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Atmospheric Chemistry and Physics Discussions

Interactive comment on "OH reactivity in a South East Asian Tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project" *by* P. M. Edwards et al.

Anonymous Referee #1

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This paper describes measurements of total OH reactivity conducted during the 2008 Oxidant and Photochemical Processes (OP3) campaign in Borneo. The authors find that the measured total OH reactivity is significantly greater than calculated based on measured concentrations of OH sinks, a result similar to that found in other studies. Through both a simple conceptual model as well as a more detailed model constrained by observed BVOCs, the authors demonstrate that the missing reactivity in this environment is likely due to unmeasured isoprene oxidation products.

Unfortunately, the authors are unable to fully reproduce the observed missing reactivity using their constrained box model. However, they demonstrate that uncertainties

associated with the physical loss processes of these intermediate species as well as uncertainties associated with the overall lifetime of these intermediate species relative to the lifetime of isoprene may explain the inability of the model to reproduce the observations. The authors emphasize the need to develop instruments capable of measuring the concentration and physical loss properties of these intermediate species in order to be able to accurately close the OH reactivity budget.

The paper is well written and suitable for publication in ACP after the authors have addressed the following comments:

1) The authors describe a new metric α as the ratio of total OH reactivity to OH reactivity from isoprene and show through simulations that the overall reactivity of isoprene approaches 10 times the reactivity of isoprene itself due to the reactivity and accumulation of intermediates in the overall isoprene mechanism. They attribute the factor of 10 to the number of OH attackable bonds in isoprene, and generalize it to all VOCs in section 4.6. This is not intuitive given that the reactivity of each oxidation product is different, but it likely reflects the overall reactivity of the accumulated oxidation products. It would be helpful to illustrate this relationship between α and the number of attackable bonds with a simple VOC to better demonstrate the overall applicability of this metric to other VOCs.

2) The authors focus on the discrepancy between the measured and modeled reactivity during the daytime, but there is little discussion regarding the nighttime measurements. As noted by the authors on page 5248 the simulated OH reactivity at night agrees to within the uncertainty of the measurements, suggesting that intermediates in the isoprene oxidation mechanism are not contributing significantly to the measured reactivity at night. Clearly deposition of these compounds at night likely increases as the boundary layer height decreases, but what do the nighttime measurements suggest about the lifetime of these intermediate oxidation products and the "mismatch" between the lifetime of isoprene and the lifetime of the oxidation products? The paper would benefit from an expanded discussion of the nighttime measurements.

Minor comments

Fig. 13. The multitude of lines on this figure make it hard to read, but it appears that the lines on the figure do not correspond to all of the physical lifetime simulations mentioned in the caption – there appear to be some simulations missing. It doesn't seem necessary to display all of the simulations, but the caption should reflect what is illustrated in the figure.

p. 5236, line 27, reference to Di Carlo et al., 2004 should be removed here, as the measurements at this site were not done under "high NOx" conditions. This reference is correctly included on the following page as under "low NOx" conditions.

p. 5236, line 27, reference to Dolgorouky et al., 2012. In contrast to other the other studies cited here under "high NOx" conditions, significant missing reactivity was observed during MEGAPOLI campaign similar to that observed in forested areas, and the missing reactivity was attributed to unmeasured anthropogenic oxidation products.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 5233, 2013.