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## *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 #3

Received and published: 26 April 2013

## **General Comment**

The present manuscript is written clearly and falls within the scope of the journal. It shows the measured and modelled OH reactivities during the OP3 campaign. The model is first used in a simplified setup to get insights into a few features of the chemical system. Then, a more realistic setup is used to model, although underestimating, the OH reactivity. The possible reasons for such underestimate are discussed in terms of poorly constrained physical loss of chemical species and of missing primarily emitted BVOC. However, the impact of different chemical mechanisms and model setup are likely not negligible and unfortunately have not been investigated. Therefore, I would

C1666

like the authors to perform sensitivity simulations as I outline below and, if necessary, change the discussion of the results accordingly.

## Major comments

1) One wonders how realistic are the model simulations performed here and in Whalley et al. 2011 and in Stone et al. 2011. In the very dynamical interplay between emissions, chemistry, transport and deposition the diurnal steady state for all species does not seem to be necessarily reached, does it? Furthermore, such an approach is bound to maximize (overestimate?) the accumulation of products and therefore OH reactivity. Another way of doing it is to let the model run until the photochemical age is reached like in Karl et al., ACP 2009. In isoprene-dominated environments this can be defined by the (MVK+MACR)/ISOP ratio. Thus, I would like to see first how the MVK+MACR sum and the (MVK+MACR)/ISOP ratio from the DSMACC model compare to the observations. If not close to observations the case for computing the model OH reactivity constrained by the photochemical age becomes even more compelling. Both of these results should be shown.

2) Although OH reactivity is by definition determined by the reactivity of compounds, little is said about the impact of changes in the chemical mechanism. For example, MCM v3.2 along with the epoxide formation did not implement the OH-forming channel in the ISOPO2 + HO2 reaction (Paulot et al., Science 2009). Liu et al., ACPD 2013 confirm this experimentally. Moreover, the branching ratios for the reactions of ISOPOOH with OH are very questionable. Specifically, ISOPCOOH + OH is given to yield 93% epoxide via the formation of the tertiary radical after OH addition. However, the formation of the secondary alkyl radical, which cannot form the epoxide and recycle OH, is expected to be 30-35% of the total. Similar problem is seen for the implemented chemistry of ISOPBOOH and ISOPDOOH. However, the most extreme case is for OH addition to ISOPAOOH in which instead of yielding 100% epoxide and OH it should yield 65% of RO2. This likely leads to an underestimate of the OH sink (OH reactivity). Therefore, I would like to see results from a sensitivity run in which the OH-forming channel in ISOPO2 + HO2 (Paulot et al., Science 2009, Liu et al., ACPD 2013) and realistic OHaddition branching ratios for ISOPOOH, e.g. using the SAR in Peeters et al., JPC A 2007, and subsequent chemistry are implemented.

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

C1668