

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 #1

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This manuscript describes a new instrument for measurement of NO₂, total alkyl nitrates and total peroxy nitrates. Measurements were taken over a tropical forest during the 2008 OP3 campaign, and were compared to a model. Model-measurement comparisons of total alkyl nitrates suggest that the parameters suggested in a different study (Perring et al.) do a good job in reproducing the data. The contribution of this paper to the scientific literature is the addition of new observations of reactive nitrogen oxides, and the conclusions state the "total PNs and total ANs have been successfully measured for the first time in [a tropical forest environment]". However, these obser-

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varations and conclusions are unsupported by the data and figures presented in this manuscript. I cannot recommend publication at this time.

I have four major areas of concern: (1) the paper does a particularly poor job of validating the analytical technique around which this manuscript is framed, (2) the manuscript lacks key pieces of information required to reproduce the experiment or judge the quality of the work, (3) Potential interferences within the instrument setup need to be quantified, and (4) there is a lack of explanation in the model-measurement comparison, which is weak and adds little scientific insight on isoprene nitrate chemistry.

Major Comments 1. Weak demonstration of analytical technique.

i. The major problem with this paper is that the one intercomparison (Figure 3) gives this reviewer significant doubt as to the accuracy and precision of the measurements. I am surprised that the authors describe the intercomparison as "somehow encouraging". This seems over-optimistic. The CL NO_z measurement includes organic nitrates, acyl peroxy nitrates and nitric acid, while the TD-LIF instrument includes only acyl peroxy nitrates and alkyl nitrates. Thus, the CL instrument should always measure the same or greater "NO_z" concentration, particularly considering the large (20–25%) contribution of HNO₃ to the NO_y budget shown in Figure 7 - let alone the exclusion of NO₃ and HONO from the TDLIF measurement! However, this is not the case, and the intercomparison is a shotgun blast, which includes points above and below the 1:1 line. Figure 3 does not support reliable measurements of total ANs or total PNs by this TD-LIF instrument, particularly considering the expected significant contributions of HNO₃ to the NO_y budget.

ii. Why was 19–23 July 2008 the only dates included in the intercomparison? The entire dataset (1–23 July 2008, as mentioned in the Site/Project description) should be presented as it will result in more robust statistics. Separating the intercomparisons into nighttime/daytime data could also be helpful in determining potential interferences.

iii. Note that the x-axis in Figure 3 should not read NO_z, as there is no HNO₃ mea-

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surement. This axis should read PNs + ANs.

iv. I disagree with the use of the n-propyl nitrate tank to demonstrate instrument specificity: the tests do not demonstrate specificity, as NO₂ was detected alongside n-propyl nitrate. Further, no demonstration of a peroxy nitrate measurement was shown to demonstrate that the instrument actually measures that type of compound. Was the NO₂ detected at exactly the same concentration by both the LIF and another instrument measuring the same gas flow? Was the n-propyl nitrate added to an inlet with exactly the same length and configuration as used in the field experiment? If not, then there is potentially an interference. One way to exclude such an interference is to show a field intercomparison of NO₂ from the chemiluminescence detector and NO₂ from the LIF. Please include such a figure.

v. The n-propyl nitrate addition (Figure 2) shows a particularly disturbing feature: as the temperature increase above 350C, the concentration levels off at 2 ppb, with a short 3-point spike between ~380C-400C of 2.3 ppb, before decreasing back to 2ppb. What was the exact concentration introduced? (Text only says '~2.3 ppb') Why was there a dip after 2.3 ppb? This feature suggests some sort of interference near the oven setting temperature, and/or a potentially strong sensitivity to oven setting. This feature and results need to be explained. They most certainly do not suggest a specific, accurate or precise measurement of alkyl nitrates.

2. Lacking information. There are several analytical questions that cannot be resolved with the information present in this paper:

i. What was the inlet setup for the CL NO_y detector? ie, was it adequate for HNO₃ detection? Did the detector measure both aerosol and gases, or gases-only? This setup affects the interpretation of the "NO_z" intercomparison.

ii. What is the sensitivity and Detection Limit for SPNs and SANs during the campaign? As this is the first description of this particular instrument, these parameters must be included.

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iii. Figure 1 shows some puzzling design features which should be either corrected or explained: - why is there a 3-way valve in the NO₂ calibration line (i.e., a unidirectional flow)? - the lengthy curved inlet suggests that multifunctional alkyl nitrates, such as hydroxyalkyl nitrates produced from isoprene oxidation, may be lost on the way into the ovens. Why was the curve introduced? What steps were taken to ensure that no nitrate loss occurred?

iv. The explanation of Figure 7 is confusing. The pie charts compare NO_y species between the models and the measurement: however, there are no measurements of HNO₃ described, so how does the second pie chart include observed NO_y species?

3. Potential interferences The authors describe Day et al's instrument as having inlet interferences that are <5%. However, this interference rate was site specific, as it depended on the presence of other radicals and relative humidity. The interference rate is potentially higher in other environments. More importantly, secondary chemistry in the inlet lines is minimized in the Day et al. instrument using a pinhole at the end of the ovens, which reduces pressure and thus interfering reactions and secondary chemistry. The authors describe using a PFA swagelok connector to reduce pressure, but this is not the same as a pinhole. What was the air pressure after the PFA connector? What was the flow rate in the tubing to the LIF connector?

While I understand that field experiments cannot be repeated, for future experiments, I strongly recommend using standard additions of calibration gases in order to determine the presence of interferences or secondary chemistry in the inlet lines.

4. Model-measurement comparison. i. What could be causing the model-measurement discrepancy in total PNs outside of the afternoon window? Perhaps the model is getting total PNs correct for the wrong reason?

ii. The altered model parameters to 5% yield with 70% recycling do indeed improve the model-measurement comparison, but still show a large (~50%) discrepancy in the afternoon. This discrepancy needs to be explained.

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Additional Comments 1. Organizational structure of manuscript. As written, the combined Results and Discussion section is difficult to read. I suggest these are separated into a Results section and a Discussion section. Further, the model description belongs in a different section, likely under following the Site and Instrument descriptions (which should similarly be separated).

2. Oven temperature explanation. p.4805, line 20 and p.4901, line 4: The authors do not seem to realize that the temperature setting at which bond dissociation will occur with unit efficiency is a function of both bond energy and residence time within the oven. Thus the temperature setting for this instrument is likely to be different from that of Day et al.'s instrument. What is this residence time, and what is the flow rate through the ovens?

3. The manuscript and caption of Figure 3 are contradictory as to whether the r or r^2 is 0.64 for the 'NO_z' intercomparison.

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