

## **General Comments:**

The paper by Kim et al. examines how well the main known sources and sinks of OH and HO<sub>2</sub> and an explicit 0D chemical box model (UWCM) are able to account for the observed ambient concentrations of OH and HO<sub>2</sub> during the BEACHON 2010 field campaign held at the Manitou Forest Observatory, Southern Colorado, USA. At this forested site, the dominant VOCs are 2-methyl-3-butene-2-ol (MBO) by day and monoterpenes (MT) by night, resulting in a chemical environment dominated by MBO and MT. Such a study is novel and interesting because previous forested site studies focusing on HO<sub>x</sub> budgets have been made primarily in isoprene dominated forests (e.g. Lelieveld et al., 2008, Whalley et al., 2011) or monoterpene dominated forests (e.g. BFORM Campaign, Sinha et al., 2010 ES&T and HUMPAAC-COPEC Campaign in Finland, Williams et al., 2011, ACP).

The authors find that in contrast to the isoprene dominated forest sites, where OH concentrations were significantly underestimated by models, a steady state model constrained by photolysis rates of O<sub>3</sub> (derived using J<sub>NO2</sub> and measured concentrations of O<sub>3</sub> and H<sub>2</sub>O), the measured reaction rate of NO + HO<sub>2</sub>, and the measured OH reactivity, was able to reasonably simulate both the diel measured concentration levels of OH as well as the diel trend (Fig.3). On the other hand a well constrained zero dimensional box model (UWCM) constrained by 30 min averaged chemical and meteorological observations significantly underestimated the measured OH (by a factor of 5) and HO<sub>2</sub> (by as much as a factor of 8). When constrained by the measured HO<sub>2</sub> concentrations, the same model appeared to reproduce the observed OH levels better, except for the early morning hours, purportedly due to the effect of HONO, which was not constrained in the model. Next, by using a simplified steady state model in which the OH production was constrained only by the NO + HO<sub>2</sub> reaction (the primary channel from O<sub>3</sub> photolysis being neglected as it was about 20 times lower than the former pathway for OH production; Fig 5) the authors showed that the modeled OH concentrations are again in reasonable agreement with the measured OH, proving thereby that HO<sub>2</sub> controls the OH levels through NO, and there must be a significant missing source of HO<sub>2</sub>. Several hypotheses are discussed to explain the missing HO<sub>2</sub> source including photolysis of short-lived VOCs and transport of HO<sub>2</sub> vertically and horizontally. Finally, on the basis of these results, the point is made that recycling reactions of the isoprene peroxy or acetyl peroxy + HO<sub>2</sub> type which have been reported to be important in low NO forest environments, are not of significance in this MBO and MT dominated low NO forest environment.

Overall the manuscript is concise and well written. It addresses an exciting area of current atmospheric chemistry research and would be of great interest to the ACP readership. However, I find some major areas of concern in the analysis, interpretation and discussion that need to be addressed by the authors before it can be recommended for publication in ACP. Please find these below.

## **Major Comments:**

- 1) HO<sub>2</sub> measurements: The authors describe the OH measurements adequately but there is not much information pertaining to the HO<sub>2</sub> measurements except for the citation and measurement uncertainty mentioned in Table 1. Since one of the major stated findings of this study is a large missing HO<sub>2</sub> source in the MBO and MT dominated forested site, the data quality assurance for the HO<sub>2</sub> measurements, including interference tests need to be provided in as much detail as the OH measurements. Please also address the following related point:

Figure 2 shows that the OH maximum was observed at 15:00 MST whereas the HO<sub>2</sub> maximum occurred 2 hours earlier at 13:00 MST. In Figure 2, I also note that both NO and the OH reactivity levels (i.e. the total loss rate of OH) (also shown in Fig 2) appear rather unchanged at 13:00 MST and 15:00 MST. If the OH production is controlled by the HO<sub>2</sub> +NO recycling reaction, as you remark later, I would expect the maximum of the OH to occur at the same time as the maximum in the HO<sub>2</sub>, since the NO levels and OH reactivity do not change significantly.

- 2) It is stated in the paper (Lines 27, Page 15959) that the modeled OH reactivity is within 30% of the observations. I did a quick calculation based on the measured MBO and MT mixing ratios reported in your study. Considering the daytime average OH reactivity value of 5 s<sup>-1</sup> observed in this study (Fig 2) (daytime is the only period relevant for OH in your study as nighttime OH levels were below detection limit), the average daytime MBO mixing ratio of 1.6 ppbV (Line 18, Page 15956 and Fig 2) alone would contribute about 4 s<sup>-1</sup> of OH reactivity ( $k_{MBO+OH} = 9.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; Cometto et al., 2008, J Phy Chem) while 0.5 ppbV of MT (Line 17, page 15956) would contribute 0.8 s<sup>-1</sup> (assuming most of it reacted at the rate of alpha pinene + OH). With just MBO and MT making up 4.8 s<sup>-1</sup> of the 5 s<sup>-1</sup> could you please clarify the above remark? This is very important because if just two species are able to account almost completely (~96%, not even counting measurement uncertainty) for the directly measured OH reactivity of 5 s<sup>-1</sup>, adding the contributions of other OH reactants such as CO, CH<sub>4</sub>, NO<sub>2</sub>, HCHO to name just a few would clearly make your calculated OH reactivity higher than the directly measured OH reactivity with the LIF method. This begs the question of whether the LIF based OH reactivity method maybe be possibly underestimating the actual OH reactivity due to artifacts? Has the instrument been tested with different terpenes +O<sub>3</sub> mixtures to account for their OH reactivities in the reactor?

If the directly measured OH reactivity is inaccurate and lower than the actual OH reactivity of the ambient air, then it implies that the [OH]<sub>SS</sub> > [OH]<sub>MEAS</sub>. It follows that then the major conclusions in the paper would also stand on very weak ground. I therefore suggest that the authors clarify this issue and provide sufficient details pertaining to the OH reactivity measurements to convince the readers regarding the accuracy of the OH reactivity measurements. The authors may also want to refer to Mogensen et al., 2011, ACP where a model was used to examine the OH reactivity

budget in an MT dominated boreal forest site. Please also clarify the exact MT composition observed in your study in terms of alpha pinene, limonene, carene contribution to the total MT mixing ratio, if the information is available.

- 3) I could not find the line showing the predicted HO<sub>2</sub> levels when constrained by measured OH in Figure 6.
- 4) Figure 3: Please clarify why the [OH]<sub>UWMC\_HO2\_Constrained</sub> values (black triangles) are missing from the plot during several hours of the day (e.g 8, 8:30, 10, 11, 11:30)..If there are so many breaks, it is difficult to conclude anything with confidence. Also please clarify the runtime of the model (2 h or 3 h?) Line 25 and Line 28, Page 15954
- 5) Page 15958: For a discussion of OH reactivity measurements from forested environments, the authors refer to the Lou et al., 2010 paper which is good reference for studies reported until early 2010. Since then a number of OH reactivity studies have been conducted in VOC rich environments (e.g. Dolgorouky et al., 2012, ACPD, Sinha et al., 2012 ACPD) and MT dominated forested sites (e.g. Sinha et al., 2010, ES&T and Noelscher et al., 2012, ACPD). The authors should atleast discuss the studies done in the MT dominated forested sites in this section. Note that in both Sinha et al., 2010 ES&T and Noelscher et al., 2012 under normal boreal forest conditions, the ratios of measured to calculated OH reactivities were about 2, implying 50% missing OH reactivity.
- 6) The NO levels in your study appear to be higher than the levels observed in the OP3 campaign held in Borneo (Whalley et al., 2011) and the GABRIEL campaign held in Suriname (Lelieveld et al., 2008). Please can you clarify how this may affect your conclusion regarding the importance of recycling reactions proposed in those studies? Accordingly, also please revise the conclusion regarding non isoprene BVOCs not causing an amplification of the oxidation capacity.

In Fig 2, I note that the maximum of the J<sub>NO2</sub> and the maximum of the [HO<sub>2</sub>] occur at 13:00 MST. This may lend greater support to the hypothesis of VOCs that could photolyse rapidly as the main source of the missing HO<sub>2</sub> among all the hypotheses discussed by the authors for a missing HO<sub>2</sub> source (Pages 15959-15960). The authors may want to pursue this line of thought further in their discussions. Are photolysis reactions of species like RONO (R= CH<sub>3</sub>etc..) included in the model's reaction scheme?

#### **MINOR/TECHNICAL COMMENTS**

Page 15950, Site description: Please mention the range of ambient temperatures experienced during the study and precipitation events if any. The cities of Denver and Colorado Springs are mentioned. In what wind direction from the station were the cities and how often did wind come from there during the study period?

Page 15951, Line 15: I could not find the cited reference Karl et al., 2012 in the list of references at the end. If it is in preparation then it must be stated as such.

Page 15951: In the Reaction R1, the first H<sub>2</sub>O on the RHS needs to have the 2 in the subscript.

Page 15953: R5, R6 and R7 There should be a gap between the rate coefficients and the product (e.g.  $O(^1D)J_{O_3}$  should be  $O(^1D), J_{O_3}$