

***Interactive comment on “Branch-level measurement of total OH reactivity for constraining unknown BVOC emission during the CABINEX (Community Atmosphere-Biosphere Interactions Experiments)-09 Field Campaign” by S. Kim et al.***

**Anonymous Referee #2**

Received and published: 5 May 2011

Summary:

This paper describes the measurements of the total OH reactivity of four tree species (red oak, white pine, beech and red maple) using the branch enclosure technique to assess the unknown BVOCs emissions at the PROPHET tower. Besides the branch measurements of OH reactivity, this paper reports model simulations using atmospheric measurements at the same site made some years before to assess the contribution of

C2758

the first generation oxidation products of isoprene to ambient OH reactivity. The idea of measure direct total OH reactivity at branch level using the enclosure technique, in my opinion, it is great and would be really helpful to find possible unmeasured BVOCs, but measurements of OH reactivity and measurements of BVOCs concentrations (to calculate OH reactivity) must be simultaneous, otherwise any difference between calculated and measured OH reactivity can be ascribed to changes of physical parameters during the switch from one measurements to the other. Therefore alternate measurements of OH reactivity and BVOCs concentrations and the time resolution of the measurements avoid to understand how to reconcile the discrepancy between observed and calculated OH reactivity. I think that the same experiment reported here with simultaneous measurements and quantitative analysis of the observations (here the analysis is to qualitative) will improve our knowledge of BVOC emissions as well as possible unmeasured BVOCs and their role on the total OH reactivity.

Problems:

1) The CRM method is a great tool to measure OH reactivity but using only one PTR-MS to switch between measures of OH reactivity and of BVOCs concentrations, as was done in this experiment, avoids simultaneous observations that are crucial when temperature and PAR change very fast, because these two parameters control the BVOCs emissions that are the main purpose of the experiment. Moreover, 20-min average data is a really poor time resolution to study OH lifetime. 2) Page 7788 lines 7-9 The Authors wrote: “The variations of measured OH reactivity can be reasonably explained by the calculated OH reactivity variations from isoprene concentrations measured by PTR-MS except on 5 July.” First at all what does it mean “..can be reasonably explained..”? there are a huge number of statistical tools to quantify quantitatively (with numbers) if it explains or not something: to give a strong conclusion you need the support of a deeper analysis, yours is too qualitative and subject to personal interpretations. In fact figure 3 that is used to support the conclusions above is not decisive: a) for all the data of the 3rd July measured OH reactivity is systematically higher than the calculated, only 2

C2759

calculated OH reactivities are similar to what measured. b) All the calculated OH reactivities of the 4th of July are lower or similar to the adjacent measured OH reactivities, except for the highest one when the calculated are a bit higher than the measured. c) For the 5th July there are some calculated OH reactivities that are a magnitude higher than the measured, really strange and hard to understand, so the Authors wrote (page 7788, lines 25-27): "Thus, we can understand that the significant disagreement on 5 July was actually caused by rapidly changing physical parameters that result in calculated and measured OH reactivity measurements that cannot be directly compared". This is why I claimed above that simultaneous measurements are needed to do a good job, otherwise the measured and calculated OH reactivities cannot be compared if in the mean time temperature and PAR has changed, because you are comparing two measurements of two environments completely different in terms of emitted BVOCs. Unfortunately you cannot check this because when you were measuring OH reactivity you did not measure BVOCs concentration but from temperature and PAR changes recorded, you are sure that the BVOCs concentrations is changing. d) On the 24th of July there are only 3 data of calculated OH reactivity that are a bit higher or similar to the adjacent measured OH reactivity. From the observations of this Figure 3 I do not think that there are sufficient evidences that measured OH reactivity are in agreement with the calculated one. Again only statistical tests of the two datasets and simultaneous measurements with higher time resolution would give a definitive response. 3) Figure 4 is a further support to what I said previously: on the 4th of July in more than 3 hours of observations there are only 4 data points of calculated OH reactivity and 11 of measured OH reactivity, while PAR changes more than 35 time ranging from 0 to 1200: How you can compare measured and calculated OH reactivity of periods with so high variability of a crucial parameter such as PAR. Similar considerations can be done for the 5th of July. 4) Page 7788 line 18 the Authors wrote: "...OH reactivity variations are comparable..." If you are so vague and qualitative I can say that for me, looking at the plotted data, they are "incomparable", please be quantitative. 5) Figure 6 and page 7789 lines 4-16: In this figure the Author wrote that they used 1-minute aver-

C2760

aged measured and calculated OH reactivity, please if you have these data use them also for the previous figures. 6) Page 7789 (lines 11-12) the Authors wrote: "...the plots clearly indicate that the difference of the measured and calculated OH reactivity in the 5°C temperature bin can be explained by the differences in PAR." This is hard to understand: the Authors at the beginning of this paragraph wrote (page 7789 lines 4-6) : "To quantitatively compare the measured and the calculated OH reactivity for the same conditions of PAR and temperature..." this means that in this case measured and calculated OH reactivity are plotted as function of the temperature and PAR to see if there is a dependence from these two parameters. Now if you have a difference between measured and calculated OH reactivity that depends on the temperature or PAR you can try to make some conclusion, if the differences are not a function of these parameters you have other conclusion, but you cannot say that the difference between measured and calculated OH reactivity can be explain by PAR difference, what does it means? That you are comparing measured and calculated OH reactivity for different environments (different PAR)? If it is right you cannot compare measured and calculated OH reactivity, as claimed before (page 7788, lines 25-27), or you mean that when PAR changes you expect an effect of PAR changes on measured OH reactivity different of the effect on emitted BVOC (consequently on measured OH reactivity). If you mean the latter I do not understand why. 7) Page 7789 lines 12-16, Authors wrote: "This comparison demonstrated the good agreement between measured and calculated OH reactivity. These results suggest that there is no significant missing OH reactivity associated with primary BVOCs emissions for red oak and white pine" Again if you are so qualitative, I can say for me is not a good agreement since some measurements are higher than some calculated OH reactivity so it is not so evident what the Authors conclude. Another issue with this figure 6, is the average: it is possible to show a figure with 1 degree C running average so in place of only 5 points you can have 20 points where you can apply a bit of statistics to find out if they are quantitatively in agreement or not, otherwise here (Fig6a) we have 2 points where measured and calculated OH reactivity are simila, 2 points where calculated is higher than measured OH and one point where

C2761

measured is higher: hard to make a conclusion, same story for Fig6b. Moreover, since data points are reported every 5 °C I suppose that it is the average of all the points in the interval ( $T-2.5^{\circ}\text{C}$  Æ  $T+ 2.5^{\circ}\text{C}$ ) looking at the measured OH reactivity at 35°C (Fig 6b) in the interval 32.5-37.7°C there are no more than 2 points: which is the statistical significance of this averaged points? I think that on the running average if in one interval you have 2 points and in the other you have 200 points the average calculated using 2 points has a less statistical significance than the average calculated using 200 points so it is hard to compare the derived averaged data. 8) Page 7790 lines 9-19 and Figure 7b: I think that the data reported in Fig. 7b do not support this conclusion. Even without any quantitative support, even with the inclusion of  $\alpha$ -farnesene, I do not see a clear agreement between measured and calculated OH reactivity, there are several points where measured are higher than neighboring calculated OH reactivity, a couple where is the opposite and very few when they are similar, also here without a statistical significance level it is hard to give a conclusion. 9) The Paragraph 1.5 describes the model simulation using atmospheric measurements made years before the campaign describe here. I think that it does not give further information on this work. I think that a paper with good results on branch enclosure observations does not need a paragraph of atmospheric model simulation unless using enclosure data, only in this case I see a consistency. There are several papers that use atmospheric observations to assess the first generation oxidation products of isoprene to BVOC emission budget and OH reactivity. 10) The enclosure would need a better characterization: measurements of CO<sub>2</sub> and H<sub>2</sub>O inside the enclosure would help a lot to be sure that the branch is functioning normally and the addition of the enclosure did not alter its physiology.

Minor Comments:

Page 7786 lines 6-9 Since PTR-MS is not able to speciate monoterpenes which is the uncertainty in the measured OH reactivity? Page 7787 line 19: Probably you mean 2009 and not 2010. Page 7788 line 19: "...temperature drop in the..." please change with "...temperature drops in the..." Page 7806 figure 6 Remove "the blue"

C2762

and "the red" because the color of the triangles and the circles change as function of PAR. Page 7790 line 1 Probably here "...higher than measured..." is "...higher than calculated...".

---

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7781, 2011.

C2763