

We appreciate both reviewers' constructive comments. While the review processes have been progressed, there were some updates for the trace gas concentration dataset especially NO, critical to assess recycling rates of OH from HO₂. In the revised dataset, the overall NO level gets higher due to updated calibration factors. We updated all our figures and model calculations based on the revised dataset. In general, the main findings we presented in the submitted version have not been changed but the specific discussions have changed in the revised manuscript. Specific responses to each comment and descriptions how the measurement dataset updates affected the specific discussions are:

REVIEWER 1

- 1) Figure 6 is missing the line to show the HO₂ prediction when OH is constrained in the MCM. This is a particularly vital piece of information.

We added predicted HO₂ in the Figure 6.

- 2) When the authors use a box model (MCM) constrained with the suite of observed parameters (CO, O₃, NO, NMHCs, OVOCs, physical values, etc.) to predict OH and HO₂, they find both of these are under-predicted (by factors 4-8). While constraining HO₂ gives reasonable predictions of OH, constraint of OH in the MCM results in an under-prediction of HO₂, with the authors concluding that an additional source for HO₂ is required. What is critically missing here however, is a direct comparison of OH reactivity predicted by the MCM model to those measurements. Page 15958, line 23 states that “a preliminary analysis indicates that ~50% of measured OH reactivity cannot be explained by the suite of VOC measurements (Nakashima et al., 2011)”, and then later (p. 15959, line 27), “Given that the modeled OH reactivity is within 30% of observations...”. An increase in the OH reactivity in the model of up to a factor of 2 could potentially shift the HO₂/OH ratio significantly, affecting predicted concentrations of HO₂.

We added discussion about how model predicted OH reactivity is affected by the various model scenarios that we applied. As shown in Figure 7, in the revised manuscript, the OH and HO₂ constrained scenarios result in over predicted OH reactivity levels. However, the over prediction levels is significantly (10 - 20 %) less than improvements in the model prediction of OH when HO₂ is constrained. Also, the differences between model simulated and observed OH reactivity can be accounted by the uncertainty in the OH reactivity observation (~12 %).

- 3) The authors state that the deficit in the HO₂ source is ~1-4 ppb/h, which is described as “5-20 times larger than the total HO₂ production in the base model”. Here, it would be very useful to see a more detailed budget analysis of the HO_x sources and cycling between OH and HO₂. I suspect

that the “missing” HO₂ source is 5-20 times the primary HO₂ production, rather than the total HO₂ production; HO₂ generated by OH reactions with NMHCs (particularly MBO), CH₄, CO, O₃, etc should be several ppb/h. It would be helpful to see the HO₂ source deficit relative to the full budget, and especially to see how uncertainties in measurements of some of the key species and reaction rates might contribute to the uncertainty in the total HO₂ source (e.g., uncertainty in MBO measurement, uncertainty in assumption for CH₄ of 1.77 ppm, uncertainty in OH reactivity measurement, uncertainty in HO₂+NO reaction rate).

We added the suggested discussion in the revised manuscript. As shown in the Figure 8, The required extra HO₂ production rates to explain the observed OH level is about 3-4 times higher than the HO₂ production rates from the known photochemical processes. This improvement comes from the higher NO level in the revised dataset. Still, this is a significant discrepancy that should be resolved. Conventionally, uncertainties for rate constants are estimated below 10 % (Atkinson et al., 2006, ACP). However, Atkinson (2008, Atmospheric Environment) discussed a need for re-evaluating the RO₂ + NO reaction rate because most of the literature values are based on the laboratory experiments with alkane originated peroxy radicals. Therefore, these two uncertain factors – kinetic constants and unknown photochemistry should be addressed to resolve the discrepancy we found. This discussion is included in the revised manuscript.

- 4) The authors state that the modeled total peroxy radical concentrations agree moderately well with observations in the run with OH constrained (p. 15959, line 26). This is potentially an important piece of information, and it would be very helpful to see a plot of this.

We added this plot on the revised manuscript in Figure 6.

- 5) It is speculated that because the total peroxy concentration is well reproduced but that HO₂ is under-predicted, that the modeled partitioning of RO₂/HO₂ may be incorrect. A conversion of RO₂ to HO₂ by a reducing agent is presented as a possibility for a missing source of HO₂. It would be a simple task to put an artificial conversion rate of RO₂ -> HO₂ into the MCM model to test that theory. The authors need to determine if such an enhanced conversion will result in a sufficient increase in HO₂, leading to an increase in OH, as to be consistent with observations. In addition, an artificial external source of HO₂ (or OH) could also be easily introduced into the model. It is important to show that these speculated sources can indeed potentially reproduce both the total HO_x abundance and the HO₂/OH partitioning.

We agree the model handling of RO₂/HO₂ partitioning may be a significant issue that causes the discrepancies we observed.

In this context, we are actually preparing a follow-up publication examining RO₂ to HO₂ conversion mechanisms based on these observational dataset. We realized that we should deal with 100 individual RO₂ species in MCM 3.2, a near explicit chemical mechanism. We added this discussion point in the revised manuscript.

- 6) The major conclusion of this work is that non-isoprene BVOCs do not cause an amplification of the oxidation capacity that have been reported in environments with high isoprene and low NO. Most of these environments are very low NO (<10 pptv) while this study represents moderate NO levels (~100 ppt), which would mask the processes dominant in a lower NO environment. It should be stated that the conclusions remain to be tested in very low NO environments, where the impact of additional HO₂-to-OH recycling due to BVOCs would be most effective

In the recently published analysis on discrepancies in [OH]_{OBS} vs [OH]_{MEA} (Lu et al., 2012) clearly shows that up to 4 times of discrepancies were found in the observation dataset from the Pearl River Delta China where NO concentrations were observed in similar or higher levels than what we observed at the BEACHON site. We clarify this point in the revised manuscript.

- 7) A comparable site mentioned in terms of NO environment is the Pearl River Delta site. Those HO_x measurements were made with LIF (as do many of the other studies cited with model under-predictions of OH). Mao et al., ACPD 12, 6715-6744, 2012 recently raised the potential of an LIF OH instrument unknown interference related to high BVOC environments. It would be useful for the authors to comment on this.

We added the discussion about the new insights on the LIF measurement techniques in the revised manuscript.

Specific Comments

Section 2.3.2 beginning line 25: What is the runtime for the model? I see both 3h and 2h mentioned (p.15954 line 25 and line 28).

P. 15956 line 20: Where does Figure 2 show the dominant sinks for OH?

Figure 2 – it is difficult to see some of the values due to the scales (e.g., 2b for NO). Can the scales on this be adjusted?

We clarified the specific comments by the reviewer

- 1) HO₂ measurements: The authors describe the OH measurements adequately but there is not much information pertaining to the HO₂ 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 HO₂ source in the MBO and MT dominated forested site, the data quality assurance for the HO₂ 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 HO₂ 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 HO₂ +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 HO₂, since the NO levels and OH reactivity do not change significantly.

We included adequate technical details on HO₂ in the revised text. Since an article about HO₂ and RO₂ observations during the BEACHON campaign is in preparation, the more thorough discussion will be appeared on that paper.

We updated the plot with the revised final dataset, updated after the initial submission. As described in the responses to Reviewer 1's comments, main differences are higher NO concentrations in the updated dataset. We also updated the OH concentration dataset, which no longer shows the highest point around 3 pm. The intention we presented Figure 2 was to introduce overall observation dataset and how each observation is compared with other published results. As described in the manuscript, we presented all the available dataset in Figure 2 so 1:1 comparison for each dataset as the Reviewer 2 suggested may not be suitable. We rather thoroughly filtered out dataset for the steady-state calculations and UWCM calculation to see how HO₂-NO-OH-OH reactivity relationships can explain ambient OH level we observed. We clarify this discussion point in the revised manuscript.

- 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⁻¹ 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 (Line18, Page 15956 and Fig 2) alone would contribute about 4 s⁻¹ of OH reactivity ($k_{MBO+OH} = 9.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; Cometto et al., 2008, J Phy Chem) while 0.5 ppbV of

MT (Line 17, page 15956) would contribute 0.8 s⁻¹ (assuming most of it reacted at the rate of alpha pinene + OH). With just MBO and MT making up 4.8 s⁻¹ of the 5 s⁻¹ 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⁻¹, adding the contributions of other OH reactants such as CO, CH₄, NO₂, 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 +O₃ 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]_{SS} > [OH]_{MEAS}. 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.

It seems that Reviewer 2 assumed the standard temperature and pressure conditions for the OH reactivity calculations. The ambient pressure at the BEACHON site was observed 760 to 775 mbar due to its high altitude (2250 m above the sea level). Therefore, if the pressure considered, OH reactivity from MBO is around 2.9 and MT is 0.61. Those two accounts about 3.5 which is around 56 % (daytime average OH reactivity is ~ 6.2). All the other compounds that Reviewer 1 listed explain around ~ 14 % of OH reactivity, which added up ~ 70 % of OH reactivity from the known compounds. The instrumentation, deployed for the BEACHON campaign, was well characterized in the laboratory and the results are presented in the peer-reviewed paper (Sadanaga et al., 2004). Therefore, we do not believe that the concern Reviewer 2 is raised is not valid.

We added more specific discussion on monoterpene speciation but as above simple calculation results indicates during the daytime, MBO is the most dominant OH chemical sink and contributions from monoterpene is considerably lower. This is obviously big differences from the observations in the boreal environments where hemiterpenoid emissions are not observed.

- 3) I could not find the line showing the predicted HO₂ levels when constrained by measured OH in Figure 6.

We added the HO₂ temporal variation in the figure.

- 4) Figure 3: Please clarify why the [OH]UWMC_HO₂_Constrained 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

In the submission version, we notified some issues in average processes in the data analysis routine. We corrected and updated the figure.

- 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.

We updated literature review in the revised manuscript

- 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 JNO₂ and the maximum of the [HO₂] 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 HO₂ among all the hypotheses discussed by the authors for a missing HO₂ 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= CH₃etc..) included in the model's reaction scheme?

In the revised manuscript, we make it clear that the NO_x conditions at the BECHON site were higher than those observed by Whalley et al. (2011) and Lelieveld et al. (2008) but similar or lower than those observed by Hofzumahaus et al. (2009) and Tan et al. (2001), who also reported significant underestimation of observed OH levels by the box model.

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 H₂O 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)JO₃ should be O(1D), JO₃

We corrected all the Minor/Technical Comments in the revised manuscript.