Author response

In addition to the changes listed in the point-by-point response, the following changes were made:

1. An error was discovered in how the 0-D photochemical modeling was conducted. The revised model results are used in the revision. The conclusions of the paper remain unchanged. The main difference between the original modeling and the revised modeling is that the relative speciation of peroxy radicals predicted by the four chemical mechanisms (RACM2, RACM2-LIM1, MCM 3.2, and MCM 3.3.1) is now very similar as described in the following two paragraphs from section 3.3 of the manuscript:

"Measured and MCM 3.2 modeled concentrations for 16, 22, and 24 July are shown in Fig. 8. On all three days the relative contributions from the various types of peroxy radicals are comparable. At 15:30 –when concentrations are highest – the modeled peroxy radicals comprised 30% $C_5H_8(OH)O_2$, 35% HO_2, 26% CH_3O_2 and 7% $CH_3C(O)O_2$. The four chemical mechanisms vary little in the predicted relative speciation (SI). The $[XO_2]/[HO_2*]$ ratio modeled by MCM 3.2 between 15:00 and 16:00 is 1.4 for 16 and 22 July and 1.45 on 24 July. The measured $[XO_2]/[HO_2*]$ ratio is close to unity on 16 and 22 July, and between 1.2 and 1.5 on 24 July. Increasing these measured ratios by 20% to account for the calibration comparison produces adjusted measured $[XO_2]/[HO_2*]$ ratios of 1.2 on 16 and 22 July and 1.4 to 1.8 on 24 July. After accounting for the 20% calibration difference, the modeled and measured ratios agree to within the experimental and model uncertainties.

Measured $[XO_2]$ mixing ratios are 20 to 30% lower than the MCM 3.2 $[XO_2]$ on 16 and 22 July but agree more closely on 24 July (measured/modeled ratio varies from 0.8 to 1.15). The comparison between measured $[HO_2*]$ and modeled $[HO_2*]$ for these three days exhibits more variability (Fig. 8). Although all four chemical mechanisms predict a very similar relative speciation, there are variations in the absolute peroxy radical concentrations predicted. MCM 3.3.1 concentrations are very similar to those from MCM 3.2, but RACM2 and RACM2-LIM1 predict 26% and 42% higher peak concentrations, respectively. Further details can be found in the SI."

2. We have revised the following section in order to address the open comment from Dr. Andres-Hernandez:

"Similarly, XO_2 measurements from two CO-based chemical amplifiers during the airborne African Monsoon Multidisciplinary Analysis (AMMA) campaign differed by factors of 2-4 when the usual relative humidity-dependent calibration (Mihele and Hastie, 1998) was used for the chemical amplifier data, though the performance of one of the instruments was not assessed with in-flight calibrations (Andrés-Hernández et al., 2010). The relative humidity dependence of the chemical amplification technique is addressed in a variety of ways. Most research groups characterize their instrument's amplification factor (chain length) as a function of relative humidity (RH) which they then apply to their measurements based on the ambient RH. In some cases, because the RH in the amplification chamber can be lower than ambient because of reduced pressure and higher temperatures, the variability in RH can be considered negligible compared to other experimental uncertainties (Andrés-Hernández et al., 2010;Kartal et al., 2010). In one case the need to apply an RH-dependent calibration was disputed (Sommariva et al., 2011) despite strong experimental evidence (Butkovskaya et al., 2007;Butkovskaya et al., 2005;Butkovskaya et al., 2009;Mihele et al., 1999;Mihele and Hastie, 1998;Reichert et al., 2003)."

3. We have changed the method by which the linear fit was determined for figure 6 – only data between 09:00 and 22:00 are now used due to the low signal-to-noise of the nighttime measurements. This is further described on page 5 of this document.

Our responses to the comments from reviewer #1 are below:

This manuscript details the results of an intercomparison carried out in the field which compares total peroxy radicals using a chemical amplification system with HO2* (which comprises HO2 and a fraction of RO2 radicals) measured by the FAGE technique. Although we may expect HO2* and total RO2 to be well correlated, the comparison presented here is the detected sum of ambient RO2 by two instruments which do not measure different RO2 radicals with the same efficiency, and so is a tricky undertaking. The authors have employed a variety of models with differing chemical mechanisms to predict the composition of peroxy radicals present and from there predict the ratio of total RO2 : HO2* for comparison with the observations. I think on the whole, the approach taken to compare these two observations has led to a meaningful comparison and has demonstrated the performance of the new ECHAMP instrument in the field. I recommend publication once the following comments have been addressed:

Abstract: One concerning result is that the XO2:HO2* ratio is periodically less than one, which the authors themselves note is not possible and must indicate a problem with one or both instruments. A ratio of 0.8 is mentioned in the abstract, but no comment on this low ratio is given until the final pages of the manuscript. I suggest the authors are more upfront about this problem and comment on ratios <1 indicating instrumental issues in the abstract and conclusion.

We have added the following sentence to the abstract:

"Time periods in which the ambient ratio was less than one are definitely caused by measurement errors (including calibration differences) as such ratios are not physically possible."

and to the abstract:

"The measured $[XO_2]/[HO_2^*]$ ratios usually differed from the ratios predicted by zero-dimensional photochemical modeling by less than the combined measurement and modeling uncertainties, though the lowest ratios observed (0.8) are not physically meaningful and therefore must be due to measurement errors."

Pg 3, line 18: 'Measurements of OH by laser-induced fluorescence technique can be affected by a sampling related interference which can exceed the actual concentration of OH..'. This interference is very much dependent on the FAGE instrument design. There are several FAGE instruments in operation that do not observe an OH interference and so this statement needs to be qualified to make this clear.

We have edited that sentence as follows:

"Measurements of OH by the laser-induced fluorescence technique can be affected by a sampling-related interference which can exceed the actual concentration of OH (Mao et al., 2012), though the magnitude of this interference and even its presence varies greatly depending on instrument design."

Pg 3, line 25: '~90%' is slightly misleading. In many of the FAGE instruments tested, α is not as high as 90% for the β-hydroxy peroxy radicals; α was as low as 17% in the cited 'Whalley et al., 2013' paper.

We have edited that section as follows:

"The sensitivity of the LIF-FAGE technique to each type of organic peroxy radical varies with the amount of NO added for the conversion and is instrument-dependent but in general is highest (up to ~90%) for β–hydroxy peroxy radicals derived from alkenes and lowest for those derived from small alkanes (Fuchs et al., 2011;Lew et al., 2018;Whalley et al., 2013). This RO_2 interference can be greatly reduced by use of lower NO concentrations or reaction times, yielding conversion efficiencies for isoprene-RO_2 under 20% (Feiner et al., 2016;Fuchs et al., 2011;Tan et al., 2017;Whalley et al., 2013)."

Pg 7, line 16: please provide the typical Li used for the ambient measurements.

The previous sentence has been edited to clarify that equation 2 is not used to calculate ambient measurements:

"Including a sampling loss term, the sensitivity "α" of ECHAMP to individual organic peroxy radicals relative to that of HO_2 can be estimated using Equation 2:"

Later in that paragraph and in the SI, the sampling losses are described.

SI, section S3: Could the authors comment on whether the loss rate of radicals is solely dependent on residence time? Does the shape of the sampling cross and the PFA tees (the sampled air has to flow around corners) impact the loss rate? This could perhaps be determined if the transmitted radical signal was plotted against residence time in the 4 lengths of tube. An intercept would indicate additional losses in the cross piece.

Section S3 describes two types of radical loss tests: 1. measuring the transmission of HO_2 through four lengths of tubing, and 2. measuring the HO_2 signal when sampling through the sampling cross compared to sampling directly at the reaction chamber. As stated in the SI,

"Similarly, the second method – comparing the ECHAMP signal when sampling a radical source through the sampling cross or directly into one of the reaction chambers – indicated overall losses of less than 4% for an HO_2 source."

Further details of the sampling losses (including loss rates onto several types of material) are the subject of a separate manuscript currently under preparation.

Pg 7, line 23: The authors discuss the impact of alkyl nitrate and alkyl nitrite formation on the sensitivity of ECHAMP to individual RO2 species, but could the authors also comment on the expected sensitivity of ECHAMP to RO2 species which are generated

from alkene + NO3 reactions, so contain an NO3-adduct? ROxLIF instruments are
expected to have a low sensitivity to these types of RO2 (Whalley et al. ACP, 2018).
If a similarly low sensitivity for these RO2 is expected in ECHAMP, could the authors
discuss how this may influence the measured vs modelled ratio during the night?

We have not yet conducted experiments in the lab to determine the sensitivity of ECHAMP to RO2 produced from NO_3 reactions, though we do expect that when mixed with NO and ethane these peroxy radicals will lead to increases in NO_2. We have added the following sentence regarding the sensitivity of ECHAMP to these radicals at the end of section 2.2:

"We estimate an elevated uncertainty of ~50% for the measurements at night as we have not investigated the sensitivity of ECHAMP to peroxy radical produced by ozonolysis and NO_3 reactions."

We are reluctant to comment on the measured vs. modelled ratio during the night for two reasons: 1. The measurements (of both peroxy radicals and the crucial compound NO) had much lower signal-to-noise ratios and higher uncertainties at night, and 2. The measurement height was only 3 meters which complicates the interpretation of the data since the air was usually stagnant.

Pg 8, line 20: Could the authors make it clear which conversion efficiencies were measured and which have been estimated.

The sentence has been re-worded to clarify:

"The conversion efficiencies for other major RO_2 radicals are estimated as 5% for CH_3O_2 and…"

Pg 8, line 22: The authors reference the Fuchs et al., 2011 work on RO2 interferences
in FAGE instruments. 'α' is very much dependent upon the specific FAGE instrument
and experimental conditions used, however. Using α determined using another FAGE
instrument would likely bias the HO2* model measurement comparison. The authors
need to make it clear how α was estimated for the RO2 species not experimentally
tested with the IU-FAGE. Specifically, how was α = 0.7 derived in equation 5 on page
14, line 21?

The sentence on pg 5 has been edited as follows:

"The conversion efficiencies for other major RO_2 are estimated as 5% for CH_3O_2 and the acetyl peroxy radical ($CH_3C(O)O_2$), 8% for ethyl peroxy radical ($C_2H_5O_2$), and 31-55% for RO_2 compounds from the OH oxidation of high-molecular-weight hydrocarbons based on comparisons to several other interference tests (Fuchs et al., 2011;Griffith et al., 2016;Lew et al., 2018)."

The value of 0.7 for the "other" category was chosen since light alkanes, which have low values of α, comprise a minor component of the OH reactivity and most other RO_2 compounds have α values near 0.7.

We have added the following sentences:

"The α values for ECHAMP are based on the calculated yields of alkyl nitrates and alkyl nitrites as described in section 2.2. For LIF-FAGE, the α value for $C_5H_8(OH)O_2$ was measured and α for CH_3O_2 and $CH_3C(O)O_2$ are based on measured yields to several similar instruments all of which have measured values less than 5%. An α of 0.7 is assume for the "other" category since most alkenes have α values between 0.5 and 0.9, and small alkanes, which have lower values, account for a small portion of the OH reactivity (Lew et al., in preparation)."

Pg 12, line 12, fig 3: Add the limit of detection of XO2 to the figure. Also make it clear in the figure caption which instrument measured HO2+RO2

The limit of detection (LOD) depends on the relative humidity and the variability in the ambient ozone concentration as described in Wood et al. 2017. To exactly determine the LOD at any given time requires operating both reaction chambers in background mode, precluding simultaneous knowledge of the exact LOD and the ambient concentrations. Rather than add an estimated limit of detection to the figure, we have added the following text to the caption:

"The sum of $[RO_2]$ and $[HO_2]$ was measured by the ECHAMP instrument, with a detection limit typically between 1 and 2 ppt (signal-to-noise ratio of two)."

Pg 12, section 3.3: The authors acknowledge that comparing the 30 min averaged ECHAMP measurements to a single FAGE measurement made during the 30 minute bin is not ideal. I worry that this approach could introduce bias into the comparison, given that the peroxy radical concentrations will generally be increasing throughout the morning hours and then decreasing during the afternoon and evening. Are the FAGE HO2* measurements made at the midpoint of each 30 minute bin? Does the gradient XO2 vs HO2* vary if the FAGE measurement falls at the start of a 30 minute bin? I think the authors need to explore the robustness of this averaging approach used for the ECHAMP data to satisfy the reader that the two measurements are comparable at the times they are taken.

We have majorly revised the paragraph below. We have also changed the averaging time used for the linear regression:

"A bi-variate linear regression of the XO_2 and HO_2^* measurements between 09:00 and 22:00 yields the relationship $[XO_2] = (1.08 \pm 0.05) [HO_2^*] – (1.4 \pm 0.3)$ ppt (Fig 6.). The regression is restricted to this window of time because of the degraded precision of the ECHAMP measurements at night due to the higher relative humidity. The $[XO_2]/[HO_2^*]$ slopes were highest on the last two days of measurements – 24 and 25 July, with slopes of 1.25 and 1.08, respectively, or 1.5 and 1.3 after adjusting for the calibration difference. These two days were characterized by the highest mixing ratios of peroxy radicals, O_3, isoprene, and the anthropogenic VOCs ethene and ethyne. The lowest $[XO_2]/[HO_2^*]$ ratios were observed on 13 July during which a passing thunderstorm led to low concentrations during mid-day with higher values before and after the storm. The higher $[XO_2]/[HO_2^*]$ ratios observed later in the field campaign may simply be the result of a change in sensitivity in one of the instruments. These linear are difficult to interpret, however, since the XO_2 measurements are 30 minute averages and the HO_2^* measurements are 1-minute averages taken every 30 minutes. A regression of the binned data shown in Fig. 5 gives the relation $[XO_2] = 1.0 \pm 0.14 [HO_2^*] + (1.5 \pm 1.6)$ ppt; accounting for the calibration difference gives an adjusted slope of 1.2. The $[XO_2]/[HO_2^*]$ ratio using the binned data was highest between 9:45 and 10:45 (Fig. 5), but was between 0.9 and 1.1 between 14:45 and 19:15. This overall temporal trend is apparent in several days (Fig. 4). Applying a 30-min offset to the XO_2 data largely removes this trend and leads to

fewer time periods when $[XO_2]/[HO_2^*]$ was less than 1.0, but such an offset does not agree with the synchronized time-base of both measurements. The two instruments' different averaging times and precision levels preclude further assessment and conclusions regarding possible time offsets."

Page 13, line 6 - 8: the authors report the highest XO2:HO2* ratio on days when isoprene and ethene concentrations were most elevated. This is unexpected, given the high sensitivity of FAGE to alkene-derived RO2 species. Could the authors comment on this finding?

We have edited that sentence:

"These two days were characterized by the highest mixing ratios of O_3, isoprene, and the anthropogenic VOCs ethene and ethyne. The high $[XO_2]/[HO_2^*]$ ratios observed those days may simply be the result of a change in sensitivity in one of the instruments."

Page 13, line 10: The data in figure 5 has already been binned and then averaged over 9 days. Does the linear regression on the figure 5 data provide a reduced uncertainty relative to the data presented in figure 6? Errors on the fit should be included. I may have misunderstood, but don't both linear regressions use the same data (just one if further averaged into a diurnal)? Does the change in the regression slope as the data is averaged further suggest that the binning approach is biasing the correlation?

The binning is useful because there are occasional gaps in the time series (e.g., the morning of 14 July). Without the binning, the morning data is slightly "underrepresented" because of that gap. We have changed the caption as follows (including the fit errors):

"Figure 6. Correlation of ambient $[XO_2]$ measured by ECHAMP with $[HO_2^*]$ measured by IU-LIF-FAGE. The linear fit is for data between 09:00 and 22:00, indicated by the points with green circles. The equation of the fit is $[XO_2] = (1.08 \pm 0.05) [HO_2^*] - (1.4 \pm 0.3)$ ppt."

Additionally, we have edited the section below discussing the point of using the binned data:

"These linear regressions are difficult to interpret, however, since the XO_2 measurements are 30 minute averages and the HO_2^* measurements are 1-minute averages taken every 30 minutes. *Furthermore, the regression with all of the data gives equal weight to each (daytime) measurement, which due to occasional gaps in the time series (e.g., the morning of 14 July), can result in certain times of day being underrepresented.* A regression of the binned data shown in Fig. 5 gives the relation $[XO_2]$ = 1.0 ± 0.14 $[HO_2^*]$ + (1.5 ± 1.6) ppt; accounting for the calibration difference gives an adjusted slope of 1.2. *Using the binned data gives equal weight to each 30-minute time period (between 09:00 and 22:00).* $[XO_2]/[HO_2^*]$ ratio using…"

That is, the change in regression slope is not due to the binning approach biasing the correlation but rather results from the different weightings as discussed in the text above.

Page 13, line 23: Although I appreciate that the authors do not know the reason why the measurements diverge on the 22nd, the possible explanation 'a transient interference in the HO2* measurement when sampling ambient air..' is rather vague. Could the authors elaborate on what they think this transient interference may be or what it may be related to?

We agree that the explanation of a "transient interference" is vague. We have removed the "transient interference" text and changed that sentence as follows:

"Measurements of VOC composition and NOx do not support such a fast change in peroxy radical composition, suggesting that these observations were more likely the result of an instrumental issue, though we are unable to identify the cause."

Pg 13, line 25 –Pg 14, line 4: I suggest moving this paragraph to the start of section 3.3. It is important that the α of two instruments to different RO2, and how the ratio is expected to change as ambient RO2 types vary, is set out at the beginning of this section.

We agree and have made that paragraph the 2nd paragraph of section 3.3 in the revision.

Section 3.3: in general, there is a lot to consider when comparing HO2* and XO2 measured and modelled. The ratio varies with RO2 type present and calibration differences also need to be considered. A table detailing the measured HO2*, XO2 and XO2:HO2* and the 4 modelled HO2*, XO2 and XO2:HO2* on the individual days and campaign average would help to clarify the text.

We hope that the majorly revised paragraph quoted earlier (starting with "A bi-variate linear regression…") has clarified these issues. For the revision we conducted and have presented modeling using only the three days with measurements of HO$_2$* (LIF), XO$_2$ (ECHAMP), and NO: July 16, 22, and 24. We have added the requested table to the SI (and below) that summarizes the daytime (13:00 – 18:00) concentrations for measured HO$_2$*, XO$_2$, and their ratio, along with the same quantities from the 4 models. We have not added additional text as the existing sentence should be sufficient: "*Further details can be found in the SI." (pg 16, line 23)*

Table S1. Summary of modeled and measured concentrations and ratios between 13:00 and 18:00.

	16 Jul	22 Jul	24 Jul
Measured $[XO_2]$	28.4	38.9	58.6
$[HO_2*]$	26.9	34.5	41.5
$[XO_2]/[HO_2*]$	1.06	1.13	1.41
MCM32 $[XO_2]$	38.1	44.1	55.2
$[HO_2*]$	29.8	31.4	38.3
$[XO_2]/[HO_2*]$	1.39	1.41	1.45
MCM331 $[XO_2]$	49.8	47.5	57.2
$[HO_2*]$	35.2	32.8	38.9
$[XO_2]/[HO_2*]$	1.42	1.46	1.48
RACM2 $[XO_2]$	66.1	56.7	69.4
$[HO_2*]$	50.3	42.4	51.1
$[XO_2]/[HO_2*]$	1.32	1.34	1.36
RACM2-LIM1 $[XO_2]$	81.3	67.4	79.2
$[HO_2*]$	60.3	49.3	57.5
$[XO_2]/[HO_2*]$	1.35	1.37	1.38

Figure 4: The caption on the figure is obscuring the top x-axis
This has been fixed in the revision.

Figure 5: There does not seem to be a measured ratio for each 30 min point? Between the hours of 4 – 8, there are only 3 points?

Because of the low signal-to-noise ratios for the nighttime measurements (especially by ECHAMP), the ratio of the measured $XO_2/[HO_2*]$ varies greatly at night, from 0.3 to 2.1, and so some of those points were off-scale (the graph's axis was from 0.8 to 1.8). For the revision, we only show the ratio for time periods between 08:00 and 22:00, with the following revised caption:

"…The upper plot shows the $[XO_2]/[HO_2*]$ ratio - both measured by the two instruments and modeled using the MCM 3.2 chemical mechanism. The measured ratio is only shown for time periods between 08:00 and 22:00 due to the poor signal-to-noise ratios for the night-time measurements."

Figure 4 – Figure 8: It is unclear whether the ECHAMP data has been corrected for the calibration comparison or not? This should be clear in each figure caption

We have added the following sentence to section 3.3 to clarify:

"No adjustments have been made to either of the datasets in Fig. 4 (or any other figures) to account for the calibration difference."

Reviewer #2's comments:

The paper describes the measurement of peroxy radicals (HO2, RO2) with two different techniques. The LIF-FAGE technique by Indiana University was originally designed to measure solely HO2 radicals by chemical conversion with NO to OH, which is then detected by LIF. However, different experimental studies (including a study by authors of this paper) have shown that the technique is also sensitive to specific RO2 radicals with different sensitivities when the instrument is tuned for maximum HO2-to-OH conversion efficiency. The measured quantity is called HO2*. The new ECHAMP technique, a chemical amplifier using ethane instead of CO, is designed to measure the sum of HO2 and all RO2 species. Due to different amplifier chain lengths for different radical species, the resulting quantity XO2 is a proxy for the total peroxy radical concentration. Comparing the measurements by the two techniques sounds like comparing apples with oranges. The present paper demonstrates that such a comparison can be done in a meaningful way, if the instruments are carefully characterized and additional information about the peroxy radical speciation is available (here from box model calculations constrained by measured trace gases). The direct comparison of the conceptually different calibration methods (photolysis of water vapor vs. photolysis of acetone) and the field comparison show that the measurement techniques yield consistent data within the specified experimental uncertainties. These findings suggest that the two described methods can also be used for meaningful tests of atmospheric chemistry models, if the measured peroxy radicals (HO2*, XO2) are appropriately simulated by the model by taking RO2-specific weighting factors of the instruments into account. This requirement should be explicitly stated in the conclusions.

Furthermore, recent progress in the measurement of HO2 by LIF-FAGE instruments should be mentioned. It has been shown that the interference by RO2 can be avoided by reducing the concentration of NO that is used for conversion to OH (e.g. Fuchs et al., 2011; Whalley et al., 2013; Feiner et al., 2016; Tan et al., 2017).

This section has been re-written as follows:

*"The sensitivity of the LIF-FAGE technique to each type of organic peroxy radical varies with the amount of NO added for the conversion and is instrument-dependent but in general is highest (up to ~90%) for β–hydroxy peroxy radicals derived from alkenes and lowest for those derived from small

alkanes (Fuchs et al., 2011;Lew et al., 2018;Whalley et al., 2013). This RO_2 interference can be greatly reduced by use of lower NO concentrations or reaction times, yielding conversion efficiencies for isoprene-RO_2 lower than 20% (Feiner et al., 2016;Fuchs et al., 2011;Tan et al., 2017;Whalley et al., 2013)."

We have also inserted the following sentence into the conclusion:

"For this type of comparison of modeled to measured peroxy radicals to be meaningful, it is crucial that the model output concentrations be weighted according to both measurement techniques' sensitivities to each class of peroxy radicals."

Overall, the paper is thoroughly and well written. It is suitable for ACP, but could have been submitted to AMT as well. The authors and editor should consider whether the paper should appear as a "Technical note" in ACP. I recommend publication after the following minor comments have been addressed.

We agree that the paper could have been suitable for AMT as well. We chose to submit to ACP because we think that the comparison of the measured concentrations with those by the models provided information beyond that of an instrument assessment and provided information on our community's understanding of HOx chemistry in low-NOx, high biogenic VOC environments, which has historically been problematic.

(1) Introduction: as the topic of the paper is an instrumental intercomparison, I suggest to provide a more complete list of previous intercomparisons. For instance, Mount et al. (JGR vol.102, no.D5, p6437, 1997), Zenker et al. (JGR vol 103, no Dll, p13,615, 1998), Ren et al. (JGR vol 108, no D19, 4605, 2003), Fuchs et al. (AMT 5, 1611–1626, 2012), Onel et al. (AMT 10, 4877–4894, 2017), Sanchez et al. (Atmos. Env. 174, 227–236, 2018).

We have added the suggested references.

(2) In the experimental section, the authors point out that the use of ethane instead of CO offers advantages. Safer operation is obviously a plus. However, I don't understand why the choice of ethane reduces the sensitivity on relative humidity. Is this due to the reduced chain length? Is there evidence for water influence on the OH+CO reaction? To my knowledge, the water effect has been attributed to the reaction HO2+NO (e.g., Mihele et al. 1999, Butkovskaya et al., 2007). Why is the amplification factor lower, if ethane is used? Another advantage of ethane could be mentioned, although it is probably not relevant in a forest environment. Ethane avoids possible interferences from ClOx, which can lead to amplification in CO/NO systems (Perner et al., J. Atmos. Chem. 34, 9, 1999).

We have added the following text to briefly clarify the important issue of RH-dependence:

"The cause of the RH-dependence of the CO-based amplification chemistry is the RH-dependence of the main radical termination step: the reaction of HO_2 with NO to form HNO_3 (Butkovskaya et al.,

2007;Butkovskaya et al., 2005;Butkovskaya et al., 2009;Mihele et al., 1999;Reichert et al., 2003), with a smaller contribution from the RH-dependent wall losses of HO_2. These two RH-dependent radical termination steps affect the ethane-based amplification chemistry as well, but the most important terminations steps are from the formation of ethyl nitrite and ethyl nitrate – neither of which depends on relative humidity."

(3) Page 9: "For this project, [O3] was instead quantified by the ECHAMP CAPS NO2 sensors after conversion to NO2 by reaction with excess NO". A few details should be explained: is the flow in the calibrator laminar or turbulent? Where is the NO added (upstream, downstream of the calibrator)? Is the NO2 measured after it has been passed through the FAGE cell or is it measured in the air that bypasses the inlet of the FAGE cell? How much NO is added and how large is the resulting NO2 mixing ratio?

We have edited the following section in order to provide more information on this quantification:

"For this project, $[O_3]$ was instead quantified by the ECHAMP CAPS NO_2 sensors after conversion to NO_2 by reaction with excess NO. This was accomplished by having the IU calibration source overflow the ECHAMP inlet. ECHAMP was operated without the ethane flowing, so that each reaction channel sampled 1 LPM of air from the cal source into which 80 sccm of 21 ppm NO was added. This resulted in a diluted concentration of 1.7 ppm NO, which is high enough to react with 99% of the O_3 formed during the transit from the inlet to the CAPS detectors. This produces a very precise measurement of the sum of $[O_3]$ and $[NO_2]$ (1σ precision of 22 ppt for 10 second averages). The accuracy of this ozone determination is thus ultimately traceable to the CAPS NO_2 calibration (see SI). Typical $[O_3]$ values measured were between 0.4 and 2.0 ppb.**"**

(4) Page 9, line 18: is the water vapor correction based on laboratory characterization of the LIF-FAGE instrument, or on theoretical calculations using published data for the OH fluorescence lifetime and cross sections for quenching?

It is based on laboratory characterizations. The new sentence:

"The sensitivity of the instrument is corrected for fluorescence quenching by water vapor as per laboratory characterization"

(5) Model constraints: was atmospheric CO measured? Which formaldehyde data were used (GC-FID or DNPH)?

CO was not measured but was estimated based on published emission ratios of CO with benzene. Formaldehyde was only measured using the DNPH cartridges.

The relevant sentences were edited as follows:

"…cartridges to measure carbonyls, including formaldehyde (which was not measured by the GC-FID system), acetaldehyde and…"

and

"Measured VOC concentrations (every 90 min) were interpolated on to this 30 min time resolution. Carbon monoxide was not measured but instead estimated based on emission ratios of CO with benzene (Warneke et al., 2007)."

I see large gaps in the measured time series of NO in the first half of the campaign. Was NO (when available) used as a constraint, or was NO calculated by the model using NO2 as a constraint?

The comparison to the models is heavily focused on the three days when there measurements of NO, XO_2 (by ECHAMP) and HO_2* (by LIF-FAGE) as described in the text:

"Due to gaps in the NO data because of problems with the Thermo chemiluminescence sensor, there are only three days for which we have model results and measured peroxy radical concentrations by both ECHAMP and LIF-FAGE – on the 16th, 22nd, and 24th of July. The model was run for these three days, and also a diurnal profile for the entire campaign was run using diurnal average concentrations of constrained species."

The box model was constrained with 30 minute average mixing ratios. As peroxy radicals show a strong non-linear dependence on NO, using 30 minute average values as constraint can lead to systematic bias in the model results. I would like to see the model results that are averaged to 30 minutes after the model has been run at the much higher time resolution of the NOx measurements.

While the NOx data is available on a shorter averaging time, that is not the case for the VOC measurements, which were measured every 90 minutes. We have interpolated those measurements on a 30 min time scale, but feel that it would not be particularly meaningful to conduct modeling with the faster (10-second) NOx data given how much interpolation would be required for the VOC measurements. If the results were different, it could just as easily be attributed to artifacts resulting from the high degree of interpolation done for the VOC measurements.

(6) Figure 4 - 6: Is it meaningful to adjust the result of the linear regression for the calibration difference (section 3.1)? This would only make sense, if the calibration would be done for the same peroxy radical speciation as encountered during the measurement days in the field.

We have intentionally included in the text both the "raw" regression/ratio results and those corrected for the calibration difference, and argue that the correction is justified since the calibration comparison was conducted with compounds to which both ECHAMP and LIF-FAGE are sensitive (high α) – HO_2, butane-RO_2, and isoprene RO_2. Had the calibration comparison been conducted using a peroxy radical for which the two techniques had very different α values, for example CH_3O_2 for which LIF-FAGE is insensitive, then in that case we would agree that such a correction would be inappropriate.

(7) Figure 1: what is the scale of the map?
The caption has been updated to address this:

"The arrow represents a distance of 1 km."

(8) Figure 3: what is causing the noise and spikes on the NO data? Is it measurement precision or atmospheric variability from nearby NO sources?

The data shown in figure 3 are the 5-minute averaged NO concentrations which have a 1σ precision of approximately 100 ppt. The "spikes" in the figure are actually of 15 to 60 minute duration, and thus are from atmospheric variability (mostly during the early morning).

(9) Figure 3 and 4: vertical dotted lines = midnight ?

Yes. We have updated the figure captions to clarify:

"The vertical grid lines indicate midnight for odd-numbered days, in local time."

(10) Figure 5: the shown error bars (1sigma precisions) seem too large compared to the variability of the shown data

In the caption for figure 5 we had erroneously described the error bars as indicative of the 1σ precision of the measurements when they actually just describe the distribution of the measured concentrations. We have changed that sentence in the caption to the following:

"The error bars indicate the ± one standard deviation of the measured concentrations in each 30-minute time bin during those nine days."

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