Atmospheric
Chemistry
and Physics

Discussions

Open Access

EGU

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.

Arnaud P. Praplan (Referee)

arnaud.praplan@gmail.com

Received and published: 26 March 2020

General comments:

The manuscript "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 Sanchez et al., present results from OH reactivity measured in spring 2016 in a Research Forest Station of Korean pine located

roughly 35km from the centre of Seoul. This site is influenced by both local biogenic emissions and transported anthropogenic emissions. OH reactivity measurement were operated with a CIMS-CRM instrument and Volatile Organic Compounds (VOCs) were monitored with a high resolution Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS). The authors found in addition to the most commonly monitored VOCs, 346 unidentified peaks that got assigned in three different categories in order to estimated their potential contribution to the observed missing OH reactivity. The missing reactivity is defined as the difference between measured total OH reactivity and the OH reactivity calculated from the known species quantified in the same air masses. While the addition of previously unexplored VOCs to the analysis decreased the amount of missing OH reactivity, still 42.0% of missing reactivity remained. The authors hypothesis is that this might be due to oxidation products from both biogenic and anthropogenic compounds.

I found the manuscript clear and concise. The introduction places this study in context in a comprehensive fashion. The methods and the results are mostly well explained and are sound. I found a few places, where the manuscript could benefit from further clarifications (see specific comments below), in particular explaining some assumptions taken for the calculations of OH reactivity from unidentified PTR-ToF-MS pseaks. Therefore, I would recommend ACP to publish this manuscript after minor corrections have been done.

Specific comments:

- p.3, ll.61-66: Are the authors aware of the more recent publications by Nölscher et al. (2012) and by Praplan et al. (2019) for additional OH reactivity measurements in Hyytiälä? Their findings were similar to the ones of Sinha et al. (2010) in terms of missing reactivity. Nölscher et al. found for instance that the highest missing reactivity values occurred during a period of higher temperature (labelled "stress" period). Praplan et al. also found among other things that including modelled oxidation compounds from the Master Chemical Mechanism only decreased the missing fraction by about

7% at most.

- p.8, ll.180-182: Fuchs et al. (2017) also found that some CRM instrument see an interference with additional O3 introduced from ambient air in the reactor. Has this interference also been investigated in the UCI CIMS-CRM? It would be a good thing to explicitly mention that this effect can be ruled out.

- p.9, ll.189-193: I understand that the detailed calibration procedures are detailed in another publication, but I believe that some additional information regarding the total OH reactivity instruments could be included. For instance there is no indication about what the pyrrole-to-OH ratio is during this campaign (and if it is the same as for the laboratory calibrations). Also from the Supplementary Material in Sanchez et al. (2018), if understand Fig. S1 correctly, the instrument response (without unit, but is it OH reactivity?) is about a quarter of what is expected and this is consistent over a wide spectrum of kOH values. I personally would find value in summarizing this in a couple of sentence in the present manuscript. Consequently, should we understand that the multi-point calibrations performed during the campaign were consistent with the measurements in Sanchez et al. (2018)?

- p.9, ll.202-203: Out of curiosity, is there a reason that the authors did attempt CIMS-CRM calibrations with the PTR-ToF-MS calibration mixture? (possibly before or after the measurement campaign, not necessarily during the campaign, as I understand that the instruments were physically located in two different shacks)

- p.11, ll.236-246: Category I: My main issue here is that, even if I am not familiar with the PTRwid software, I assume that it delivers "calculated molecular formula" (and not chemical structures) as mentioned by the authors. Looking at Table S2 of the Supplementary material I understand that for some of the molecular formula, there is only one sound structure possible. Could the authors discuss the chances that they found only one match in the NIST database, while other chemical structures, for which the database contain no data, could be possible? I also fail to understand how a

SAR-based estimate can be given for compound without any given "Possible ID". I understand that it is a lot of work to compile all these reaction rate coefficients, but the authors definitely ought to explain their assumptions better. Do authors rely on previous studies with the same instrument? Previous studies at the same site? I also could not find where the NIST value for k comes from for C4H4H+, for instance. Is it just in the wrong column? And why were the authors not able to use the SAR method for maleic anhydride? Is it a limitation of the method?

- p.11-12, ll.252-264: Category II: Should there be a regression adjusted to the m/z of isoprene for m/z 116.036 in Table S3, which is correlating with isoprene? (Also there is no mention of Table S3 and S4 in the main text)

- pp.12-13, ll. 278-281: Does this assumption rely on the fact that light hydrocarbons are not emitted locally? Can the authors be sure that there is no strong vertical gradient for these compounds regardless of the evolution of the boundary layer height?

Technical corrections:

p.27, Table 1, 3rd row: "Scientific" instead of "Scien8fic"

pp. 21-27: Check the format of the references. Sometimes "Doi" is used, sometimes "DOI", sometimes nothing; one link appears, "–" (l. 699) should probably be fixed, etc.

Supplementary material, Tables S3 and S4: I would use "peaks" instead of "compounds" in the tables' captions.

References:

Fuchs, H.; Novelli, A.; Rolletter, M.; Hofzumahaus, A.; Pfannerstill, E. Y.; Kessel, S.; Edtbauer, A.; Williams, J.; Michoud, V.; Dusanter, S.; Locoge, N.; Zannoni, N.; Gros, V.; Truong, F.; Sarda-Esteve, R.; Cryer, D. R.; Brumby, C. A.; Whalley, L. K.; Stone, D.; Seakins, P. W.; Heard, D. E.; Schoemaecker, C.; Blocquet, M.; Coudert, S.; Batut, S.; Fittschen, C.; Thames, A. B.; Brune, W. H.; Ernest, C.; Harder, H.; Muller, J. B. A.;

Elste, T.; Kubistin, D.; Andres, S.; Bohn, B.; Hohaus, T.; Holland, F.; Li, X.; Rohrer, F.; Kiendler-Scharr, A.; Tillmann, R.; Wegener, R.; Yu, Z.; Zou, Q. & Wahner, A. Comparison of OH reactivity measurements in the atmospheric simulation chamber SAPHIR Atmos. Meas. Tech., 2017, 10, 4023-4053.

Nölscher, A. C.; Yáñez-Serrano, A. M.; Wolff, S.; de Araujo, A. C.; Lavrič, J. V.; Kesselmeier, J. & Williams, J. Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity Nature Comm., 2016, 7, 10383.

Praplan, A. P.; Tykkä, T.; Chen, D.; Boy, M.; Taipale, D.; Vakkari, V.; Zhou, P.; Petäjä, T. & Hellén, H. Long-term total OH reactivity measurements in a boreal forest Atmos. Chem. Phys., 2019, 19, 14431-14453.

Sanchez, D.; Jeong, D.; Seco, R.; Wrangham, I.; Park, J.-H.; Brune, W. H.; Koss, A.; Gilman, J.; de Gouw, J.; Misztal, P.; Goldstein, A.; Baumann, K.; Wennberg, P. O.; Keutsch, F. N.; Guenther, A. & Kim, S. Intercomparison of OH and OH reactivity measurements in a high isoprene and low NO environment during the Southern Oxidant and Aerosol Study (SOAS) Atmospheric Environment, 2018, 174, 227-236.

Sinha, V.; Williams, J.; Lelieveld, J.; Ruuskanen, T.; Kajos, M.; Patokoski, J.; Hellen, H.; Hakola, H.; Mogensen, D.; Boy, M.; Rinne, J. & Kulmala, M. OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions Environ. Sci. Technol., 2010, 44, 6614-6620.