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Atmospheric
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Discussions

Interactive comment on "Observations of total peroxy nitrates and total alkyl nitrates during the OP3 campaign: isoprene nitrate chemistry above a south-east Asian tropical rain forest" *by* E. Aruffo et al.

Anonymous Referee #2

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The manuscript by Aruffo et al. discusses the measurements of Total Peroxynitrates (TPN) and Total Alkylnitrates (TAN) using an LIF technique during the OP3 campaign. The measurements were made to investigate the role of NOx – VOC chemistry above a tropical rainforest. Comparisons with model simulations of the chemistry are presented. The use of the multi-channel LIF technique to provide data on broad classes of organic nitrates has provided interesting insights in the potential role of multifunctional organic nitrates on atmospheric chemistry, and this data set has the potential to be very interesting, too. However, I find it difficult to tell if the data is of sufficient quality

to be useful for this sort of analysis.I think the authors need to provide more detail to characterize their measurements and the associated uncertainties.

First, I think there should be some discussion not just about detection limits, but about total analytical uncertainty. Is this 20 – 25% uncertainty shown for Figure 1 typical of the measurement on all channels? Is it known if the uncertainty is the same for multifunctional nitrates, compared to the relatively easy to handle n-propylnitrate? Has the inlet passing efficiency been tested for isoprene and/or terpene nitrates?

Though it is not specifically stated, it appears that the measurement of each thermal dissociation channel also includes the species in the lower temperature channel. Thus, TAN = TAN +TPN + NO2, TPN = TPN + NO2, and NO2 = NO2, so successive subtractions are necessary to determine the TPN and TAN. I would be interested in how the errors propagate in this calculation.

Once the expected uncertainties are clarified, it is then important to discuss the remarkable (not in a good way) comparison shown in Figure 3. If the LIF measures only a fraction of NOy (about 50 – 65% according to Figure 7), then the CL method should always measure equal or greater concentrations of NOz. Figure 3 seems to show that this is true only about half of the time. (I am also puzzled by the reason for comparing medians instead of means for this figure.) This apparent difference deserves some more detailed investigation and discussion if the data are to be deemed credible. Perhaps the CL system is the source of the problem, but until the differences are evaluated and discussed, then the data remain suspect. In my evaluation, this problem needs to be resolved before any subsequent discussion of comparing chemical model data to the measurements.

Regarding the modeling, it is unclear if all of the monoterpenes are included in the model calculation, or if only a-pinene is modeled (as shown in Table 1). While a-pinene appears to be the most significant monoterpene, others are potentially important too. Other papers from OP3 suggest that OH reactivity from total monoterpenes is about

40% of the reactivity due to isoprene. Can this be clarified?

I don't know what to make of the daytime model comparison in Figure 6. With some optimization, the modeled and measured curves appear to coincide for some period, though the trends are not similar. (I am curious how the optimization works for such poorly matched profiles.) The addition of uncertainty analysis to this comparison and a discussion of why the trends might not track would be instructive. For example, I am curious about the claim that high values of TAN at night are due to NO3 oxidation of isoprene (and presumably other terpenes). Though the nighttime measurements of TAN appear to go through 2 maxima at night, the model shows low levels of TAN in the morning. What happened in the model to remove these nighttime oxidation products?

I didn't understand the data shown in Figure 7. Could the authors specifically state what was actually measured in Fig 7B? I didn't see any measurement of HNO3 mentioned, and the TAN were not speciated by the measurement into isoprene and other categories. Some clarification is needed.

The basic measurements are potentially interesting if one could have more confidence in understanding the uncertainties. It is an interesting comment that these measurements are lower than previous studies over forested areas, but that comparison makes little sense without some discussion of the VOCs at the different sites. The final summary statement that suggests "an important role of the isoprene nitrates chemistry in the ozone production and aerosol budget" may be true, but the authors do not make a good case for that conclusion (or even discuss this connection in the paper).

Finally, there were a number of typos: Fig 1. Swagelok not Swagelock; Fig 2. Propyl not Propil; Fig 3. Chemiluminescence not Chemiluniscence; Fig 4. PN and AN, not Pn and An; P.4802, l22, ICARTT not ICARITT.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4797, 2012.