

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

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Re: "Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest" by L. K. Whalley et al.

Comment by J. Peeters, T. Stavrou and J.-F. Müller

The authors conclude that the OP3-I [OH] data and the complementary [HO₂] data from OP3-III cannot be satisfactorily reproduced at the same time by the new isoprene mechanism proposed by Peeters et al., 2009 and Peeters and Müller, 2010. Rather, the authors suggest an unidentified additional HO₂ + X → OH + XO conversion reaction, which at an optimized rate of 0.15 s⁻¹ allows to obtain MCM-modeled [OH] and [HO₂]

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concentration profiles in good accord with the observations.

First, already in the two papers cited above it was pointed out that the secondary chemistry following hydroperoxy-methyl-butanal photolysis has a major impact on both the OH and HO₂ budgets, and it was proposed that "of the order of one OH" (rather than "1 OH") could be regenerated overall per isoprene + OH step.

More importantly, using the IMAGESv2 global chemistry transport model, the new chemistry as implemented in a first version of the Leuven Isoprene Mechanism, LIM0, was shown to reproduce within 25% both the high [OH] and [HO₂] observed in the GABRIEL (Lelieveld et al., 2008) as well as the INTEX-A (Ren et al., 2008) airborne campaigns (see Stavrakou et al., 2010). Using the same CTM for OP3, constrained by the [NO], [O₃], [isoprene] and photolysis rates measured during OP3-I, we find that LIM0 leads to an [HO₂] overestimation by more than a factor 2, in agreement with the findings presented by Whalley et al. However, LIM0 is found to reproduce within 20% the average daytime [OH] concentration of OP3-I, and at the same time also the [HO₂] of OP3-III provided an additional HO₂ sink is introduced with rate 0.02 s⁻¹. This sink is much slower than the HO₂ → OH conversion at 0.15 s⁻¹ needed with the MCM mechanism.

Focusing on the various concentrations and rates around noon (11.30 to 12.30 hrs), it may be noted that the 0.15 s⁻¹ HO₂ sink suggested by Whalley et al. implies an HO₂ + X → OH + XO volume rate, and hence also a lower limit for the total HO₂ production rate, of 3.5 × 10⁷ cm⁻³ s⁻¹. This rate turns out equal to the total OH reaction rate of 3.5 × 10⁷ cm⁻³ s⁻¹, as found from the measured noontime [OH] of 1.75 × 10⁶ cm⁻³ and OH reactivity of 20 s⁻¹. As each reacted OH results in either RO₂ or HO₂, this in turn implies that there is no room for any RO₂ formation by the OH reactions, unless there is another unidentified RO₂ + Z → HO₂ + Prod reaction that forms HO₂ with a high volume rate of several times 10⁷ cm⁻³ s⁻¹. Furthermore, the suggested HO₂ + X → OH + XO reaction at rate 0.15 s⁻¹ is not only at least 5 times faster than the combined known HO₂ sinks (by NO, RO₂, HO₂, O₃ and OH), but would also be

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the by far fastest oxidation process in OP3, even 3.5 times faster than the isoprene + OH reaction with its rate of $1.0 \times 10^{**7} \text{ cm}^{-3} \text{ s}^{-1}$. Moreover, provided that the missing OH source in OP3 is directly linked to isoprene as found in several other campaigns (e.g. GABRIEL, Martinez et al., 2010), one would need here at least 3 or 4 species "X" formed (or otherwise available) per isoprene + OH step.

On the other hand, the much slower additional HO₂ sink at 0.02 s^{-1} required by LIM0, without need for OH production thereby, might more readily be attributed to as yet unidentified HO₂ reactions at canopy level. One could speculatively suggest (so far unknown) H-abstractions by HO₂ from specific monoterpenes featuring "super-allyl"-activated C-H bonds with BDE only about 70 kcal/mol (Vereecken and Peeters, 2001).

References

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