

Interactive comment on “Contributions to OH reactivity from unexplored volatile organic compounds measured by PTR-ToF-MS – A case study in a suburban forest of the Seoul Metropolitan Area during KORUS-AQ 2016” by Dianne Sanchez et al.

Anonymous Referee #3

Received and published: 1 May 2020

This manuscript reports a comparison of OH reactivity measurements performed during the KORUS-AQ 2016 field campaign to OH reactivity values derived from the measurement of trace gases. In this study, the authors observed a large amount of missing OH reactivity, similar to that observed in previous campaigns focusing on areas impacted by biogenic emissions. The authors propose a procedure to assess the contribution of unidentified species detected by a high resolution PTRMS to the missing OH reactivity.

C1

This reviewer thinks that this work is of interest for the scientific community and deserves publication. However, several aspects of this publication need to be straightened, especially the measurement quality of the CIMS-CRM instrument. I therefore recommend publication in ACP after the authors address the following comments:

Major comments:

L183-185: “This included a laboratory-built catalytic converter (Pt-wool at 350 °C) that minimized the interferences due to changes in air to prevent the interference from the difference in humidity for the zero air characterizations.” – Heated Pt-wool will not remove NO_x and may even lead to a higher NO_x concentration at the output of the catalytic converter due to the oxidation of organic nitrate species present in ambient air. This has been reported in Hansen et al. (2015) where the authors used filters made of Purafil and activated charcoal upstream the catalytic converter to remove NO_x. If NO_x is not removed from the VOC-free air provided by the catalytic converter, the CRM measurements will be biased low. How did the authors remove NO_x from the VOC-free air generated by their catalytic converter?

L186-189: “Additionally, interference from the OH recycling reaction of HO₂ with NO in the glass chamber was prevented by removing OH reactivity data points that corresponded with ambient NO levels that exceeded 5 ppb to reflect results from a laboratory characterization study (Sanchez et al., 2018).” – The reviewer checked in Sanchez et al. (2018) but did not find the laboratory characterization mentioned in the above sentence. The authors should provide some information about the tests performed on the UCI CIMS-CRM instrument to characterize OH recycling. It is stated that OH reactivity measurements performed when NO was larger than 5 ppb were discarded. However, OH recycling does not stop below 5 ppb NO and still impacts the OH reactivity measurements. The impact will be instrument dependent and it is important to assess it on the UCI CIMS-CRM. Fuchs et al. (2017) report corrections of 10-20 s⁻¹ at 10 ppb NO for 3 CRM instruments. Assuming that the correction scales with NO on this small range of concentrations, 5 ppb of NO would lead to a correction ranging from 5-10 s⁻¹

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for the instruments used in Fuchs et al., which is significant compared to the range of OH reactivity observed in the present study (20-50 s⁻¹). In addition, NO₂ was observed to generate measurement artifacts on some CRM instruments (Michoud et al., 2015; Fuchs et al. 2017), requiring corrections of 1.6-3 s⁻¹ at a NO₂ mixing ratio of 10 ppb. For the present study, Figure S2 reports mixing ratios ranging from 2-60 ppb for NO₂. Was this issue investigated on the UCI CIMS-CRM?

L189-193: The authors refer the reader to Sanchez et al. (2018) for details on calibration procedures. The reviewer agree with the comments from the first reviewer that additional information on calibration procedures is needed in the present publication. What was the pyrrole-to-OH ratio in the CRM reactor during calibration experiments reported in Sanchez et al. (2018)? Why is there a significant intercept of 3.9 s⁻¹ on the calibration curve (Sanchez et al., 2018)? What was the range of pyrrole-to-OH ratios during the field measurements reported in the present publication? Previous studies have shown that the CRM response can depend on the pyrrole-to-OH ratio (Michoud et al., 2015; Zannoni et al., 2015) and calibrations have to be performed over the range of pyrrole-to-OH ratios observed during field measurements. Can the authors comment on this aspect for the UCI CIMS-CRM?

L236-246: When a molecular formula was determined by PTRwid, how did the authors choose between the different possibilities for isomers? The reviewer checked how the OH rate constant would change between different isomers for C₃H₆O₂ detected at the nominal m/z 75 (methyl acetate 3.5E-13 cm³/molecule/s; propanoic acid 1.2E-12; hydroxyacetone 3E-12; hydroxypropanal 3.5-5.5E-11; and others). The OH rate constant can span 2 orders of magnitude for these isomers. Could the authors comment about the choice made in Table S2 to use a kOH value of 1.2E-12 cm³/molecule/s for this molecular formula? This issue is even worse for ions detected at higher masses since more isomers have to be taken into account. What methodology did the authors used to select the rate constants reported in Table S2?

Minor comments:

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L57-59: “Di Carlo et al. (2004) conducted a study in a mixed forest near Pellston, Michigan where they reported missing OH reactivity larger than observational uncertainty.” – Please be quantitative. How much larger?

L115: The authors reviewed part of the OH reactivity literature for forested areas showing that variable agreements were observed between measured and calculated OH reactivity (from trace gas measurements or constrained O-D modeling), the disagreement being sometime attributed to (i) unknown emissions of VOC, (ii) oxidation products of primary VOC, or (iii) both. The reviewer would have liked to see a short discussion on the current limits in the identification of the missing OH reactivity. How can additional studies help improving our understanding of the missing OH coreactants? This will help motivating the present work.

L149-L151: “The OH reactivity and NO_x analyzers were located in another nearby air-conditioned shack (3 m apart) and sampled air through an extended Teflon inlet line of 4 m ($\frac{1}{4}$ ” OD) from the ground with a flow rate of 4 sLpm resulting in a 0.5 second residence time.” – Please indicate the height of the sampling inlet for the OH reactivity instrument and the NO_x analyzers.

L161-162: The authors indicate a pyrrole+OH rate constant of 1.45E-10 cm³/molecule/s at 298 K. The rate constant recommended by Dillon et al. (2012) and Atkinson et al. (1984) is 1.2E-10 cm³/molecule/s at the same temperature. Why did the authors use a different rate constant?

L212-213: “we determined the VOC sensitivities using equation 1 (Eq 1)” – Equation 1 is not used to derive the VOC sensitivity but to calculate the concentration of uncalibrated species. Please rephrase.

L219: Equation 1 is confusing. Is “ncps(benzene)/ppb” the normalized signal (corrected for mass discrimination) generated by 1 ppb of benzene? What is the factor of 11.94? Please clarify this equation. How was the ion transmission curve characterized on the PTRMS to correct the normalized VOC signals for mass discrimination?

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L247-251: Please indicate the range of R2 factors for the correlations. Also indicate R2 factors in Table S3.

L253-255: “The compounds were grouped into 5 m/z bins and the average kOH of each bin was calculated. The green triangles represent 5 m/z binned averages from these compounds plotted with their respective average kOH.” – The reviewer does not understand what was done here. Please clarify this section. Also provide additional information on what is shown in Figure S2. What is the purpose of the different regression lines?

L371-374: The authors are discussing the potential species detected at m/z 83.085. This mass is not shown in Figure 6 and the authors may want to add it.

L417-420: “As NO_x illustrates a conspicuous temporal variation that appears to correlate with the fraction of missing OH reactivity, while observed OH reactivity and calculated OH reactivity from VOCs indicate a less pronounced diurnal difference. “ - The reviewer does not understand what is meant here. Please clarify/rephrase this sentence.

L428-430: “Moreover, due to the different inlet configurations for OH reactivity and VOC observations, their contributions towards observed and calculated OH reactivity may not have been consistently evaluated.” – This sentence also need to be clarified. Are the authors discussing the impact of the inlet on the measured trace gases and OH reactivity?

Table 1: Please include detection limit and time resolution for each instrument. Brand and model of PTRMS?

Figure 2: How did the authors assess the uncertainty associated to the calculated OH reactivity? What were the sources of errors factored in the calculations? What uncertainty did the authors consider on the OH reactivity from categories I-III?

Figure 3: The authors indicate an uncertainty of 20.1% for the missing OH reactivity?

C5

Since the uncertainty stated for the OH reactivity measurements is 16.7%, a quadratic propagation of errors allows calculating that the authors considered an uncertainty of approximately 11% (1 sigma) on the calculated OH reactivity. This seems a bit low since this uncertainty should account for errors associated to measured trace gases and tabulated reaction rate constants, the latter being already in the range 10-25% at 1 sigma. For the measured trace gases, it is stated that the error on NO_x, which account for a large fraction of the OH reactivity, is 20% at 1 sigma. While the uncertainty associated to PTRMS measurements of calibrated compounds is within 5-10%, the uncertainty on mixing ratios derived from masses where a default proton transfer rate constant of 3E-9 cm³/s was used will not be better than 25% (1 sigma). How was the uncertainty on the calculated OH reactivity derived?

Edits:

L74 : “Alkanes, alkenes and other observed trace gases such as...” should read “alkanes and alkenes and other observed trace gases such as...”

L358: “m/z 101” – Should it read “m/z 101.10”.

L 458: “Further study is required ...” should read “Further studies are required ...”

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