

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

Anonymous Referee #2

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The paper reports HO_x concentration and OH reactivity measurements obtained in a tropical rain forest in Borneo during the OP3-I campaign. The measured OH is compared to steady-state concentrations calculated from the major known OH sources (photolytical sources and HO_2+NO recycling) and OH reactivity (reciprocal OH lifetime). A significant discrepancy between measured and calculated OH is found, indicating a large missing OH source. The result is of high relevance as it indicates a major gap in our understanding of atmospheric chemistry at tropical latitudes. The result is solid since the comparison is entirely based on experimental data without need of a sophisticated chemical model (although HO_2 was taken from a later measurement period, OP3-III, at similar chemical conditions). A model sensitivity study suggests that

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the missing source is most likely a radical recycling reaction that converts HO₂ to OH. This conclusion is consistent with similar observations reported from other field studies in forested areas. Thus, the present work expands, in a geographical and chemical sense, the set of observational data that may serve as a benchmark to test and develop new chemical mechanisms for atmospheres that contain a large amount of biogenic VOCs. The paper is well suited to be published in ACP. However the following comments should be considered in the discussion.

Specific Comments

Like in other related paper (e.g. Lelieveld et al., 2008; Archibald et al., 2010; Stavrou et al., 2010), much of the discussion is focused on the role of isoprene oxidation as a potential source of OH recycling. However, Fig. 1 shows that the maximum mean value of measured isoprene (3 ppbv) explains only one third (7.5 s^{-1}) of the total OH reactivity ($20\text{--}25 \text{ s}^{-1}$). Why then should isoprene dominate the chemistry of OH? Where does the other reactivity come from and how large is the fraction of reactivity that cannot be explained by measured trace gases? There is an analogy to k'_{OH} from the Suriname rain forest, where isoprene, isoprene oxidation products, acetone and acetaldehyde make up only 35% of the measured OH reactivity (e.g., Sinha et al., Atmos. Chem. Phys., 8, 2213–2227, 2008). The k'_{OH} measurements at OP3 and Suriname indicate that the postulated OH recycling may be related to biogenic VOCs other than isoprene. This issue should be addressed in more detail.

Fuchs et al. (Atmos. Meas. Tech. Discuss. 4, 1255–1302, 2011) report an interference in their HO₂ measurement by LIF which is caused by partial chemical conversion of RO₂ radicals in their detection system. This interference causes a systematic bias in the measured HO₂ data, which may become larger than the true ambient concentration. Is this interference also expected for the Leeds instrument? If so, the authors should discuss the impact on the PSS calculation and the conclusions drawn from Fig. 3.

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Minor comments

page 5787, line 21–23: The statement is too broad and not all references are adequate. Please be more specific! Thornton et al. studied the budget of peroxy radicals (not OH) in a city plume (not forest). Carslaw et al. and Tan et al. performed their measurements at middle latitudes, not in the tropics. The paper by Hofzumahaus et al. (2009) (HO_x study at tropical latitudes) could be mentioned here as well.

page 5788, line 13–18: The mechanism of Peeters et al. (2009) postulates a potential OH yield of about one. The papers by Peeters and Muller (Phys. Chem. Chem. Phys. 12, 14227–14235, 2010) and Stavrou et al. (2010) assume that even a yield of three is possible. Only with a yield of three (not one), the model underprediction could be largely reconciled.

page 5788, line 19–20: Delete 'However' and 'any such'.

page 5788, line 19: PRIDE-PRD

page 5789, line 22: Which kind of VOCs were measured? Did they include HCHO and other OVOCs?

page 5792, line 6: In the paper by Ingham et al (2009), a flow tube made of glass is mentioned. Can you briefly explain why a PVC tube has been used at OP3? I wonder whether the wall material absorbs/desorbs reactive gases and/or accumulates dust (by electrostatic charging) that may change the zero decay rate during the course of the campaign?

page 5795, line 1–3: It would be worthwhile to include k'_{OH} in the comparison between OP3 and GABRIEL. Were the OH reactivities similar during both campaigns?

page 5797, line 23: Reaction → Equation

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

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