

Interactive comment on “Variability of OH reactivity in the Landes maritime Pine forest: Results from the LANDEX campaign 2017” by Sandy Bsaibes et al.

Sandy Bsaibes et al.

sandy.bsaibes@gmail.com

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We thank referee (3) for the valuable comments.

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

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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⁻¹ (page 12, lines 363- 364, new version of the paper). For OH reactivity measurements, samples were collected through 1/8"-OD sulfinert lines, heated up to 50°C with a sampling flow rate of 1- 1.2 L min⁻¹ (page 7, lines 199- 205). As mentioned in the answer on 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 HO₂, 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 4x10¹³ to 3.7x10¹⁴ cm⁻³, corresponding to OH reactivity from 10 to 90 s⁻¹) are injected in the photolysis cell. In absence of NO, HO₂ is not recycled in OH and does not interfere with the OH

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measurement.

This is clarified in 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 4×10^{13} to 3.7×10^{14} cm⁻³ in humid zero air are injected in the photolysis cell, allowing to measure reactivities ranging from 10 to 90 s⁻¹ and to determine (using a linear regression: $R^2 = 0.97$) a rate constant of $k_{\text{CO} + \text{OH}} = (2.45 \pm 0.11) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, in good agreement with the reference value of 2.31×10^{-13} cm³ molecule⁻¹ s⁻¹ (Atkinson et al., 2006) at room temperature. Under these conditions (absence of NO), HO₂ 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, NO_x, O₃ and SO₂ 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.

- NO_x 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 (new version), however their contribution to OH reactivity was estimated and discussed in page 28, lines 750-753, together with O₃ calculated OH reactivity and CO estimated OH reactivity. No SO₂ 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 β-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.,

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2013).

6- It is well known that PTR sees higher MT than 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 (new 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. New version, page 17: Figure 2. Time series of total OH reactivity measured by UL-FAGE (dark blue) and LSCE-CRM (light blue) instruments from the 18th to 19th of July 2017, at the same

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location inside canopy. This figure is in the attached file.

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

New version of the legend of figure 4 (b), also in the attached file: ...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 s⁻¹ offset but the text description says otherwise. Please make them consistent! In addition, even without the intercept, there are ~20 % 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 (New 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 ± 0.02 , an intercept of 4.2 ± 0.4 s⁻¹ and a R² of 0.87. This high intercept is statistically significant at 3σ 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 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 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 s⁻¹ is possible for this study leading to an underestimation of the ambient

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OH reactivity by 3 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: New version, page 13, lines 381- 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 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 m/s. 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:

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

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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 new version, page 30, line 830- 31, line 842:

Interestingly, isoprene, acetic acid and MVK+ MACR+ISOPOOH 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+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. Even

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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 (Figure 10).

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-548/acp-2019-548-AC3-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-548>, 2019.

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