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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Long-term total OH reactivity measurements in a boreal forest" *by* Arnaud P. Praplan et al.

Anonymous Referee #2

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General Comments: The paper by Praplan et al. presents total OH reactivity measurements alongwith OH reactant measurements carried out in a boreal forest environment during the months of April, May, June and July in 2016. Measurements of total OH reactivity over a four-month period are indeed rare at any atmospheric environment and without doubt the suite of VOC measurements are impressive. However, there are several issues which I think the authors need to address through substantive revisions. Major Concerns: 1) Experimental methods: The description of the OH reactivity measurement method with the multiple corrections listed by the authors (only to later surmise that many of those corrections were not necessary for their ambient conditions is confusing and at times also misleading. Though they cite the original method paper published in Atm Env (Praplan et al. 2017) which was set up for urban measurements in high NO environment, I have to say that there are several issues pertaining to their treatment of the details. The authors seem to make strange assumptions concerning the competitive kinetics occurring inside the reactor. While they consider the potential for OH production inside the reactor through O3 and NO2 photolysis as well as NO + HO2 reactions, I could not find any discussion of compensating effects in such reactions. Firstly, the C1-C2 signal is a direct measurement of the OH in the reactor available for competitive reactions during the C3 stage when ambient air is sampled and this already takes into account ozone formed from the UV lamp in the absence of ambient air being sampled. When ambient air containing 50-60 ppb of ozone is sampled into the reactor it also gets diluted so the moot question really is how much OH do the authors think can be produced near the reaction zone which is just where photons from the lamp and the ambient air reactants mix in. The lifetime of OH radicals just against pyrrole molecules is few milli-seconds and while the lamp position will make some difference, I wonder how much additional OH the authors think can come from the Ozone photolysis when those same photons have about 3 times higher number of pyrrole molecules and several times higher number of water molecules to compete against?? Can they show a simple calculation for all these relative channels? Now coming to the NOx reactions the authors also do need to consider compensatory reactions that can mitigate the OH reformation as well which they have simply ignored. . .for example when NO2 photolyzes to NO, they should also consider that the 100's of ppb of ozone inside the reactor will convert the NO back to NO2 really fast as well. The additional NO2 can be a sink of the additional OH, thereby cancelling some of the extra "OH" effect. While NOx may not be important for the forest measurements, the general point is that such compensatory reactions can have a "benign" influence and before launching "detailed" box model simulations focusing on only a subset of reactions to understand the chemistry inside the CRM, the authors need to consider such aspects more thoroughly (both in the 2017 work and this work). For each of the interferences they mentioned a simple set of experiments with varying NOx or O3 or humidity in the reactor with the probe sampling the air into the GC-FID from the reactor at different distances from the lamp would have revealed more on how significant these effects could turn out to be. The authors do acknowledge that the chemistry inside the reactor and the box model analysis of the chemistry inside the reactor are not completely understood. . .in such case it would have been better to rely on experimental calibrations which better validate the method then to rely on more uncertain model corrections just because these models give the sense of being “detailed”. So my suggestion is that the authors stick to only those interferences which are relevant for the forest environment measurements in their study and do a thorough job of addressing them also considering compensatory effects in the revised version. It would also be nice to know whether authors tested the GC FID signal for humidity interferences of pyrrole detection. The concept paper by Noelscher et al. 2012 did mention this as a GC-FID “detector “ specific issue for CRM measurements.. How often during the four month deployment was the sensitivity drift in the GC-FID characterized through calibrations and corrected for ? How often were CRM calibration experiments performed in the four month period? Were there any major changes in the detection sensitivity ? This is important to address as the June data seems to be quite dissimilar relative to other months despite no obvious changes in the co-measured OH reactants.

Corrections for deviation from pseudo first order conditions: The authors mention quite a lot about this but I could not find exactly what molecule they used as a proxy in their simulations to determine the correction factor. Was it propane? If so, then this is not the ideal choice for a forested environment where terpenes form a major fraction of the ambient reaction mixture as typically terpenes are 10-100 times faster on per molecule basis with the OH radical. The correction factor depends quite strongly on the choice of the molecule with higher correction factors for propane and lower/no correction required for a terpene compound like isoprene or alpha –pinene. It would be good to have some discussion of this sensitivity as it has a direct bearing on the measured and missing OH reactivity calculations. . . 2) Box model for understanding chemistry inside CRM: This is the part that I found to be scant on details and sensitivity runs . . .I had little confidence in this analysis after reading the scanty description of how the box model was set up and the tenuous statements made on its basis for example didn't make me understand it any better: "This box model is far from taking into account the complex processes in the CRM reactor, but it is a useful tool to test hypotheses (such as NO2 and O3 photolysis) and to extend the validity range of correction factors that depend on pyr:OH to conditions that were not available experimentally. . ." I would suggest complete removal of this part of the analysis unless the authors can refine it and also show what useful and critical info came out of this. . . Given the published literature on CRM , the experimental corrections listed in Noelscher et al. 2012 and the original Sinha et al. 2008 paper are sufficient for this study.

3) Interpretation of ambient measurements: Most of the figures showing the ambient data were not easy to read and seemed to be too cluttered. I request the authors to improve the figures. . .for e.g. there is hardly any need to show multiple traces of measured OH reactivity with different stages of corrections ..they can list these magnitude ranges in the experimental section and show the final values they used. . . I also found the June data quite surprising (Table 1). Measured MT were lower than May but measured total OH reactivity was highest as was the fraction of missing reactivity (which the authors attribute to lack of co-measured OH reactants). Surely there may be few days of data in June that have better coverage which can be used instead of the monthly average? The authors mention alkyl amines as a source from soil. Can they rule out the contribution of biomass fires during the four months, esp in June? Kumar et al., 2018 Sci Reports have reported amides and amine in biomass burning plumes while trying to explain their missing OH reactivity and the authors may want to check out this possibility. Also it is surprising that no PTR-MS measurements from the SMEAR station were included in the analyses. Online measurements at high temporal resolution of acetonitrile or acetaldehyde would have bene useful but perhaps they can still look at the CO data if PTR-MS measurements were unavailable? Finally some comment is warranted to justify the SOSAA model comparison with the measurements made at very different heights from the height at which the model is simulating the chemistry. . ...can't vertical gradients confound such comparisons?

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I hope that with the above revisions that address the major points raised above, the paper can become suitable for publication in ACP as the novelty of the work and the need for such data is high.

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Discussion paper