

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 #2

Received and published: 25 April 2013

General Comments:

The paper by Edwards et al. reports a novel 12 day dataset of OH reactivity from an East Asian Tropical Rainforest in Borneo from measurements performed in April–May 2008. The authors compare the measured OH reactivity with the calculated OH reactivity due to the individually measured OH reactants and find that approximately 40% of the measured OH reactivity is unexplained, pointing to a significant gap in our understanding of the composition of reactive compounds present in forest air. This result is consistent with results of high missing OH reactivity from forested environments where primary biogenic emissions dominate the chemical composition of the air. In

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their paper, the authors also investigate potential reasons for the missing OH reactivity employing a variety of sensitivity tests and using models with varying degrees of detail in chemical and physical parameterization. They conclude on the basis of these analyses that oxidation products of primary emissions such as isoprene can likely make up the missing OH reactivity in the forest air.

The manuscript is well written and will be a valuable addition to existing OH reactivity datasets in the literature. While the authors were unable to unravel the identity of the missing OH reactivity in this work, the analyses are novel and they also propose directions for future research to improve our understanding of the missing OH reactivity. I enjoyed reading the interesting paper and recommend publication in ACP after the following comments have been addressed.

Major Comments:

Abstract: Line 20–23: “Notable in these calculations is that the lifetime of OH reactivity is significantly longer than the lifetime of isoprene and critically depends on the chemical and physical lifetime of intermediate species.” The wording in the above lines is quite confusing. OH reactivity is the inverse of the chemical lifetime of the hydroxyl radical under steady state conditions. So what is meant by “lifetime of OH reactivity”? Please clarify.

Abstract: Page 5236: “A clear argument for a significant missing flux of primary emitted VOC compounds to account for the unmeasured reactivity is not found and the development of techniques for the measurement of secondary multifunctional carbon compounds is needed to close the OH reactivity budget” Based on the information and analyses contained in the manuscript, the above statement appears to be too strong. Can the authors rule out the potential contribution of unmeasured primary reactive species (say 20–30) emitted at few ppt level with reactivity comparable to isoprene (several hundred such species exists, see for e.g. Goldstein and Galbally, ES&T, 2007)? These would not have been captured by the suite of VOC instrumentation (etection

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limits would be a challenge) deployed in OP3 but could all together still contribute significantly to the missing OH reactivity and also scale with the isoprene reactivity (which as the authors note is also a proxy for primary emissions).

If one cannot rule out the above possibility then it should be made clear that both unmeasured oxidation products and primary biogenic emissions could together account for the missing OH reactivity. This should be clarified both in the abstract and elsewhere in the manuscript.

Page 5237; Lines 1-4; "between measured and calculated OH reactivity are usually found under low NO_x conditions in the presence of elevated levels of Volatile Organic Compounds (VOC), typical of those found in forested locations (Di Carlo et al., 2004; Sinha et al., 2008, 2010)."

Significant missing OH reactivity has also been observed in aged urban air masses in France (e.g. Dolgrouky et al, 2012) which the authors cite in error as a study where the OH reactivity budget was well understood. Very high OH reactivity has also been observed in aged urban air masses containing very low NO_x levels in Spain (Sinha et al., ACP, 2012). The authors should include these works in their Introductory section and clarify that missing OH reactivity and high OH reactivity has also been observed in urban sites when influenced by aged air masses and not only in forested sites.

Page 5238; Lines 18-24: The Kim et al. 2011 paper only studied four tree species (red oak, white pine, beech and red maple), and therefore conclusions derived in that study cannot be generalized to the most bio-diverse natural forest ecosystem, namely the rainforest. This should be noted in the discussion.

Mogensen et al. 2011, ACP included secondary species in their modeling analysis of the boreal forest OH reactivity but were still unable to explain the 30-50% missing OH reactivity. They even assessed uncertainties in rate coefficients as a contributory factor and the authors should discuss how their approach fares better/differently in comparison to the modeling analysis of Mogensen et al. as it would benefit the readers.

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Figure 5: The correlation plot does not look that good to me and the trend lines tend to be determined at the extremes by just 1-3 points. While the authors have certainly used a novel approach here and I appreciate it, some comment is warranted on why at OH reactivity of ~ 75 /s, the isoprene reactivity is only 12 /s while at a total observed OH reactivity of 40 /s, isoprene reactivity is as much as 22/s. Could this be due to unmeasured primary biogenic reactive emissions during the instances you observe close to 75/s ? Some comment is required regarding this feature. Perhaps colouring the data points by the intensity of the solar radiation or by the ratio of MVK+MACR/isoprene might help to elucidate the relative importance of primary emissions versus oxidation products?

Section on "Missing OH reactivity owing to primary emitted species": The authors highlight the limitations of different analytical techniques in this section. This section could benefit from a specific discussion regarding the detection of green leaf volatiles (GLV) such as hexenols and hexenals? How well would the triad of GC-FID, GC-MS and PTR-MS be able to measure/constrain these seemingly ubiquitously produced GLVs in the forest air?

MINOR/TECHNICAL COMMENTS

Abstract, Line 1: "OH reactivity the reciprocal of its lifetime..." As it is the first line of the abstract it is necessary to specify that OH reactivity is the reciprocal of the chemical lifetime of the hydroxyl radical rather than use the pronoun "its".....

Abstract, Line 8: Please mention in parenthesis the typical % contribution of isoprene to the measured OH reactivity

Abstract, Lines 11-12: Maximum multiplier for what?

Page 5239; Lines 15-18: Please mention the make /model of j(O₁D) Filter radiometer or provide a citation if it is not a commercial instrument.

Figure 1: Why do both isoprene and monoterpenes show a dip at around 0.6 fraction of

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day before rising again? The plot for propene goes till -50 pptV. What does this suggest about the measurements? Figure 1: Were the isoprene oxidation products methyl vinyl ketone and methacrolein measured using the PTR-MS? If so, their profiles should also be shown in Figure 1. The ratio of these compounds to isoprene could also be a good tracer for oxidation of isoprene.

Figure 3: There seem to be large breaks in the dataset. What are these due to?

Page 5245: The phrase .. "This reduction is due to the breaking of certain emitted isoprene bonds by photolysis I suggest replacing "emitted isoprene bonds" by " bonds within the isoprene molecule and/or its oxidation products". I found "emitted isoprene bonds" bit odd

Figure 13: The colours of the traces and the simulations they correspond to are not clear. Please revise the Figure for better readability. At what first order loss is the closest agreement found between the measured and calculated OH reactivity?

Figure 11: The features (rising, peaks and fall) in the day time modeled and measured mean OH reactivity profiles do not appear to be in phase and neither does the trend seem to mirror. Can the authors speculate why?

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