranging between LOD ( $3\text{ s}^{-1}$ ) and  $99\text{ s}^{-1}$  inside canopy and between LOD and  $70\text{ s}^{-1}$  above canopy, with maximum values of OH reactivity mostly recorded during nights. These OH reactivity levels are larger than other measurements performed in forested environments (Yang et al., 2016, Dusander and Stevens, 2017), with maximum values of approximately  $80\text{ s}^{-1}$  reported for the tropical forest (Edwards et al., 2013).

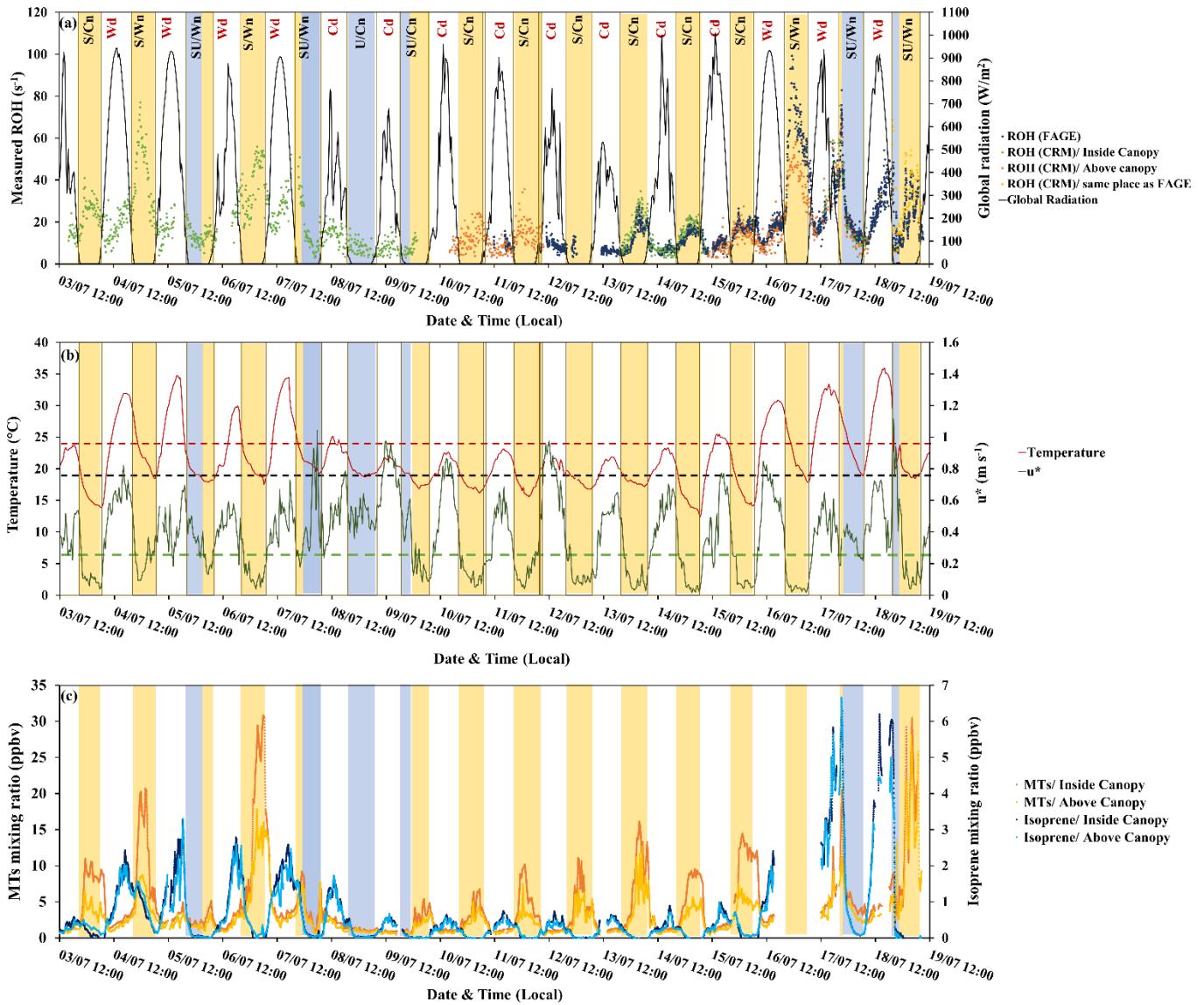
The predominant meteorological parameter that had a role on OH reactivity levels was the friction velocity. It traduces the vertical turbulence intensity that was high during the day (mean day-time  $u^* \geq 0.4\text{ m s}^{-1}$ ) and lower during most nights (mean night-time  $u^* \leq 0.2\text{ m s}^{-1}$ ). Based on this parameter, night-time OH reactivity (between 21:00 and 06:00 local time of the next day) was separated in 3 classes:

- Class S: Stable atmospheric conditions (mean  $u^* \leq 0.2\text{ m s}^{-1}$ )
- Class U: Unstable atmospheric conditions (mean  $u^* \geq 0.4\text{ m s}^{-1}$ )
- Class SU: Stable and unstable conditions during the same night.

The lower vertical turbulence intensity, observed for “S” nights as well as for some hours of “SU” nights, led to a lower boundary layer (Saraiva and Krusche, 2013) and a significant nocturnal stratification within the canopy, with higher concentrations of primary compounds within the canopy (Fig. 5(c)). These stable atmospheric conditions, together with no photochemical oxidation of BVOCs, resulted in higher total OH reactivity during these nights due to higher BVOCs concentration even though their emissions are lower compared to day-time (Simon et al., 1994).

Another important parameter to consider is ambient temperature, which is known to enhance BVOCs emissions during the day when stomata are open, and which also plays a role for night-time emissions due to permeation, even though stomata are closed in the dark (Simon et al., 1994). Considering temperature, 2 sub-classes can be added to night-time OH reactivity classification: the sub-class “Wn” corresponding to warm nights (nights with mean  $T \geq 18.9\text{ }^{\circ}\text{C}$  which is the mean night-time temperature over the whole campaign) and the sub-class “Cn” that includes cooler nights (nights with mean  $T < 18.9\text{ }^{\circ}\text{C}$ ). Thus, comparing “S/Wn” nights and “S/Cn” nights, it can be seen that, for similar turbulent conditions, the magnitude of the measured OH reactivity was temperature dependent. Indeed, higher OH reactivity values were linked to higher ambient temperatures: nights of the 4<sup>th</sup>-5<sup>th</sup>, 6<sup>th</sup>-7<sup>th</sup> and 16<sup>th</sup>-17<sup>th</sup> of July (S/Wn) were characterized by an average temperature of  $21\text{ }^{\circ}\text{C}$  compared to  $16.6\text{ }^{\circ}\text{C}$  for the nights with lower OH reactivity (S/Cn).

605



**Figure 5.** Variability of measured OH reactivity by LSCE-CRM and UL- FAGE, inside and above the canopy with (a) global radiation (black), (b) temperature (red), friction velocity (green) and with c) monoterpenes and isoprene concentrations. Yellow stripes indicate stable night-time atmospheric conditions (S nights with mean  $u^* \leq 0.2 \text{ m s}^{-1}$ ) and blue stripes indicate unstable night-time conditions (U nights with mean  $u^* \geq 0.4 \text{ m s}^{-1}$ ). Class SU includes nights with stable and unstable atmospheric conditions (blue + yellow stripes). Wn and Wd stand for warm nights and warm days respectively. Cn and Cd stand for cooler nights and cooler days respectively. Red dashes and black dashes indicate the temperature thresholds to distinguish warm and cool days and nights, respectively. Green dashes indicate the friction velocity threshold to distinguish stable and unstable nights.

Regarding the period when measurements were done simultaneously at both heights (15<sup>th</sup> to 18<sup>th</sup> of July, LSCE-CRM above canopy and UL-FAGE within canopy), we can analyze the effect of turbulence on the above-within canopy differences keeping in mind a potential instrumental offset of a few  $s^{-1}$  between the two methods (sect. 3.1). For the night of the 16<sup>th</sup>-17<sup>th</sup> of July (S/Wn) when the vertical turbulence was relatively low, total OH reactivity measured above the canopy (LSCE-CRM) was lower than the one measured inside the canopy by a mean factor of 1.6 (UL-FAGE reactivity) despite similar general trends. For the night of the 17<sup>th</sup>-18<sup>th</sup> of July (SU/Wn), stable atmospheric conditions started to settle at the beginning 615 of the night (20h30 local time) inducing a similar stratification to that observed on the previous nights. However, this situation did not last the whole night since these stable conditions were disturbed by higher turbulences around 21h00. This led to a decrease in OH reactivity values going to similar levels inside and above the canopy. A similar event occurred 620 during the night of the 18<sup>th</sup>-19<sup>th</sup> of July, where three OH reactivity peaks showed up, not correlated neither with variation of turbulence intensity nor with temperature changes. **However, it is worth noting that during this night, an intense wind, rain 625 and thunders occurred, which could have led to the observed bursts of BVOCs (Nakashima et al., 2013), leading to distinct peaks of BVOCs and total OH reactivity and thus relatively high total OH reactivity compared to other nights from the same class.**

Total OH reactivity also increased during the day, although on a lower extent than during night-time, and reached a day-time maximum of up to  $74.2\text{ s}^{-1}$  inside the canopy and  $69.9\text{ s}^{-1}$  above the canopy, following the same trends than 630 temperature and solar radiation. Temperature appeared to be an important driving factor of total OH reactivity during day-time hours, therefore, day-time OH reactivity was divided into 2 classes: Class “Wd” with warm conditions (mean daytime  $T \geq 24\text{ }^{\circ}\text{C}$ ) and class “Cd” with cooler temperatures (mean day-time  $T < 24\text{ }^{\circ}\text{C}$ ) indicated on Fig. 5. The solar irradiation also played a role on day-time OH reactivity since it is responsible of initiating the emission of some compounds like isoprene, 635 that is light and temperature dependent. Thus with the first rays of sunlight, the emission and the concentration of isoprene increased leading to an increase in total OH reactivity.

Examining BVOC profiles (Fig. 5 (c)), we can see how the variability of primary BVOC concentrations can explain the day/night variability of total OH reactivity. Indeed, monoterpenes, which are the main emitted compounds in this ecosystem, were influenced by vertical turbulence and night-time temperature, exhibiting a diurnal profile with maxima 640 during stable nights and minima during day-time. Under stable atmospheric conditions (class S), monoterpenes concentration started to increase at the beginning of the night (between 20h and 21h local time) corresponding to the time of the day when the turbulence intensity started to drop and the nocturnal boundary layer started to build up. Maximum mixing ratios were reached in the middle of the night, corresponding to a lower dilution in the atmosphere and a lower oxidation rate (low OH concentrations, nitrate radical mixing ratios lower than the LOD (3ppt/min) most of the time, and BVOC’s chemistry with ozone generally slower than during daytime (Fuentes et al., 2002)). Finally, the monoterpenes concentration dropped as soon 645 as the first sunlight radiations broke the stable nocturnal boundary layer inducing lower levels of OH reactivity. Under these

conditions, the concentration of monoterpenes inside the canopy was higher than above the canopy, showing a clear stratification, consistent with differences seen on total OH reactivity at the different heights. On the contrary, during turbulent night hours (Class U and SU), the concentration of monoterpenes was lower inside the canopy and similar to that observed above, leading to lower and closer night-time OH reactivity at both measurements heights.

650 At the end, even though BVOC emissions are more intense during the day (Simon et al., 1994), the higher turbulence observed compared to night-time led to a faster mixing within the canopy and thus similar levels of isoprene and monoterpenes inside and above the canopy. These day-time levels were lower than those observed at night for monoterpenes and higher for isoprene, the latter being light and temperature dependent.

655 To conclude, these observations show that on one hand, lower turbulence inducing stable atmospheric conditions during the night explains the observed stratification in terms of monoterpenes levels and thus in terms of OH reactivity levels within the canopy, when on the other hand, higher turbulence during day-time leads to higher mixing within the canopy and a vertical homogeneity, with similar BVOCs concentrations and OH reactivity levels at both heights. **Diurnal average values of total OH reactivity, for inside and above canopy measurements are given in Table S9.**

### 660 3.3 Measured and calculated ROH within and above the canopy

Figure 6 shows that there is a good co-variation of the measured total OH reactivity by the CRM instrument with the values calculated from the PTR-MS data (22- 24 % (2 $\sigma$ )). However, a certain fraction of the measured total OH reactivity remains unexplained by the considered compounds (Table 3). Diurnal variations of OH reactivity were observed within the canopy, during the major part of the campaign, with maximum values recorded during most nights and averages of  $19.2 \pm 12.8 \text{ s}^{-1}$  and  $19.3 \pm 16.3 \text{ s}^{-1}$  measured by the LSCE-CRM and UL-FAGE instruments, respectively. This diurnal cycle was also observed above canopy where the average total OH reactivity was  $16.5 \pm 12.3 \text{ s}^{-1}$ , which is higher than observations made in other temperate coniferous forests (Ramasamy et al., 2016) where the reported OH reactivity ranges from  $4-13 \text{ s}^{-1}$  (campaign average).

670 During the first part of the campaign (3<sup>rd</sup> – 10<sup>th</sup> of July), when the LSCE-CRM was measuring alone inside the canopy, total OH reactivity varied between LOD ( $3 \text{ s}^{-1}$  at  $3\sigma$ ) and  $76.9 \text{ s}^{-1}$ , while the calculated reactivity ranged between  $1.4 \text{ s}^{-1}$  and  $60 \text{ s}^{-1}$ . During the second period (13<sup>th</sup> – 15<sup>th</sup> and 17<sup>th</sup> – 18<sup>th</sup> of July), similar maxima were recorded by the LSCE-CRM ( $74.2 \text{ s}^{-1}$ ) and the UL-FAGE instruments ( $78.9 \text{ s}^{-1}$ ), when both were measuring at two different locations within the canopy. Regarding the calculated OH reactivity, it varied between  $2.6 \text{ s}^{-1}$  and  $59.3 \text{ s}^{-1}$ . During this same period, the FAGE instrument measured alone within the canopy from the 15<sup>th</sup> to the 17<sup>th</sup> of July and recorded total OH reactivity values ranging between  $3.6 \text{ s}^{-1}$  and  $99.2 \text{ s}^{-1}$ , however the PTR-MS data were not taken into account for the period going from the 16<sup>th</sup> 15:00 to the 17<sup>th</sup> 12:00 due to an electrical failure. Finally, during the last two days (18<sup>th</sup>- 19<sup>th</sup> of July), total OH reactivity showed a particular behavior as mentioned in section 3.2. It started to increase in the afternoon, reached a maximum at the beginning of the night

that was suddenly broken by turbulences and showed three peaks during the night corresponding to more stable conditions observed for both the measured and calculated reactivity.

680 Regarding above canopy measurements, the measured OH reactivity varied between LOD and  $35.7 \text{ s}^{-1}$  between the 10<sup>th</sup> and the 12<sup>th</sup> of July, whereas the calculated reactivity varied between 1.2 and  $14.5 \text{ s}^{-1}$ . A similar trend was observed for the second period of measurements performed above the canopy (15<sup>th</sup> - 18<sup>th</sup> of July) during which higher OH reactivity was recorded with a maximum of  $69.9 \text{ s}^{-1}$ , which is 1.7 times higher than the calculated OH reactivity ( $40.8 \text{ s}^{-1}$ ).

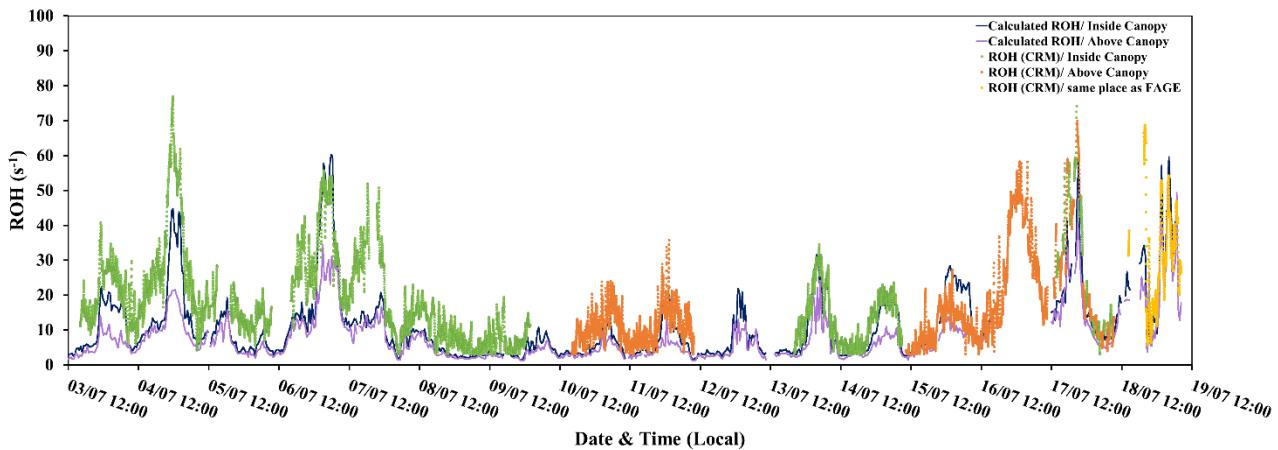


Figure 6. Variability of measured ROH (LSCE-CRM) and calculated ROH (PTR-MS) at 6 and 12 m height.

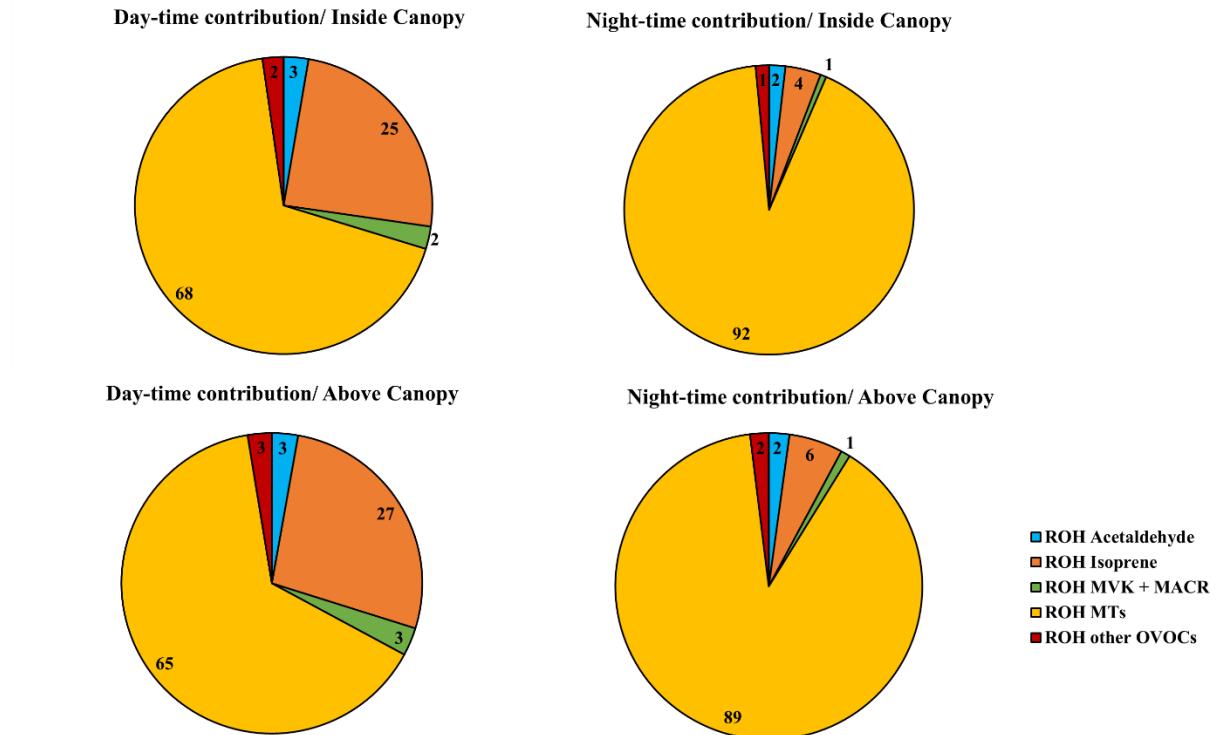
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### 3.4. Contribution of VOCs (PTR-MS) to calculated OH reactivity within and above the canopy

Figure 7 shows the breakdown of trace gases to the calculated OH reactivity during day-time and night-time at the two heights, taking into account the whole measurement period (campaign average). We note that primary BVOCs (monoterpenes, isoprene) are by far the main contributors to the calculated OH reactivity, representing 92- 96 % of the 690 calculated OH reactivity on average.

Monoterpenes exhibited the most prominent contribution to the calculated OH reactivity. These species had a similar contribution within and above the canopy, but significant differences between day-time (68- 65 %) and night-time (92- 89 %). Next to monoterpenes, isoprene had a maximum contribution during day-time and represented on average 25- 27 % of the calculated OH reactivity, followed by acetaldehyde (3 %) and MACR + MVK (2- 3 %) at both measurements heights. 695 However, during night-time, isoprene accounted for only 4 -6 % of the OH reactivity measured within and above the canopy, acetaldehyde contributing for approximately 2 % and MACR + MVK around 1 %.

Thus, we can conclude that no substantial difference in the atmospheric chemical composition existed between the two sampling heights, even when we only consider stable nights (monoterpenes relative contribution is around 92 % inside and above the canopy).



**Figure 7.** The components of calculated OH reactivity within and above the canopy during day -time and night-time.

### 3.5 Description and investigation of potential missing OH reactivity during the LANDEX campaign

710 The missing OH reactivity was calculated as a difference between the total OH reactivity measured by LSCE-CRM, since it was operated over the whole campaign and at both heights, and the OH reactivity calculated from PTR-MS data. It is worth noting that a scatter plot of the LSCE-CRM and UL-FAGE data led to a slope of 1.2 and an intercept of  $4.2 \text{ s}^{-1}$  (section

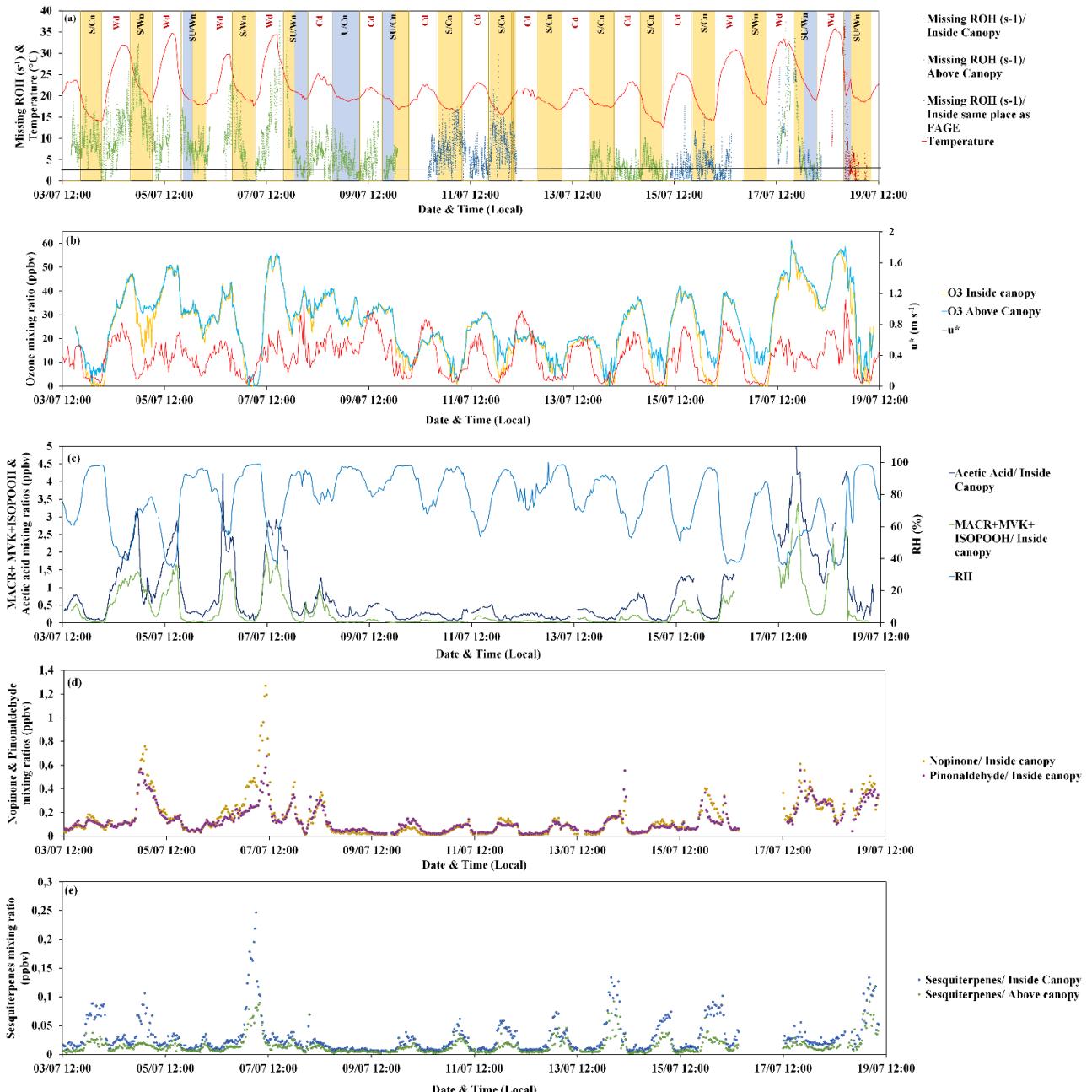
3.1.1), indicating higher OH reactivity values measured by the CRM instrument. The intercept is mainly attributed to a zeroing issue on UL-FA GE but we cannot completely rule out a bias on the CRM measurements. Considering OH reactivity  
715 values measured by the CRM instrument may therefore maximize the missing OH reactivity if the discrepancy observed between the two instruments is due to a bias in the CRM data. In the following, the analysis on the missing OH reactivity was performed when it was higher than both the LOD of  $3 \text{ s}^{-1}$  ( $3\sigma$ ) and 35% of the measured OH reactivity (uncertainty on the CRM measurements, see section 2.2).

Figure 8 shows a) the variability of the missing OH reactivity within and above the canopy, together with ambient  
720 temperature, b) friction velocity (red), and ozone mixing ratios within (yellow) and above (blue) the canopy. The ozone variability is discussed below as ozone chemistry can dominate night-time chemistry of BVOCs observed at this site ( $\alpha$ -pinene,  $\beta$ -pinene) (Fuentes et al., 2002; Kammer et al., 2018).

The concentration of OH was  $4.2 \times 10^6 \text{ molecules cm}^{-3}$  on average during day-time with a maximum of  $4.3 \times 10^7 \text{ molecules cm}^{-3}$  and around  $1.5 \times 10^6 \text{ molecules cm}^{-3}$  on average during night-time (data available between the 13<sup>th</sup> and the 19<sup>th</sup>, July).  
725 However, a potential artefact on OH radical's measurements leading to a possible overestimation of OH radical's concentrations, could not be ruled out. Regarding ozone, its mixing ratio showed a diurnal cycle with maximum values during the day (max  $\approx 60 \text{ ppbv}$ , mean  $\approx 29 \text{ ppbv}$ ), that were similar within and above the canopy due to efficient mixing, and lower levels during nights, with an average of 18 ppbv inside canopy, while levels higher by 1 - 10 ppbv on average, above the canopy. Considering OH and O<sub>3</sub> average mixing ratios, the  $\alpha$ -pinene lifetime was estimated to be 1.2 hours and 4 hours,  
730 respectively, during the day, and 3.6 hours and 5.8 hours, respectively, during the night. At maximum OH and O<sub>3</sub> mixing ratios during day-time, the  $\alpha$ -pinene lifetime was reduced to 7.4 min and 2 hours, respectively. Thus, OH chemistry remained dominant compared to ozonolysis of main emitted compounds on this site (i.e.  $\alpha$ -pinene). An article on the reactivity of monoterpenes with OH, ozone and nitrate for this campaign is in preparation (Mermet et al., in preparation).

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**Figure 8.** Missing OH reactivity inside and above the canopy together with (a) temperature, (b) friction velocity (red), ozone mixing ratios inside (yellow) and above (blue) the canopy, (c) relative humidity (clear blue), MACR+MVK+ ISOOPOOH (dark blue) and acetic acid (green) inside the canopy, (d) Nopinone (yellow) and pinonaldehyde (purple) inside the canopy and (e) sesquiterpenes inside (blue) and above (green) the canopy.

When comparing measurements of OH reactivity with calculations based on PTR-MS data (see Table 3), an average of 38% (7.2  $\text{s}^{-1}$ ) and 48% (6.1  $\text{s}^{-1}$ ), remained unexplained inside and above the canopy, respectively.

750 Considering other measurements performed inside the canopy (6 m) and not included in the OH reactivity calculations, such as NO, NO<sub>2</sub>, ozone and butanol (leakage from SMPS), and assuming constant concentrations of CO (150 ppbv) and methane (2000 ppbv), their contribution can reach 3.0  $\text{s}^{-1}$  on average (maximum around 7  $\text{s}^{-1}$ ) at this level. This said, the mean missing OH reactivity was finally around 4.2  $\text{s}^{-1}$  (22%) inside canopy for the whole measurement period.

Regarding other measurements performed above canopy, online chromatographic instruments (Table 3) provided 755 information on other oxygenated VOCs (7 compounds) and non-methane hydrocarbons (36 compounds). These compounds could explain 0.48  $\text{s}^{-1}$  on average (0.43  $\text{s}^{-1}$  from NMHC and 0.05  $\text{s}^{-1}$  from OVOC measured by GC) of the missing OH reactivity between the 10th and the 12th of July. However, after the 14th of July, the GC measuring OVOC stopped working, but NMHCs alone could account for 0.5  $\text{s}^{-1}$  of missing OH reactivity on average. While O<sub>3</sub> was measured at 12 m, no NO<sub>x</sub> measurement were performed at this height, however, their contribution at the 6 m height was 0.3  $\text{s}^{-1}$  on average, suggesting 760 only a small contribution to the missing OH reactivity. Methane and CO were also considered, assuming the same mixing ratios as inside. Finally, looking at butanol measured by the PTR-MS at the 12 m height, a maximum mean contribution of 0.3  $\text{s}^{-1}$  was assessed for the nights of 10th-11th of July. Hence, considering OVOCs, NMHC, O<sub>3</sub>, CO, CH<sub>4</sub> and butanol, the mean missing OH reactivity above the canopy level was around 4.3  $\text{s}^{-1}$  (33%). However, this missing fraction exhibited a diurnal variability at both heights, that is worth discussing in details. A summary of mean missing OH reactivity values at 765 both heights, is presented in Table 4.

**Table 4.** Summary of the measured OH reactivity and the missing OH reactivity inside and above the canopy, during the day and the night, taking into account only PTR-MS data or all the data available at each height for OH reactivity calculations. These averages are calculated for the periods when CRM, PTR-MS and others instruments data are available.

	Mean Measured OH reactivity ( $\text{s}^{-1}$ )	Mean missing OH reactivity with PTRQi-ToFMS ( $\text{s}^{-1}$ )	Missing ROH considering PTRQi-ToFMS data + other measurements ( $\text{s}^{-1}$ )
<b>Inside</b>	19.1	7.2	4.2
Day	16.8	7.3	4.7
Night	22.0	7.1	3.6
Stable cool nights	20.5	5.5	< LOD
Stable warm nights	41.6	10.7	6.7
Unstable cool nights	7.9	4.5	< LOD
Unstable warm nights	13.5	6.8	3.6
<b>Above</b>	12.8	6.1	4.3
Day	10.7	5.1	3.3
Night	15.5	7.5	5.6
Stable cool nights	14.8	7.5	5.7
Stable warm nights	---	---	---
Unstable cool nights	---	---	---
Unstable warm nights	20.5	7.1	5.2

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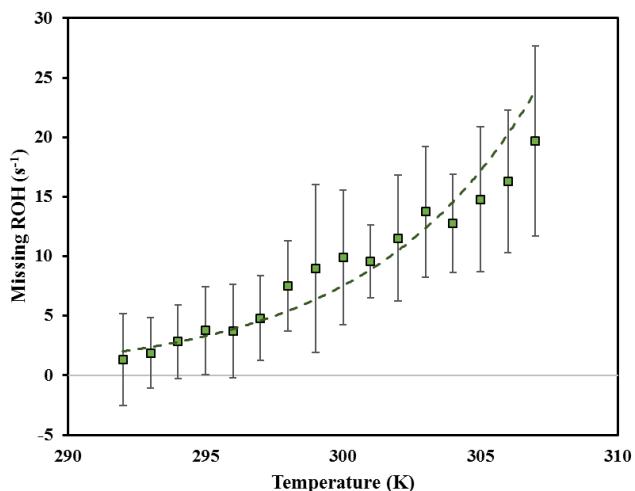
- Day-time missing OH reactivity

Analyzing the behavior of missing OH reactivity during day-time for inside canopy measurements, Fig. 9 shows that it increases exponentially with temperature. Indeed, the average missing OH reactivity was around  $7.5 \text{ s}^{-1}$  for “Wd” days, after taking into account other available measurements at this height (NO, NO<sub>2</sub>, O<sub>3</sub>, butanol and estimated CO and CH<sub>4</sub>), whereas no missing reactivity was seen for cooler days (< LOD). As reported in Di Carlo et al. (2004), the missing OH reactivity was fitted with an equation usually used to describe temperature-dependent emissions of monoterpenes (Guenther et al., 1993):  $E(T) = E(293) \exp(\beta(T-293))$ , where  $E(T)$  and  $E(293)$  represent the emission rate at a given temperature  $T$  and at 293K, respectively. In this equation,  $E(T)$  was substituted to MROH( $T$ ) and  $E(293)$  by MROH (293) with MROH representing the missing OH reactivity (Hansen et al., 2014). The value of  $\beta$  determined from the fit of the data for the 6 m height (day-time), is around 0.17, higher than the values attributed to monoterpenes emissions from vegetation (0.057 to 0.144 K<sup>-1</sup>). Higher  $\beta$ -values were also obtained by Mao et al. (2012), Hansen et al. (2014) and Kaiser et al. (2016), where they suggested that day-time missing reactivity is mostly linked to secondary oxidation products. However, the use of  $\beta$  factor must be made with caution, as the missing OH reactivity can be influenced by processes that do not affect BVOCs emissions (i.e. the boundary layer height and the vertical mixing). Furthermore, we cannot exclude the possibility of light and temperature dependent emissions. Indeed, Kaiser et al. (2016) also investigated the temperature dependency of day-time missing OH reactivity in an isoprene-dominated forest, reporting that part of the missing emissions could be characterized by a light and temperature dependence, knowing that temperature increases with increasing solar radiation. Regarding above canopy, most measurements were performed during cool days. Thus, it was not possible to analyze the temperature dependence of above canopy day-time missing OH reactivity.

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**Figure 9.** Day-time missing OH reactivity binned by ambient temperature for the 6 m height for temperatures ranging from 292 and 308 K. Error bars represent the standard deviation on missing OH reactivity calculated for each temperature bin.

805 Another way to investigate the origin of missing OH reactivity is by examining its covariability with compounds such as acetic acid as well as MACR+MVK+ISOPPOOH, knowing that MACR and MVK are oxidation products of isoprene. First, for higher day-time missing OH reactivity observed for Wd days (within and above the canopy), Figure 8(c) shows that the missing reactivity increases with acetic acid (mixing ratio up to 5 ppbv). Acetic acid can be directly emitted by the trees and the soil (Kesselmeier and Staudt, 1999) and could also be an oxidation product of BVOCs, including isoprene (Paulot et al.,  
810 2011). **This compound showed a diurnal cycle similar to that of isoprene (Fig. 5(c)), and was not used to calculate the OH reactivity.** Despite its relatively low reactivity with OH, this compound showed a maximum calculated OH reactivity during Wd days that was, on average ( $0.07\text{ s}^{-1}$ ), 4 times higher than that of Cd days. Thus it could explain, with other compounds exhibiting a similar temporal behavior, part of the missing OH reactivity seen during warm days. MACR+ MVK + ISOPPOOH showed a general trend with higher values during the day and lower values during the night, suggesting that  
815 oxidation products of isoprene could be responsible of the day-time missing OH reactivity. These levels were generally higher for Wd days than for Cd reflecting a higher yield of secondary products and a more intense photochemistry during warm days.

#### - Night-time missing OH reactivity

820 On average the highest night-time missing OH reactivity inside canopy ( $13.1\text{ s}^{-1}$ ) was observed on the stable/ warm night of the 4<sup>th</sup>- 5<sup>th</sup>, July. Whereas, during stable/cool and unstable/warm nights, no significant missing OH reactivity was found ( $\leq\text{ LOD}$ ). Interestingly, the stable/warm night of the 6<sup>th</sup>-7<sup>th</sup>, July, did not show a significant missing OH reactivity, meaning that the missing fraction inside canopy during night, was not only influenced by meteorological parameters, even if, as shown before, BVOCs concentrations and total OH reactivity were. So what was the difference between these two nights  
825 with similar meteorological conditions?

Checking monoterpenes' oxidation products variabilities (nopinone and pinonaldehyde), both nights exhibited higher concentration levels of these species, however their contribution to OH reactivity remained relatively low, and did not exceed  $1\text{ s}^{-1}$ , on average for both nights, keeping in mind that this is a lower limit of their contribution (since the reported measurements do not account for potential fragmentation in the PTR-MS). Thus, only a small fraction of the missing fraction  
830 can be explained by these species. Interestingly, isoprene, acetic acid and MVK+ MACR+ISOPPOOH exhibited higher concentration levels during the night of the 4<sup>th</sup>- 5<sup>th</sup>, July, which was not the case for the 6<sup>th</sup>-7<sup>th</sup>, July night. Indeed, these species marked relatively high nocturnal/ inside canopy levels. When looking at air masses backward trajectories (Fig. 10), the 4<sup>th</sup>-5<sup>th</sup> night was characterized by an air mass originally coming from the ocean, which spent at least 48 hours above the continent before reaching the site. This could have led to the enrichment of the air mass with species emitted by the widely  
835 spread Landes forests and their oxidation products. Thus, the significant missing OH reactivity observed during the mentioned night is likely related to unconsidered compounds of biogenic origin characterized by a similar behavior to that of

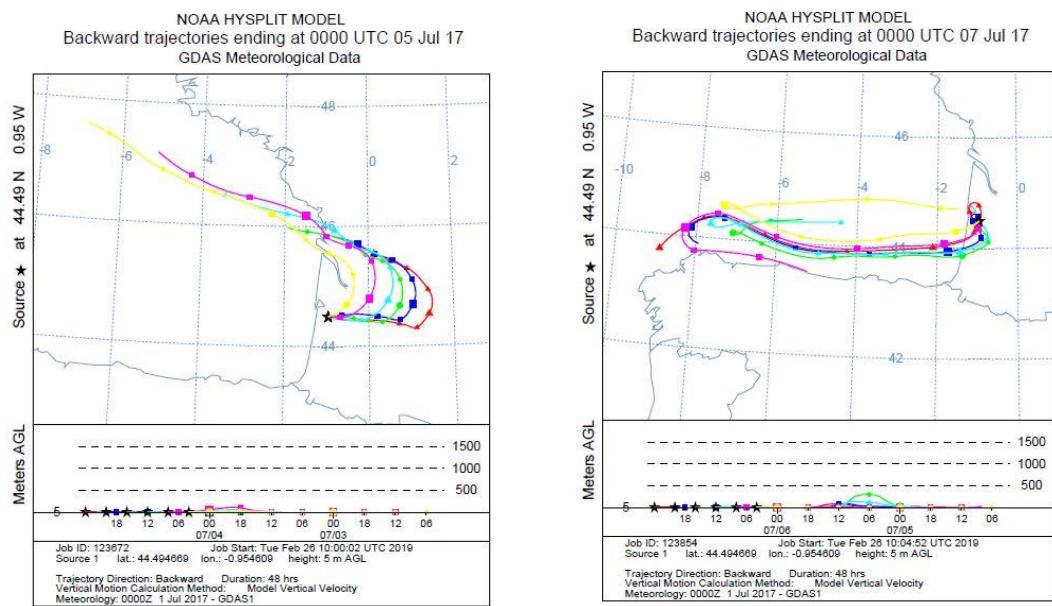
isoprene, acetic acid and MVK+MACR+ISOPOOH, which accumulated in the stable nocturnal boundary layer. In contrast, air masses spent approximately 12-18 hours above the continent during the 6<sup>th</sup>-7<sup>th</sup> of July, with more time above the ocean. Marine air masses are generally known to be clean, with relatively low levels of reactive species. Even though, the night of the 5<sup>th</sup>-6<sup>th</sup>, July shows similar air mass backward trajectories to the night of the 4<sup>th</sup>-5<sup>th</sup>, the higher turbulence during this night prevents the accumulation of reactive species (including long-lived oxidation products) due to a higher boundary layer height, lowering the reactivity and the missing OH reactivity (Fig. 10).

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**Figure 10.** Air masses backward trajectories for the 4<sup>th</sup>-5<sup>th</sup> and the 6<sup>th</sup>- 7<sup>th</sup>, July nights. Red lines represent air masses arriving around mid-night UTC (around 02:00 local time), to the site. The time difference between 2 points is 6 hours.

Regarding above canopy measurements (10<sup>th</sup>- 12<sup>th</sup> and 15<sup>th</sup>- 18<sup>th</sup>, July), the night-time average missing OH reactivity was 5.6 s<sup>-1</sup> (all the nights were characterized by stable/ cool atmospheric conditions). Monoterpenes oxidation products had similar concentration levels above and inside canopy. Their maximum contribution was around 0.4 s<sup>-1</sup> on average for the SU/W night of the 17<sup>th</sup>-18<sup>th</sup>, July. Therefore, these monoterpenes night-time oxidation products are only responsible for a small fraction of the missing OH reactivity observed above canopy during the night. Sesquiterpenes (SQT) exhibited a similar temporal trend than monoterpenes, showing higher mixing ratios during night-time. Interestingly, sesquiterpenes mixing ratios were higher inside the canopy compared to above and the difference was significant during stable nights. O<sub>3</sub> mixing ratios during these nights decreased to very low levels. Plotting the ratio SQT(above)/MTs(above) with the ratio

SQT(inside)/MTs(inside) shows a good linear correlation with a slope of 0.73 and an  $R^2$  of 0.6. Knowing that sesquiterpenes are highly reactive with ozone (Ciccioli et al., 1999), which can dominate the chemistry during dark hours, this observation suggests that a larger fraction of these species ( $\approx 30\%$ ) could be consumed by ozonolysis above canopy, leading to the formation of unidentified secondary compounds. However, sesquiterpenes were present at relatively low concentrations (max of 0.25 ppbv and 0.11 ppbv, inside and above canopy, respectively). Assuming that all sesquiterpenes are  $\beta$ -caryophyllene and considering that 30% are transformed into first generation oxidation products through ozonolysis reactions, the maximum mixing ratio of these products would be around 0.07 ppbv each assuming a yield of 1. However, it was reported by Winterhalter et al. (2009) that oxidation products of  $\beta$ -caryophyllene were much less reactive (100 times) than their precursor. Thus, the contribution of sesquiterpenes night-time oxidation products to the missing OH reactivity is likely negligible.

Finally, it is worth noting that Holzinger et al. (2005) reported the emission of highly reactive BVOCs in a coniferous forest, which is 6-30 times the emission of monoterpenes in the studied Ponderosa pine forest. This large fraction of BVOCs is subject to oxidation by ozone and OH leading to unidentified, non-accounted for secondary molecules. These oxidation products can participate to the growth of new particles. Indeed, new particle formation episodes were recently reported on this site (Kammer et al., 2018).

To summarize, higher day-time missing OH reactivity was observed for warm days (Wd), inside and above the canopy, exhibiting a dependency on temperature profiles and showing that trace gases leading to the missing OH reactivity could be linked to an enhancement of primary species as well as secondary products formation. Regarding night-time missing OH reactivity, higher levels were seen for the stable and warm night of the 4<sup>th</sup>-5<sup>th</sup>, July, showing that these conditions could have been favorable for the accumulation of long-lived species (primary and secondary species) during the transport of the air mass from nearby forests.

#### 4 Conclusion

During summer 2017, total OH reactivity measurements were conducted as part of the LANDEX field campaign, in the Landes maritime pine forest (France). During this campaign, two instruments (LSCE-CRM and UL-FAGE) were deployed to measure total OH reactivity inside and above the canopy as well as at two different locations inside the canopy level. The comparison between both instruments, based on measurements done at the same location at the end of the campaign, showed a good agreement (slope of 1.17 on a linear correlation plot). However, an offset of  $4.2 \text{ s}^{-1}$  was obtained, which is potentially linked to an overestimation of the instrumental zero for the UL-FAGE instrument. Measuring at two different locations demonstrated a good horizontal homogeneity inside the canopy, even during episodes of vertical stratification that was observed during some nights.

Total OH reactivity recorded an average of  $19.2 \text{ s}^{-1}$  at 6 m height, 1.2 times higher than that observed above the canopy level at 12 m height. It varied similarly at both heights, following a diurnal cycle with two maxima, one during day -time following

isoprene's profile and a higher one during night-time when monoterpenes concentrations reached their maxima. The later were the main emitted compounds in this forest ecosystem.

905 The variability of BVOC concentrations and OH reactivity were strongly dependant on meteorological parameters. Day -time OH reactivity was linked to ambient temperatures and light, two parameters governing the emissions of temperature and/ or light dependent compounds (like isoprene), whereas night-time OH reactivity was influenced by night-time temperatures and vertical turbulence intensity. Indeed, low turbulence, high temperature and lower oxidation rates than during day-time, led to higher concentrations of monoterpenes and thus higher OH reactivity during stable and warm nights. In addition, higher 910 differences in BVOCs levels and total OH reactivity were observed between the two studied heights particularly during stable nights.

Furthermore, monoterpenes showed to be the main contributors to total OH reactivity during both day -time and night-time. These species accounted for more than 60% of the OH reactivity during day-time, followed by isoprene (25- 27 %), acetaldehyde (3%) and MAC+ MVK (2- 3%). However, the contributions of isoprene and OVOCs were much lower at both 915 levels during the night, leading to a higher contribution of monoterpenes, which was slightly more important inside the canopy level due to the stratified conditions.

An investigation of the missing OH reactivity indicated averages of 22 % and 33 %, inside and above the canopy, respectively, over the whole campaign, when comparing the measured OH reactivity to the calculated one from PTR-MS and other available measurements. However, it showed some diurnal variability at both heights. During day -time, higher missing 920 OH reactivity was observed on warmer days inside and above the canopy. Plotted against temperature, inside canopy missing OH reactivity showed a dependency on temperature. The analysis suggested that the missing OH reactivity may be due to unmeasured primary emitted compounds and oxidation products. In this context, OH reactivity measurements from a *Pinus pinaster* Aiton branch enclosure, could be of great interest to verify the contribution of unaccounted/unmeasured BVOCs emissions to OH reactivity as done by Kim et al. (2011), for red oak and white pine branch enclosures. Furthermore, 925 higher levels of isoprene oxidation products on warmer days also suggest that the missing reactivity could be due to the formation of unmeasured oxidation products. Regarding the night-time period, the highest missing OH reactivity was found inside canopy for the 4<sup>th</sup>-5<sup>th</sup>, July night. This night was characterized by higher levels of isoprene and its oxidation products, compared to the night of the 6<sup>th</sup>-7<sup>th</sup>, July with similar atmospheric conditions. Air masses backward trajectories showed a continental origin for this night, suggesting that species, emitted by the largely spread Landes forest, could have been 930 imported to the site and accumulated due to the stable nocturnal boundary layer. These species, unmeasured by the deployed analytical instruments and hence not considered in OH reactivity calculations, could explain the higher missing OH fraction for the 4<sup>th</sup>-5<sup>th</sup>, July night. The investigation of sesquiterpenes and monoterpenes oxidation products (nopinone and pinonaldehyde) measured by PTR-MS highlighted their small contribution in terms of OH reactivity. They only explained a small fraction of the observed missing OH reactivity inside and above canopy during night. Finally, seen the time needed 935 and the data required, no modeling study was performed, however, it would be interesting to run a box model in order to get more insights into the origin of the missing OH reactivity.

### Authors contribution:

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S. Bsaibes and F. Truong set up and carried out OH reactivity measurements with the LSCE-CRM. M. Al Ajami, C. Schoemaecker, S. Batut and C. Hecquet set up and carried out OH reactivity measurements with the UL-FAGE instrument. K. Mermet, T. Léornadis, S. Sauvage and N. Locoge carried out GC-BVOC2, GC-OVOCs and GC-NMHCs measurements and provided analyzed data. V. Gros provided GC-BVOC1 analyzed data. S. Dusanter carried out PTR-MS measurements and provided the corresponding data. J. Kammer and P.-M. Flaud provided NOx data and meteorological parameters. E. Villenave, E. Perraudin and P.-M. Flaud have coordinated the LANDEX project and field campaign. S. Bsaibes prepared the manuscript with the co-authors contribution, mainly M. Al Ajami, C. Schoemaecker, D. Dusanter, and V. Gros.

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