

We would like to thank the Reviewers and Dr. G. Philips for their detailed and insightful comments that have greatly improved our manuscript. We agree with many of their suggestions and have modified the manuscript as described below. In the following, we highlight general concerns of Reviewers and of Dr. G. Philips that were common and our effort to address these concerns. We then address comments specific to each Reviewer and to Dr. G. Philips below.

Their comments are included in italics with RC#1 (Reviewer #1), RC#2 (Reviewer #2) and GP (Dr. G. Philips) followed by our responses (AC).

RC#1: 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 TDLIF instrument, particularly considering the expected significant contributions of HNO₃ to the NO_y budget.

RC#1: 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.

RC#2: 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 NO_y (about 50 – 65% according to Figure 7), then the CL method should always measure equal or greater concentrations of NO_z. 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.

GP: Why were medians compared and not means? It would really nice to plot a time series of these two measures of NO_z. The scatter plot indicates large differences between the two measurements. There are times when NO_z Chem is measuring 300 ppt and the LIF techniques measures near zero and times where the reverse, nearly 200 ppt in the LIF and near zero in the Chem. NO_z. Does the comparative time series tell us the reason for these differences? For example, does one instrument over-measure relative the other during particular circumstances? The reason given on page 4807 does not seem to me to be sufficient and the discussion would benefit from a comparison of the time-series and a discussion of the pros and cons of both techniques in particular configuration in which they were operated in the tropical forest, for example:

AC: This criticism may have arisen because the referees and Dr. C. Phillips assumed that the CL instrument had an inlet designed to minimize HNO₃ loss. Unfortunately it was not the case, therefore we do not expect only points above the 1:1 line. Actually the periods when the TD-LIF measures more than the CL instrument are an indirect proof of Σ ANs contribution to NO_z, as reported in other sites (Day et al., 2003, Perring et al., 2009a), and usually not detected by the CL. Another source for uncertainty is that the CL inlet was not very close to the TD-LIF inlet (below for details on this point). These technical and logistic issues (unfortunately not easy to solve in a “really” harsh site as it was that chosen for this campaign) allowed us to make only a “qualitative” intercomparison, reported here, with the limitation above, this is why we used the term “somehow encouraging”.

Regarding the dataset we limited the intercomparison to the period 19-23 July 2008 because before the inlet of the chemiluminescence and that of the LIF were far apart since the LIF inlet was close to the sonic anemometer for flux observations. From the 19th of July we put the inlets of the two systems as close as possible but for logistic problems they did not sample exactly at the same point: the LIF inlet sampled at about 5 meters apart and about 3 meters above from the chemiluminescence.

We thank the reviewer #1 for calling the nighttime/daytime intercomparisons to our attention. In fact making this distinction we found out that most of the points when the TD_LIF observed up to 0.2 ppbv of NO_x and the CL close to zero are during nighttime. We speculated that this is due to Σ ANs, produced during nighttime by reactions of NO₃ with isoprene and other monoterpenes, detected by the TD_LIF but missed by the CL. There are several observations (i.e. Parrish et al., 1993; Williams et al., 1997, Day et al., 2003; Day et al., 2009) that show that in the NO_z budget accounted by Chemiluminescence observations there is a “Missing NO_z” and this could be explained with the contribution of Σ ANs.

We used the medians only because the CL data were available as 10 minutes medians of the observations. For this review we got from colleagues that runned the CL instrument a not averaged data and we tried the mean instead of the median but we did not get any sort of difference. The pros and cons of both systems are reported extensively in the introduction and instrumentation section of the manuscript, so we believe that there is no need for more discussion.

Here there are the changes and improvements we made in the manuscript to clarify and respond to the questions above:

- 1) Page 4807 line 13 We add the following paragraph: “The modest correlation between TD_LIF and chemiluminescence observations are due to several factors: 1) the NO_z observed by the TD-LIF does not include HNO₃, NO₃ and HONO, 2) the chemiluminescence inlet was not heated nor specifically designed to detect HNO₃, therefore even though it can be detected, it is not know the fraction of HNO₃ lost in the inlet, 3) the TD_LIF detects Σ ANs that are not measured by the chemiluminescence, 4) due to logistics constraints the TD_LIF inlet was installed 3 meters above and 5 meters apart from the chemiluminescence inlet. Dividing the intercomparison between daytime and nighttime observations (fig. 3) is evident that during nighttime most of the time the TD_LIF measured more NO_z than chemiluminescence, this can be explain with the Σ ANs detected by the TD_LIF (produced by the oxidation of isoprene and monoterpenes by NO₃) that can be a significant fraction of NO_z not detected by the chemiluminescence (Day et al., 2003; Perring et al., 2009b).”
- 2) Page 4807 line 11 We add: “because before the TD_LIF inlet was installed too far the chemiluminescence inlet”.
- 3) We modify the Fig. 3 highlighting nighttime data; this is the new Fig. 3:

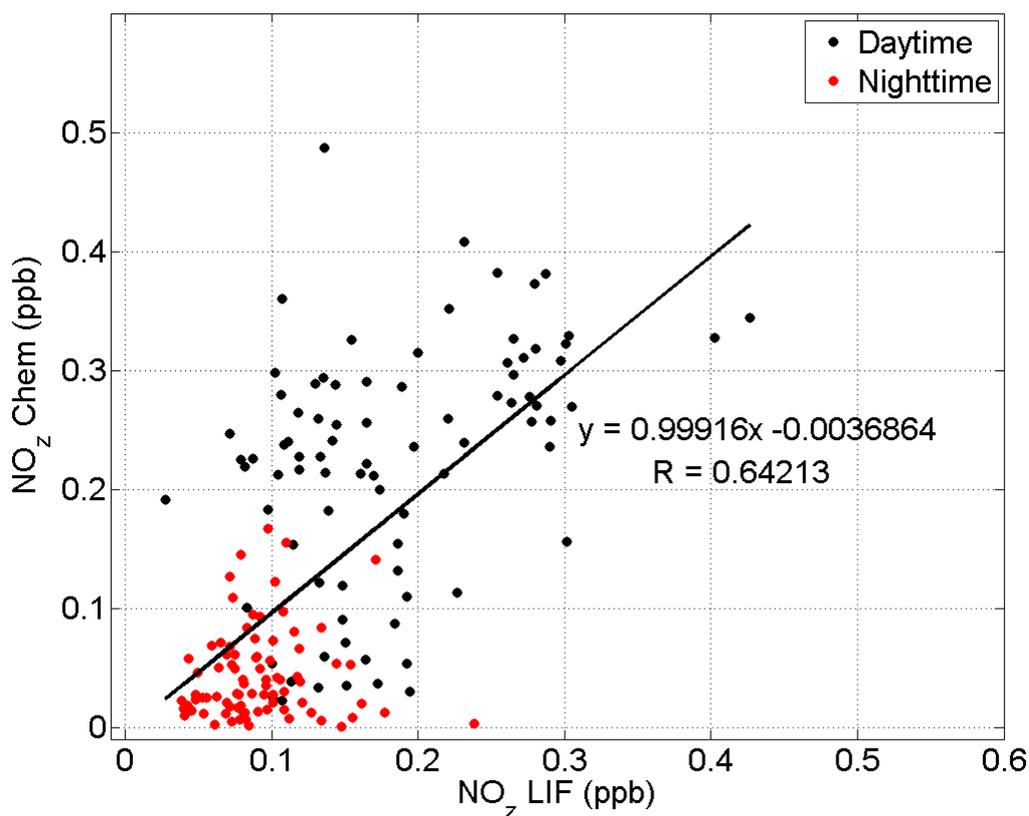


Figure 3

Intercomparison between NO_z measured by the Chemiluminescence and NO_z ($\Sigma\text{PNs} + \Sigma\text{ANs}$) measured by TD-LIF.

RC#1: 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 HNO_3 detection? Did the detector measure both aerosol and gases, or gases-only? This setup affects the interpretation of the " NO_z " intercomparison.

GP: How well does the chem. NO_z instrument measure HNO_3 ? Were there inlet losses along a long humid inlet?

AC: We agree with the Reviewer that the setup affects the interpretation of the " NO_z " intercomparison. The chemiluminescence instrument was not set up to measure HNO_3 . The inlet was not specifically designed to allow HNO_3 detection and was not heated. Therefore we cannot quantify the fraction of HNO_3 lost in the chem. instrument and the fractions detected.

Page 4807 line 13 We included this sentence: "the chemiluminescence inlet was not heated nor specifically designed to detect HNO_3 , therefore even though HNO_3 will be converted to NO and detected, the HNO_3 loss in the inlet could be significant."

RC#1: 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 HNO_3 described, so how does the second pie chart include observed NO_y species?

RC#2: 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 HNO_3 mentioned, and the

TAN were not speciated by the measurement into isoprene and other categories. Some clarification is needed.

AC: HNO₃ reported in Fig. 7 comes from a wet rotating denuder system that measured this species every hour. The Reviewer's point regarding the Σ AN speciation is correct: the TD_LIF cannot divide the Σ AN derived from isoprene from that derived from other species, therefore the Σ AN derived by isoprene was calculated using the isoprene measurements made during the OP3 campaign and assuming that the isoprene nitrates yield is 4.4% as suggested by laboratory studies (Chen et al., 1998, Sprengnether et al. 2002, Tuazon and Atkinson 1990, (corrected as discussed by Paulson et al. 1992). Actually laboratory studies above suggest an isoprene nitrates yield in the range from 4.4% to 15%, and we used the lower value.

Page 4812 line 11 We add the following paragraph: "The Σ ANs observations are not speciated, therefore the Σ ANs derived by isoprene are estimated using the isoprene measurements, made during this campaign, and assuming that the isoprene nitrates yield is 4.4% as suggested by laboratory studies (Chen et al. 2002). HNO₃ were observed every hour using a wet rotating denuder system."

We also add a reference for work done by Chen et al.:

Page 4814, Line 18: add a new reference: Chen, X., D. Hulbert, and P. B. Shepson, Measurement of the organic nitrate yield from OH reaction with isoprene, J. Geophys. Res., 103(D19), 25,563–25,568, 1998.

Responses to Referee #1

We are very grateful for the detailed and insightful comments made by the Referee that have greatly improved our manuscript. We agree with many of her/his suggestions and we have modified the manuscript as described below.

We address all of the concerns of the referee here. Many of the referee's comments were common to referee #2 and to Dr. G. Philips. Only comments not covered under the general comments section are covered here. Please see our response to the common comments above.

Below are the specific comments from the Referee #1 (RC#1) in italics followed by our response (AC):

RC#1: iii. Note that the x-axis in Figure 3 should not read NO_z, as there is no HNO₃ measurement. This axis should read PNs + ANs.

AC: In the figure caption is explained that the NO_z measured by the LIF is PNs+ANs.

RC#1: 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.

AC: We disagree with the reviewer comment for the following reasons: a) the n-propyl nitrate has been used for a long time as one of the Σ ANs to identify the heating temperature for a complete thermal dissociation into NO₂ of Σ ANs (Day et al., 2002, Farmer et al., 2006, Perring et al, 2009a; Perring et al., 2010). Usually n-propyl nitrate is synthesized in laboratory and its concentration is

not measured, because to find the dissociation temperature it is not necessary to know its amount. Using a tank of n-propyl nitrate we can report its concentrations sent to the LIF and what is measured and, since they are in agreement within the instruments uncertainties, it is a stronger proof of the selectivity and sensitivity of our system.

Regarding the demonstration of peroxy nitrate measurements we included that figure in the first submission but at the quick review the Referee suggested to remove it because the n-propyl nitrate test is enough to prove the instrument performance, because the difference between the dissociation temperature of alkyl nitrates and peroxy nitrates is constant (Day et al., 2002).

We definitively sent n-propyl nitrate to the instrument inlet with exactly the same length and configuration used in the field experiment to avoid any kind of interference.

We agree with the Reviewer that one way to exclude interferences is to compare NO₂ observations made with the chemiluminescence and the TD_LIF. This is one of the several tests we did and, as wrote in the manuscript, not reported because showed in a previous paper (Dari-Salisburgo et al., 2009). However to exclude any doubt we are including in this response the requested figure here (see below Fig. 1 supp.). From this figure is evident the agreement between the two systems.

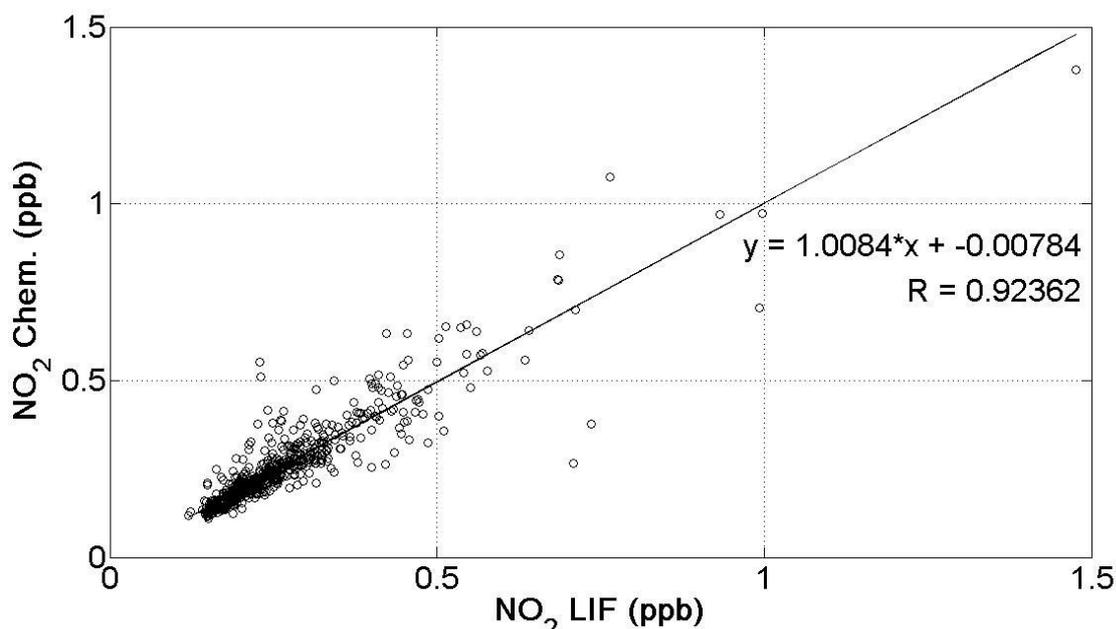


Figure 1 supp.. NO₂ measured by the chemiluminescence and by the TD_LIF during the OP3 campaign (19-23 July 2008)

RC#1: 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.*

AC: Basically the 3 points near 400°C are a bit higher than the points before and after because of an instability in the concentrations of n-propyl nitrate sent by the mass-flow controllers.

To make this clear we add the following sentence (Page 4806 line 14): “The oscillation of the NO₂ detected by the TD-LIF around 400°C was due to an instability in the concentrations of n-propyl nitrate sent by the mass-flow controllers”.

RC#1: 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.

AC: They are reported two times in the manuscript (page 7, lines 5-6 and page 8, lines 20-21).

RC#1: 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?

AC: The 3-ways valve in the NO₂ calibration line is there to purge the line. Figure 1 is a schematic of the dissociation box and to make the figure as compact as possible we drew the inlet line as close as possible to the dissociation tubes resulting in a curve of its line that is not real, since in the system it is completely straight.

RC#1: 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.

AC: We agree with the Reviewer, actually we tested for interferences and we reduced the pressure as in Day et al., after the heating tubes. This is described in page 4805 line 28.

RC#1: 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.

AC: It is clear that a connector cannot reduce the pressure, here we have forgot to write that we used a pinhole in the Swagelok connector to reduce the pressure after the heated tubes. The air pressure after the pinhole was 197 Torr (with a drop pressure of about 74%). The flow rate in each heater was 2 l/m. Page 4805 line 28: We include this sentence "where a pinhole reduces the air pressure".

Our system is equipped with a calibration system (see Dari-Salisburgo et al., 2009) that sends to the TD-LIF inlet standard NO₂ for calibration and zero air to check interference. In laboratory tests and during the field campaigns we used to send other standard gases like n-propyl nitrates, HNO₃ and NO into the instrument inlet to check for potential interferences.

RC#1: 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?

AC: Our feeling is that model-measurement discrepancy in total PNs outside of the afternoon window is caused by a couple of reasons: 1) nighttime chemistry that may have a big impact on early morning comparison and 2) dry deposition that, as pointed out in this manuscript as well as in

other ones, have a big impact on the performance of the model. Probably a further improvement is to include dry deposition that changes with the hours of the day to replace a constant value, as used here.

RC#1: 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.

AC: Here probably the Reviewer meant once again a model-measurements discrepancy in the morning. We suppose that this is mainly due to a nighttime chemistry (NO₃+isoprene and NO₃+monoterpenes) not described in detail by the model.

RC#1: 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).

AC: We agree with the Reviewer about the proposed organization, actually it was how we submitted the manuscript at the beginning, we rearranged it as it is now after the quick reviewer due to a specific request of one Reviewer.

RC#1: 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?

AC: We agree with the Reviewer that the temperature setting is a function of bond energy and residence time, therefore we determine it for all the ovens using synthetic gases produced in the lab or from a tank, as reported in figure 2. By the way the temperatures of our ovens during the observations reported here were 200°C and 400°C for Σ PNs and Σ ANs respectively, whereas Day et al. (2002) reported 150°C and 350°C. Indeed these temperatures have to be checked (as we and all the other groups that use this technique usually do) for each oven because it can be different due to construction differences. The residence time and the flow rate through the ovens are 36 ms and 2 l/m, respectively.

RC#1: 3. The manuscript and caption of Figure 3 are contradictory as to whether the r or r^2 is 0.64 for the 'NO_x' intercomparison.

AC: We changed the figure description in the revised manuscript accordingly with what reported in the text (see above the new Fig. 3).

Responses to Referee #2

We are very grateful for the detailed and insightful comments made by the Reviewer that have greatly improved our manuscript. We agree with many of her/his suggestions and we have modified the manuscript as described below.

We address all of the concerns of the referee here. Many of the Reviewer's comments were common to Reviewer #1 and to Dr. G. Philips. Only comments not covered under the general comments section are covered here. Please see our response to the common comments above. Below are the specific comments from the Reviewer # 2(RC#2) in italics followed by our response (AC):

RC#2: 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.

AC: The inlet is made using only PFA tubing and PFA junctions to minimize the wall loss. From the laboratory tests that we made using some nitrates and HNO₃ we are confident that the loss is below 5-6%. As regards the error propagation, it is evident that in the subtraction the errors of each measurements are summed using the propagation error formula:

We determine $\sum\text{ANS}$ after one subtraction: $\sum\text{ANS}(\text{signal}) - \sum\text{PNs}(\text{signal})$, the same is true for $\sum\text{PNs}$: $\sum\text{PNs}(\text{signal}) - \text{NO}_2(\text{signal})$, where $\sum\text{ANS}(\text{signal}) = \sum\text{ANS} + \sum\text{PNs} + \text{NO}_2$, $\sum\text{PNs}(\text{signal}) = \sum\text{PNs} + \text{NO}_2$ and $\text{NO}_2(\text{signal}) = \text{NO}_2$. The instrumental errors are: 8%, 12% and 18% for NO₂, $\sum\text{PNs}$ and $\sum\text{ANS}$, respectively.

Page 4804 line 22: We add the following sentence: "The instrumental errors are: 8%, 12% and 18% for NO₂, $\sum\text{PNs}$ and $\sum\text{ANs}$, respectively."

RC#2: 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?

AC: In the calculation are included a-pinene and limonene. For a mistake in table 1 we forgot to include limonene (we will include it in the revised paper). We agree that there are other significant monoterpenes, but we included only those observed during the campaign. The results reported in other OP3 papers, where they showed that the oxidation of isoprene accounts for about 40% of the reactivity (this includes all the products of the oxidation of isoprene). In our simulation we focused on the isoprene nitrate (IN) production and in particular the $\sum\text{ANs}$ produced from IN that is 5.4% and 9.5% from the model and from the observations, respectively. These simulations were made to tests results observed in other field campaigns (i.e. Perring et al., 2009a).

Table 1 we add the following row:

Compounds	Median (ppt)	Mean (ppt)	Standard deviation (ppt)	Range (ppt)
Limonene	82.8	75.4	18.1	45.9 to 95.9

RC#2: 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?

AC: The model was optimized for daytime chemistry simulations, therefore the NO₃ chemistry during the night was missed and this can explain the big disagreement during early mornings. Regarding the trends we believe that a constant dry deposition during the day and night is the big issue that avoid a good trend agreement between observations and model simulations.

RC#2: 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).

AC: We agree with the reviewer that Σ PNs and Σ ANs levels are controlled by the VOC load, however here we reported only Σ PNs and Σ ANs and the statement that they are lower than other site is true to our knowledge. A wider comparison with other sites including VOC is out of the scope of this paper. The same for the role of isoprene nitrates on aerosol and ozone studied in several regional and global models, here we reported the references but the impacts are out of the scope of this manuscript.

RC#2: 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, 122, ICARTT not ICARITT.

AC: We corrected these typos:

This is the new Fig. 1 with where “Swagelok” replaces “Swagelock”:

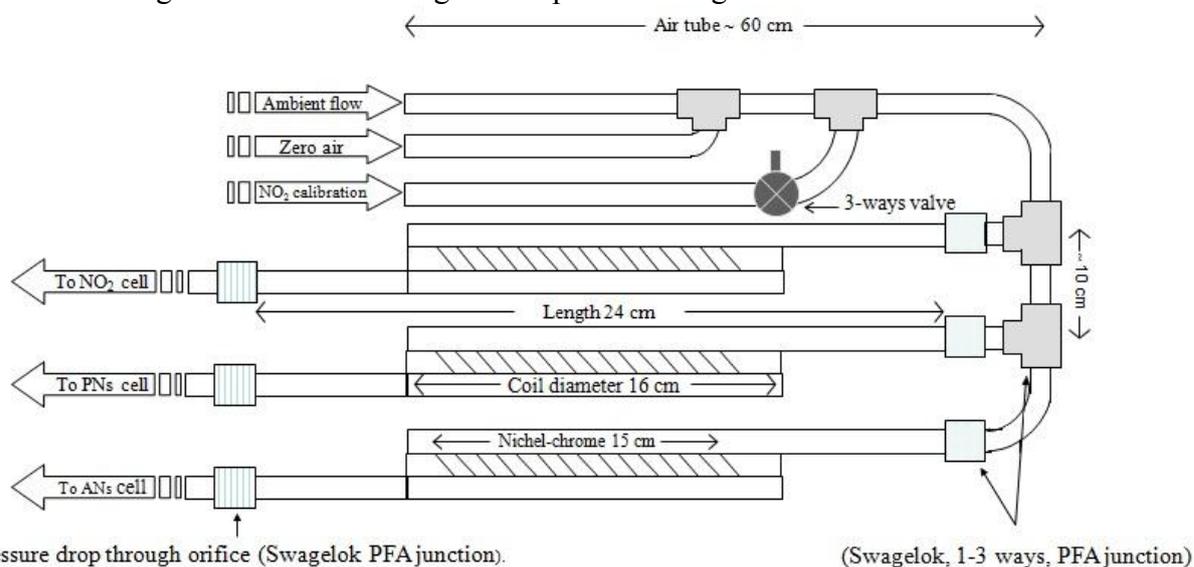


Figure 1.

Schematic of all the components of the inlet system. In the OP3 configuration were used three channels (two heated).

Page 4824 Fig. 2 caption: We corrected the typo by substituting “*Propil*” with “*Propyl*”.

Page 4825 Fig. 3 caption: We corrected the typo by substituting “*Chemiluniscence*” with “*Chemiluminescence*”.

Page 4826 Fig. 4 caption: We corrected the typo by substituting “*Pn*” with *PN* and “*An*” with *AN*”.

Page 4802 line 22: We corrected the typo by substituting “*ICARITT*” with “*ICARTT*”.

Responses to Dr. G. Philips

We thank Dr. G. Philips for his constructive comments and suggestions. Below are the comments from Dr. G. Philips (GP) followed by our response (AC):

We address all of the concerns of Dr. G. Philips here. Many of the Dr. G. Philips’s comments were common to all two Reviewers. Only comments not covered under the general comments section are covered here. Please see our response to the common comments above.

Below are the specific comments from the Dr. G. Philips (GP) in italics followed by our response (AC):

GP: Page 4807 and figure 3 Comparison of NO_z from chemiluminescence NO_z and LIF NO_z. There is a correlation value, (R or R²), which is correct, the plot or the text? What was fitting method used? Did the fit account for uncertainties in both measurements?

AC: The text is correct, we will correct the plot in the revised manuscript. We used a least squares fit and we accounted for the uncertainties in both measurements.

GP: How does the failure to measure HONO, NO₃ and HNO₃ account for the time periods where the LIF instrument measures more than the Chem. NO_z?

AC: Our hypothesis is that the Σ ANs observed by the TD_LIF is not detected by the CL. This is supported by several field observations (in different environments) where are reported high contributions of Σ ANs on the NO_z budget (Day et al., 2003, Day et al., 2008). Here we observed that the TD_LIF measured more NO_z than the CL only during nighttime, this is compatible with laboratory observations in which were reported high levels of Σ ANs as a result of NO₃+isoprene and NO₃+monoterpenes reactions (Perring et al., 2009b, Paulot et al., 2009). Field and lab observations support our hypothesis that the Σ ANs not detected by CL, but observed by the TD_LIF, can explain the nighttime discrepancy between TD_LIF and CL measurements. On the other hand we cannot exclude instruments interferences in the TD-LIF and/or the CL to explain this discrepancy, however all the tests we did or made by other groups up to now, have never showed any sort of interferences in the TD_LIF.

GP: If HNO₃ was 25% of the NO_y and the LIF did not measure it, why is there not a gradient larger than one in the comparison fit?

AC: Because chemiluminescence, as explained above, is not arranged to measure HNO₃, we do not expect a gradient larger than one in the comparison fit.

GP: The abstract and the conclusions state that the model reproduced the PNs well, but the plot of the comparison shows a disagreement for 6 out of the 10 hours. What is the definition of good

agreement? Does the model get it right for the wrong reason in the middle of the day or wrong for the right reason at either end of the day?

AC: To be quantitative in the text we use the sum of the squared differences (defined in page 4811 line 24), which is one of the methods used to compare the observations with the model simulations. On the basis of this parameter we decided the set of parameters that minimize the discrepancy between measured and modeled Σ PNs and Σ ANs. However we pointed out that the agreement for Σ PNs is good between 12:00 and 16:00, but outside of this period the model overestimates the observations (see page 4811, lines 11-12).

GP: It does not seem to me that there is any improvement in the fit between the model and the experiment for the alkyl nitrates by adjusting yields and recycling. It gets better in parts and worse in others. The whole shape of the diurnal is not particularly similar suggesting that the model is not simulating the situation well and therefore the statement regarding the recycling and yield is not supported by this data.

AC: We agree with GP comment, however we believe that using a parameter like the sum of the squared differences, we can compare different simulations being quantitative and consequently make some constraints on the parameters used in the model simulations. The diurnal shape is not well reproduced (except for some periods) and this is mainly due to a constant deposition rate during the day. We think that a time-dependent deposition rate could be a further progress to reconcile observations and model simulations.

GP: I find figure 4 very difficult to read.

AC: We improved the quality of Fig. 4, below the new Fig. 4:

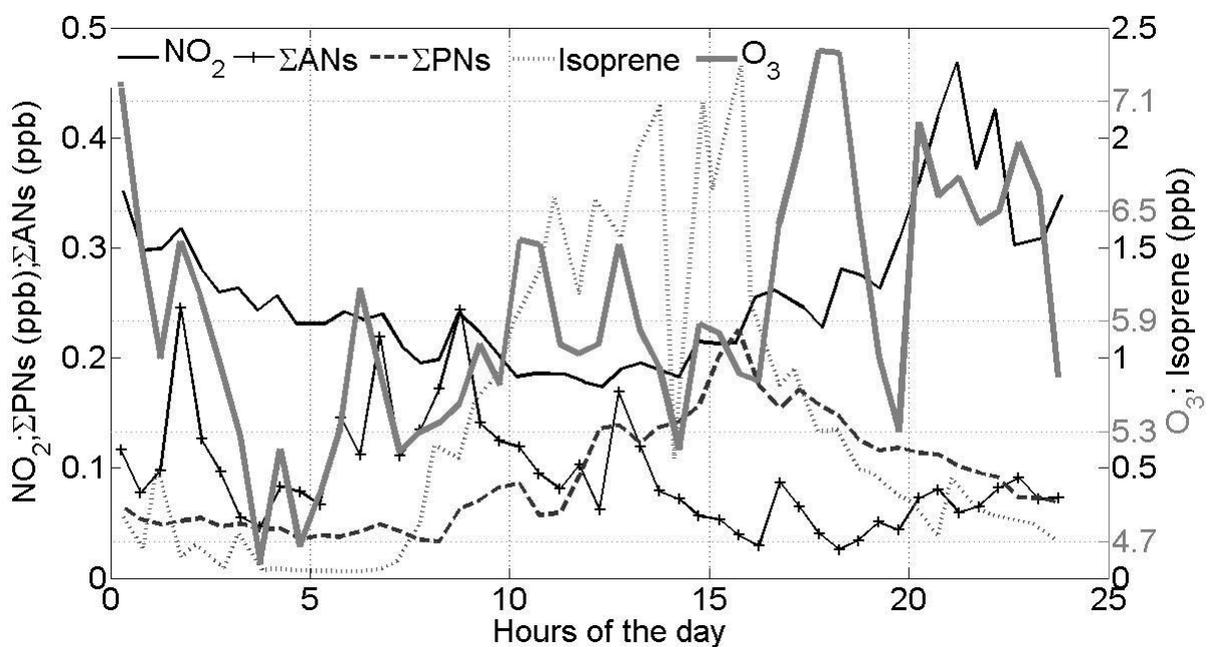


Fig. 4 Diurnal mean of NO₂, Σ PNs, Σ ANs, O₃ and isoprene observed at the Bukit Atur tower (8 m above the surface) during OP3 campaign.

GP: These are interesting measurements in a location which is rarely studied and it would be of benefit to explore the measurements in themselves in greater detail before using a box model to draw conclusions about particular specific mechanisms in model systems.

AC: We completely agree with this comment, however we believe that data in this location would contribute to reduce the uncertainties in the oxidation of isoprene nitrates raised in recent studies in other US forests (Horowitz et al., 2007, Perring et al., 2009a) and in laboratories studies (i.e. Paulot et al., 2009).

References

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