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Atmospheric Chemistry and Physics Discussions

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

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We thank referee (2) for the valuable comments.

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.

New version, page 8 (Table in the attached file), lines 237 - 240: Table 2 reports a summary of the corrections resulting from our tests and their impact on measurements. As

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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 s-1 on average. Furthermore, this factor (F) has the largest relative uncertainty, with ±36%, against ±2% for the humidity correction factor.

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 (≈50°C) sulfinert lines were used. Indeed, Kim et al. (2009), showed that losses of b-caryophyllene are negligible in heated lines with temperatures above 20°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 sulfinert 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°C as it was shown that losses of highly reactive molecules (b-caryophyllene) were negligible for temperature above 20°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 sulfinert sampling lines, similar to those used in the CRM sampling system, heated up to 50°C, with a flow rate of, at least, 1 L min-1, ensuring a short residence time of less than 8s. 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°C. All lines were 15-m long and the flow rates were adjusted to 10 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 β-caryophyllene (a sticky sesquiterpene) in a 40-m long Teflon tube (1/4”-OD) flushed at 25 L min-1. 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 β-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-1 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 b-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 NO2 / NO to the OH reactivity.

New 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 NO2 were only measured at the 6 m height. Mean NO mixing ratio was below the LOD for the measurement period and NO2 was around 1.1 ± 0.8 ppb 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 (in attachment). Errors of the measurements were not taken into account in the regression procedure.

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

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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 m s-1, higher to what was observed for stable nights (u*≈ 0.1 m s-1). The measurement period between the 15th and 17th of July corresponds to CRM and UL-FAGE measuring at two different heights.

New 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 (mean u* ≈ 0.3 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.

New version: 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 ± 0.01, an intercept of -0.69 ± 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 ± 0.17 compared to 4.22 ± 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 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.

New version P20, 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.

New 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% (2σ)).

(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 (new 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 s-1 on average and a maximum of 1.2 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 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 new 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 new 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 (≈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 b-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 ppb each assuming a yield of 1. However, it was reported by Winterhalter et al. (2009) that oxidation products of b-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.

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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.

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-548/acp-2019-548-AC2-supplement.pdf

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