

Interactive comment on “Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest” by L. K. Whalley et al.

Anonymous Referee #1

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This manuscript documents an analysis of photochemical observations at a remote surface site in Borneo. The inability to reconcile radical concentrations with current understanding builds upon the growing body of evidence indicating that BVOC oxidation (particularly for isoprene) is poorly understood and does not suppress OH as current mechanisms would predict. While mechanisms for regeneration of OH have been posited, this study further corroborates earlier findings that the OH source must involve the recycling of HO₂ since a direct source of additional OH leads to overprediction of HO₂. It is noteworthy that this unknown recycling pathway is rather large (equivalent to the impact of 0.74 ppbv NO) and does not closely follow the isoprene diurnal profile.

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This work represents an important contribution that should be published. The following comments are offered as suggestions for improving the manuscript.

1. In discussing the importance the observations, the authors emphasize the “reduction in CH₄ lifetime and increase in the rate of VOC degradation.” While I agree that these are the fundamental implications, it is important to emphasize how much of the work being pursued throughout the community relies on a satisfactory resolution to this discrepancy. For instance, any global or regional model currently able to reproduce isoprene observations should be considered suspect with the likely consequence being an underestimate of the flux of BVOCs into the atmosphere and impacts associated with their oxidation (e.g., SOA production). Likewise, the interpretation of satellite observations of CH₂O to provide a top-down estimate of isoprene emissions is sensitive to this problem.

2. The treatment of peroxides in the analysis is not entirely clear. In section 2, the authors note that peroxides, which were unmeasured, are assumed based on observations during GABRIEL and are held constant. In section 2.3, the authors discuss controlling the peroxide concentrations through the deposition lifetime. So have peroxides been calculated? If so, why is there a need to invoke the GABRIEL observations? Given the differences between GABRIEL and OP3 in terms of observed $j(\text{O1D})$ and OH, it is not clear how reasonable this assumption is anyway. It would be useful to quantify the relative importance of peroxides as a source of OH. While I expect that it is small, this would put bounds on the sensitivity of the results to this assumption.

3. The factor of two difference in noontime $j(\text{O1D})$ between OP3 and GABRIEL is of some concern, and deserves some further discussion. Both experiments were conducted at the same latitude (5N) and based on the observation dates, noontime SZA was slightly lower for OP3. While GABRIEL observations were airborne, it is easy to conduct a few calculations using quick TUV to determine that the difference in j -value between the surface and 1 km shouldn't be more than 25%. There is also little to gain in terms of overhead ozone since tropical values are pretty stable. What about clouds?

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In section 2, the authors state that cloud cover was increased in the second OP3 measurement period rather than the first, but that both periods experienced similar peak photolysis rates. Was there any opportunity to assess photolysis under clear-sky conditions in comparison to a model?

4. The conclusions offer a somewhat tepid recounting of the importance of the problem and our lack of understanding. I would like to encourage the authors to take an opportunity here to recommend next steps for the community. While I would say that this study provides the most comprehensive characterization of the problem to date, it has now been observed in numerous studies reaching back nearly a decade. Field studies have been critical to uncovering this problem, but does the next step belong in the lab or in the field? What other measurements would have been useful (e.g. CH₂O)? I also notice that peroxy radicals were measured by PERCA as well as FAGE. Should a future study include CIMS observations as well? These are just a few thoughts, but I'm sure that the authors have other ideas as well.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5785, 2011.