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

New 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 O3? Did you apply any O3 correction? Have you detected any effect of O3 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 O3 and no correction was applied to OH reactivity raw data. This information has been added in the revised version of the manuscript as:

New version page 6, lines 176- 179: In some CRM systems, corrections for potential NO2 and/or O3 artefacts are also considered (Michoud et al., 2015, Praplan et al., 2017). On one hand, NO2 is subject to photolysis leading to NO, which can subsequently react with HO2 yielding OH. On the other hand, O3 can also be photolyzed in the reactor, producing O(1D), which reacts further with H2O, yielding two OH radicals.

And page 8, lines 228 -232: NO mixing ratios were lower than 0.5 ppb (corresponding to the detection limit of the NOx 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 HO2+NO reaction. Similarly, for NO2, no correction was applied due to the low ambient mixing ratio of 1.1 $\pm$ 0.8 ppb. Regarding O3, 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-Page7, lines 27-28: Please, be more specific. What was the concentration range of isoprene and a-pinene?

New 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 isoprene+OH = 1x10-10 cm3 molecule-1 s-1, 1- 120 ppb) and α-pinene (k α-pinene+OH = 5.33 x 10-11 cm3 molecule-1 s-1, 3 -190 ppb) (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) O3 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. α-terpinene and β-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 α and β-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-1 for GC instruments and 10 L min-1 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:

New version Page 10, lines 304- 311: Measurements of VOCs (Table 3) were per-

formed at different locations (Figure 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 O3 (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 α- and β-pinene). High flow rates were applied in the sampling lines: 1 L min-1 for GC instruments and 10 L min-1 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 compare 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 thermodegradtion of monoteprenes may also occur as reported by Coeur et al. (1997).

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

New 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 new version of the paper page 11, lines 334- 335: More details about the optimization and the tests performed can be found in Mermet et al. AMTD, 2019.

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:

New 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 s-1) and 48%. (6.0 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 β 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 β of 0.09 was obtained when the missing ROH was fitted in the equation used to describe the temperature dependency of monoterpenes emissions. This β was in the range of β-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 β value was higher (0.17), which indicates that the missing is not only linked to primary emissions but is also due to secondary oxidation products (Mao et al., 2012, Hansen et al. 2014, Kaiser at al.,2016).

New 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(β(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 β 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-1). Higher β-values were also obtained by Mao et al. (2012), Hansen et al. (2014) and Kaiser et al. (2016), were they suggested that day-time missing reactivity is mostly linked to secondary oxidation products. However, the use of β 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 α-pinene lifetime (one of the major compounds) towards OH and O3 were made.

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

The concentration of OH was 4.2×106 molecules cm-3 on average during day-time with a maximum of 4.3×107 molecules cm-3 and around 1.5×106 molecules cm-3 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 ≈ 60 ppbv, mean ≈ 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 ppb on average, above the canopy. Considering OH and O3 average mixing ratios, the α-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 O3 mixing ratios during day-time, the α-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. α-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

New version (Table 1): ROH max (s-1) instead of K' max (s-1).

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.

New version: Page 11, lines 325- 326: It was used to monitor 20 C5-C15 BVOCs, including isoprene, α- and β-pinene, carenes and α-phellandrene at the 6 m height with a time resolution of 90 min.

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 new 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.

- 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. New version, page 30, lines 810- 811: This compound showed a diurnal cycle similar to that of isoprene (Fig 4.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 (O3, NOx) and above the canopy (OVOCs,NMHCs, O3, NOx 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:

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This part of the conclusion was modified:

An investigation of the missing OH reactivity indicated averages of 6.0 and 7.3 s-1 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 α-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 - 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 Léornadis, Pierre-Marie Flaud, Sandy Bsaibes, Julien Kammer, Vincent Michoud, Aline Gratien, Manuela Cirtog, Mohamad Al Ajami, François Truong, Sébastien Batut, Christophe Hecquet, Jean-Francois Doussin, Coralie Schoemaecker, Valérie Gros, , Nadine Locoge and Eric Villenave, in preparation.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-548/acp-2019-548-AC1-supplement.pdf

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