

Review of “Evaluation of HO_x sources and cycling using measurement-constrained model calculations in a 2-methyl-3-butene-2-ol (MBO) and monoterpene (MT) dominated ecosystem” by Kim et al.

This paper describes measurements of HO_x and many of its precursors during the summertime BEACHON-ROCS experiment in the Manitou Forest Observatory during August 2010. In examining directly observed quantities, the authors can show that OH is accurately simulated using only the measured OH reactivity and the recycling of HO₂ (HO₂+NO). This suggests that the source of OH from recycling of HO₂ via NO dominates its total production and that there is no additional recycling mechanism of HO₂ required to explain observed OH, as has been found in previous studies over low NO/high isoprene regions. On the other hand, there is not an adequate explanation for a source of HO₂ that can reproduce its observed concentrations. The paper was well-written and easy to read. I found this paper extremely interesting and potentially exciting. However there are a number of points that I believe require additional work and/or discussion. I recommend publication after the following major revisions are addresses.

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.

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.

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).

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.

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.

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.

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 sited 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.

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?