Atmospheric
Chemistry
and Physics

Discussions

Interactive comment on "OH reactivity and concentrations of Biogenic Volatile Organic Compounds in a Mediterranean forest of downy oak trees" *by* N. Zannoni et al.

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The authors would like to thank Anonymous referee 2 for her/his valuable comments to the manuscript. Please find below the answers to the comments and changes in the manuscript text.

1) (1) Though, the paper is well structured, I agree with the comments of Reviewer 1, that at times there are serious language issues which tend to obscure the scientific meaning/clarity of the discussion. Thus the senior authors should help revise the submission or english language editing should be undertaken for the revsied version. The full list would be very big so I shall point out just a few where the choice of the words

is not correct. e.g. 1: Page 220068; Line 15 and at other places in the MS :words like scatter and flattered ....."the signal of total OH reactivity started to scatter around 11:30 p.m., then again at 2 a.m. and flattered back to the signal of calculated OH reactivity around 4:30 a.m. (Fig. 5)." The authors probably mean the trace becomes flat?? "24 h statistics", "9 point percentage", "breakdown of reactivity " for pie charts.. (2) We are thankful to both referees for pointing out these language issues in the manuscript. We modified some parts of the text and a revision from a native English speaker of the final version will be done as well.

2) (1) Qualitative conjectures should be avoided:.... ...e.g.Page 22063; Line 11: "co-variated perfectly with PAR...." In such cases, the correlation coefficient should be mentioned... (2) This is right. We have included more information/removed some comments from the text.

3) (1) Why do the authors have such high uncertainty for the CRM OH reactivity measurements (35 %) when other CRM systems typically do a better job and the authors' own previous work (e.g. Dolgorouky et al.,2012) had less uncertainty? If it is due to specific conditions encountered in the present deployment , then the same should be discussed. (2) Yes, 35% uncertainty on the measured reactivity is a higher value than the one of the previous instrument used in our laboratory and higher than the stated uncertainties on other CRM instruments constructed in other laboratories. This number accounts also for the uncertainties on the correction factors needed to process the raw data sets of reactivity. Specifically, it includes the uncertainty on the rate coefficient of the reaction of pyrrole with OH, uncertainty on the flow rates of all gases flowing inside and outside the reactor, uncertainties on the correction factor for kinetics (which represents the largest source of error and its investigation is currently ongoing) and uncertainties on pyrrole concentration from the certified standard and pyrrole sensitivity to the PTR-MS. We also used a certified standard of pyrrole with a larger error associated to its concentration compared to the pyrrole cylinder used in the study of Dolgorouky et al.,2012. More information can be found in Zannoni et al., 2015 and the

whole calculations are provided in the supplement of the article of Michoud et al., 2015.

4) (1) How did the authors produce the C2 stage zero ? Did they try humidifying botlled zero air or was it using a catalytic scrubber? How was the humidity regulated for the reactivity measurements? These are important points to clarify because as seen in Fig 5 and Fig 6, the ambient RH covers quite a range (25% RH duirng daytime to $\sim$ 60% RH at night), and ensuring the humidity is ok between C2 and C3 stages is no longer trivial. (2) We produced the C2 stage zero by sampling ambient air through a zero air generator, which provided clean air at the same level of humidity of ambient air. Though, small differences in m/z 37/m/z 19 (here considered as tracer for absolute humidity) were noticeable between the stages C2 and C3 and a correction for humidity was applied to the data set of OH reactivity. Such correction had an impact of about 13% on the raw data of reactivity.

5) (1) The authors should discuss the magnitude of the pseudo first order correction for the measured OH reactivity values. Generally, the direction in which this correction works is to bring down the measured OH reactivity value, especially if an unreactive molecule like propane is used for inferring the correction. However in the present study, as isoprene and pyrrole both have similar reactivity with OH radicals (rate coefficients are of the order of 10-10 cm3 molecule-1 s-1), I am a little concerned that the correction applied to account for the pseudo first order effect could have caused underestimation of the measured OH reactivity, which could affect the conclusions about not having much missing OH reactivity. (2) In our study the correction for deviation from pseudo first order kinetics was estimated by testing the response of our instrument, on the field, to two specific ambient reactive tracers: isoprene, a key species in this forest environment, and propane which is less reactive to OH than isoprene and in the present study can better represent other atmospheric reactive gases sampled at the site. Additionally, tests are conducted at different pyrrole/OH ratios in order to cover the different OH fields and kinetics occurring inside the reactor during the campaign. The results from these tests will be available in the supplementary material. The magnitude of this

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correction impacted the data set of reactivity by decreasing the values by 47%. This magnitude is higher than those encountered in other field experiments with the same instrument due, to our opinion, to less OH radicals produced inside the reactor due to less intensity of the UV lamp we used for this campaign.

6) (1) The high ozone concentrations (60-70 ppb!) and its time series seem to be at variance with the finding that not much photochemistry occurs within the forest and lack of transport of anthropogenically influenced air masses to the site (which the authors state to be the case based on the benzene and acetonitrile measurements). As the author seem to have NOx measurements and OH reactivity measurements, it may benefit the discussion if they discuss the photochemical regime for ozone formation in the forest based on the ratio of NOx OH reactivity/VOC OH reactivity (see for e.g. Sinha et al., 2012," Constraints on instantaneous ozone production regimes and rates..." Atmos Chem Phys). (2) Ozone is continuously monitored at the field site and in the surrounding area (as Manosque, Marseille) by the regional air quality network. Such high levels reported in this study are usually observed at the site and in line with the levels observed at more polluted sites surrounding the area of OHP, suggesting that no specific photochemistry occurs within this forest and that this mixing ratio is rather the result of transported ozone. We thank Anonymous referee for her/his suggestion in evaluating the photochemical regime in the forest. However, it falls a bit outside the main scope of this specific article which is comparing the measured and calculated reactivity to highlight any missing component in the forest.

7) (1) What is the role of deposition of OVOCs and ozone to the forest and its implications if any for their conclusions? Some discussion on this would strengthen the MS further. (2) Previous measurements in the same forest of OCS (carbonyl sulfide) and its observed analogy with ozone, suggested that the deposition flux of ozone in this forest was mostly the result of leaves uptake (Belviso et al., now in preparation). If this is the case, it can be speculated that ozone might lead to surface reactions forming the oxygenated molecules responsible for the missing reactivity observed during nighttime.

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This could be possible since the downy oak is a broad-leaf tree species, which might enhance these processes. However, more studies at the leaf scale are needed to investigate whether this process is occurring. The discussion of the missing nighttime reactivity will be improved in the text considering also the comments of Anonymous referee 1.

8) (1) Page 22058; At 2.2 mbar and 60 degree celsius, I think the Townsend ratio would be 135 Td and not 130 Td; Can the authors please check their calculation? (2) Yes, it is checked and corrected in the manuscript.

9) (1) Fragmentation of isoprene peroxides and their contribution to m/z 71 seems new. Can the authors cite some work and add more light on it? Unless the studies reporting the fragmentation used the same Td ratio in the drift tube, can one extrapolate those results for different Td conditions? (2) It might be confusing in the manuscript but we did not separate the different components measured at m/z 71. However, since m/z 71 has been recently attributed also to ISOPOOH for unpolluted sites, we cannot neglect that we also measured these compounds at m/z 71. Since ISOPOOH have different vapor pressures and solubility compared to MVK and MACR these compounds have been separated and identified with the PTR-MS by using a water trap. As also suggested by Anonymous referee 1, we reworded this part of the manuscript to make clearer that we consider these compounds not because we separated them but because it was recently found that they also contribute to the m/z 71 (see point (3)). It is possible that these molecules can be measured at other Td conditions, their presence mostly depends on the level of NOx at the site of measurements. (3) Previous studies highlighted the presence of isoprene hydroperoxides (ISOPOOH) fragmenting at m/z 71 in the PTR-MS, and representing a major yield from isoprene oxidation for low NOx environments, such as our case study (Liu et al., 2013 and Rivera-Rios et al., 2014). Since we did not separate between these compounds, we will therefore refer hereinafter to m/z 71 as the sum of the isoprene oxidation products ISOP.OXs: methylvinyl ketone (MVK)+methacrolein (MACR)+isoprene hydroperoxides (ISOPOOH).

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10) (1) As the measurement site is a long term measurement site, where other routine measurements are performed, is there any information on the boundary layer dynamics between day and night at the site? van Stratum et al.,Atmos Chem Phys 2012 showed these to be significant for another Mediterranean site with pine trees and I wonder if that could explain the strange ozone profile. (2) Unfortunately ozone is the only parameter which is continuously monitored at the site.

11) (1) The authors may want to add some new OH reactivity measurements (average $\sim$ 50 s-1)to Figure 11 from an environment where biogenic emissions are dominated by agro-foresty of high isoprene emitting trees such as poplar and eucalyptus and isoprene concentrations are as high as 3 ppb (Kumar and Sinha, Int. J. of Mass Spectrom., 374, 55-63, 2014. http://dx.doi.org/10.1016/j.ijms.2014.10.012). (2) Yes. This is right, the results from these measurements are included in figure 11.