

General Comments:

The paper by Wolf et al. examines peroxy radical concentrations and chemistry using a detailed chemical box model constrained by a large suite of relevant chemical measurements during the 2010 BEACHON-ROCS field study. The measurements were performed in a rural forest where reactive compounds/emissions are dominated by biogenic terpenes and MBO. The observed total peroxy radical concentrations reached as high as 180 pptv with 100 pptv on an almost daily basis during the period of their observations (~ 2 weeks). The box model calculations under-predicted total peroxy radicals by as much as a factor of 3 which the authors propose are likely due to missing sources. The paper is well written and very good effort has been put in the analysis and in trying to explain possible reasons for discrepancies between the measured and modeled peroxy radicals concentrations. I enjoyed reading it. The intriguing results are certainly of relevance to ACP readers and I recommend that the paper be published after the authors have addressed the few comments and suggestions and some minor technical points listed below, which will improve the quality of the discussion and confidence in the results.

Major Comments and Suggestions:

1) I share Reviewer 1's concerns regarding the influence of strong vertical gradients in the concentration profiles of chemical species and the resultant analysis and interpretation. To be fair, the authors have acknowledged the strong impact exerted by the chemical gradients and tried to correct for it in the measurements of several key chemical species. However, the effect may still be significant and therefore affect the conclusions of the study. In Table S1, the inlet heights for the different measurements are mentioned. I see some complication here with the inlet height for the OH reactivity measurements, which were made at 4 m and therefore differ from i) the height at which other OH reactants were measured and ii) the height at which the radical measurements were made (~1.6 m). The difference is greater than 2.4 m and sometimes as much as 15 m! Notwithstanding this difference, the authors state rather strongly in Page 31731; Lines 15-19:

“While under-represented OH reactivity could have a profound impact on peroxy radical chemistry elsewhere, we reiterate that this is not a viable explanation for missing peroxy radicals in the present study.”

I think the authors cannot entirely discount this effect in particular as several studies have shown occurrence of high missing OH reactivity in forested environments. A useful thing to check how important this effect is would be through additional model sensitivity runs constrained by different ratios of the total measured OH reactivity at 4 m. For example, taking 0.5 times of the measured OH reactivities at 4 m and another run with 1.5 times of the directly measured OH reactivity at 4m from 08-16 hrs local time would be very revealing to examine how the current discrepancy by a factor of 3 between modelled and measured RO₂ changes in each case. Perhaps, the OH reactivity change could be done in the form of a new molecule that is as

reactive as MBO with OH and with similar chemistry? The non-linearity in chemistry may bring down or increase the discrepancy depending on the run.

2) Ozone production implications: Page 31724; Lines 25-30 and again in Conclusion Page 31738: The authors highlight the importance of representing radical sources and sinks accurately for getting the ozone production rates and regimes correct. Since the authors have directly measured OH, HO₂ and RO₂ and NO and OH reactivity at the site, even with the caveats associated (HO₂ is HO₂ * and inlet heights vary...), it would be very interesting to compare the “local” and potential “global” ozone production rates (see e.g. Shirley et al., ACP, 2010 and Sinha et al., ACP, 2012). This would perhaps make the reader appreciate their recommendation of using the ozone production sensor developed by Carlo and Brune, AMT, 2010 with quantitative arguments! Shirley et al. reported ozone production measurements from an urban environment, whereas the Sinha et al study was from a mixed coastal site influenced by high OH reactivity quite frequently.

3) The radical measurements reported herein are high. As the authors discuss non photolytic sources they should also discuss the results of Andrés-Hernández et al., ACP, 2013, who found as much as 80 ppt of measured RO₂ at nighttime.

4) At Page 31726; Lines 1-15 they state:

“To our knowledge, there are no published data comparing within and above-canopy peroxy radical levels; however, detailed 1-D canopy modelling results predict relatively minor gradients in HO₂ and total RO₂ at other forests (Bryan et al., 2012; Makar et al., 1999; Wolfe and Thornton, 2011; Wolfe et al., 2011a).”

This may be true for radical levels but there is at least another modelling study by Mogensen et al., 2010 that examined vertical gradients in OH reactivity from a pine forest in Finland (monoterpene rich air) using a model. The authors may find the study relevant.

MINOR\TECHNICAL COMMENTS:

1) Introduction: In R1: O₂ is missing, from VOC+OH → RO₂.

2) Section 2.1: The site is above 2000 m asl. How important are mountain winds here? How would the diel dynamics of mixing affect chemistry and chemical concentrations? A wind rose could be added to the supplement for data periods relevant to this study.

3) Lines; 1-5; Page 31720: the inlet protruding 0.5m from the trailer wall at a height of 1.6m and oriented to the southeast.

If available, a picture of the inlets would be helpful and could be added to the supplement.

4) Section 2.3: First paragraph: It would be good to give full names of PAN and PPN at the beginning of the Section.

In the discussion where the authors mention non speciated monoterpenes and then the speciated monoterpenes in the form of alpha pinene, beta pinene etc.. It was not very clear which ones the authors used

References:

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Andrés-Hernández, M. D., Kartal, D., et al. Diel peroxy radicals in a semi-industrial coastal area: nighttime formation of free radicals, **Atmos. Chem. Phys.**, 13, 5731-5749, doi:10.5194/acp-13-5731-2013, 2013

Sinha, V., Williams, J., Diesch, J. M., et al.: Constraints on instantaneous ozone production rates and regimes during DOMINO derived using in-situ OH reactivity measurements, **Atmos. Chem. Phys.**, 12, 7269-7283, doi:10.5194/acp-12-7269-2012, 2012.

Shirley, T. R., Brune, W. H., Ren, X., et al.: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003, **Atmos. Chem. Phys.**, 6, 2753–2765, doi:10.5194/acp-6-2753-2006, 2006

Cazorla, M. and Brune, W. H.: Measurement of Ozone Production Sensor, **Atmos. Meas. Tech.**, 3, 545–555, doi:10.5194/amt-3-545-2010, 2010.