

Anonymous Referee #1

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We would like to thank the reviewer for comments and questions which helped us to improve the manuscript. The reviewer comments are given below together with our responses and changes made to the manuscript.

1) The authors conduct several chemical modulation tests to measure interferences using an “improved” chemical modulation reactor (CMR). Unfortunately there are limited details on the design of the CMR and how it was improved over the previous version. The paper would benefit from an expanded discussion of the CMR, including a schematic diagram, which could be included in a supplement.

Answers:

We added a schematic plot of the CMR in the supplement. In this version, we improve the mixing of ambient air with an added agent by using a two-needle injector system.

We changed the text on Page 4 Line 26-30 to be “In the present study, an improved CMR device was used for some selected time periods during clean and polluted air conditions. The device consisted of a Teflon tube with an inner diameter of 1.0 cm and a length of 8.3 cm (Fig. S2). About 20 slpm of ambient air was drawn through the tube by a blower, of which 1 slpm was sampled into the OH detection cell. In the current design, two small stainless steel tubes (outer diameter 1/16 inches) were arranged at the entrance of the Teflon tube opposite to each other (compared to one injector in the previous version described in Tan et al. 2017)). This change of the injector system design could improve the mixing of ambient air with the injected propane.”

2) The chemical modulation experiments should have allowed a direct measurement of the ozone interference that is subtracted from the wavelength modulation signal (equation 2). Did the chemical modulation experiments confirm the correction for the ozone interference?

Answers:

We added a sentence on Page 5 Line 5 that “The ozone photolysis is a known interference in the OH measurement using wavelength modulation (Holland et al. 2003). This interference was characterized in laboratory experiments and subtracted in OH_{WM} . The background signal determined in the chemical modulation contains the information about interferences including

that from ozone. This signal is consistent with the correction applied to the OH_{WM} detection scheme. This can be seen, for example, in the good agreement between OH_{WM} and OH_{CM} during nighttime, when the ozone interference was a large fraction of the uncorrected OH_{WM} signal. ”

3) For the regression of the chemical modulation measurements versus the wavelength modulation measurements (Figure 2), the authors should clarify the regression method. They should use a bivariate regression weighted by the measurement precision of both OH chem and OH wave.

Answers:

The regression is done with a bivariate weighted method and the figure 2b is updated accordingly, which resulted in slightly different from the origin one (polyfit). We changed the sentence on Page 5 Line 14-16 “The regression is done using a bivariate regression weighted by the measurement errors of both signals, OH_{CM} and OH_{WM}. The slope of this correlation is close to unity (1.1) for the various encountered chemical conditions. Small intercept ($0.2 \times 10^6 \text{ cm}^{-3}$ smaller than the detection limit) is found indicating that no significant bias in the low concentration range...”

4) The description of the RO₂ measurements appears to be incomplete, as the addition of NO and CO would result in the measurement of both RO₂ + HO₂ + OH (RO_x as described in Fuchs et al., 2008). Measurements with CO addition only result in detection of HO_x (OH + HO₂) only. To obtain measurements of RO₂ only, the measured HO_x concentrations must be subtracted from the measured RO_x concentrations. Based on the description in Tan et al. (2017), it appears that the HO_x measurements from the other two axes are used to obtain the RO₂ concentrations from the RO_x measurements, but this should be clarified in this paper.

Answers:

We added a sentence in Page 4 Line 5 that “The measurements from the other two fluorescence cells are used to calculate the contributions from OH and HO₂ and subtracted to retrieve the RO₂ measurements.”

The same subtraction is applied to the HO₂ measurement. So we added a sentence on Page 3 Line 28 “The contribution of OH is subtracted using the measurement in the OH channel and OH sensitivity in the HO₂ channel.”

5) Related to this, it is not clear that the uncertainty for the RO₂ measurements listed in Table 2 reflect the fact that the HO_x measurements are subtracted from the RO_x measurements. Fuchs et al. (2008) estimates the accuracy of the RO₂ measurements to be approximately 20%. This should be clarified. In addition, the authors state that the measurement accuracies reflect both the “the uncertainty of the calibration source (10%, 1 σ) and the 1 σ standard deviation of the variability of individual calibration sensitivities” (page 4). However the accuracies of the OH and HO₂ measurements in Table 2 appear to only reflect the standard deviation of the variability of the individual calibration sensitivities, and do not appear to include the uncertainty associated with the calibration source. This should be clarified.

Answers:

We changed the sentence in Page 4 Line 9-11 to be “The accuracies include the uncertainty of the calibration source (10%, 1 σ) and the 1 σ standard deviation of the variability of individual calibration sensitivities (OH: 10%, HO₂: 13%, RO₂: 11%). The accuracies are calculated from Gaussian error propagation 14%, 17% and 23% for OH, HO₂, and RO₂, respectively.” We also changed the numbers in Table 1 accordingly.

6) The authors should also provide an estimate of the model uncertainty.

Answers:

We added a sentence in Page 7 Line 2 “The uncertainty of the model calculations is derived from the uncertainties in the measurements used as model constraints and the reaction rate constants. Taking into account the uncertainties of both measurements and kinetic rate constants, a series of tests based on Monte Carlo simulations show that the 1 σ uncertainty of the model calculations is approximately 40% (Tan et al. 2017).”

7) Figure 7 could be improved to better show the model/measurement agreement/disagreement. Instead of separating the plots with measurements on one side and modeling on the other, I would suggest separating them by episode (background, clean, polluted), and then showing the model results and the measurements on the same plot, including the measurement and model variability, similar to that done in Tan et al. (2017).

Answers:

In Figure 7, we try to emphasize that the observed radical concentrations are similar in all three cases while the model predicts radical concentrations that are significantly decreased in the polluted periods compared to the clean episodes. The measurement-model discrepancy is highlighted in the NO dependence (Figure 10 and 11). However, we agree that this plot is also insightful and thus we show it in the supplement.

We added a sentence on Page 9 Line 34 “In fact, the observed radical concentrations are rather comparable in all episodes, while the model predicts a suppression of radical concentrations in the polluted episodes. This is most obviously seen for HO₂ and RO₂. The comparison between observed and modelled OH, HO₂, and RO₂ concentrations for clean and polluted episodes are shown in Fig. S3.”

8) While the measured/modeled ratios illustrated in Figure 11 suggest that the increase in the modeled underestimation of HO₂ as a function of NO is similar to that observed previously (page 12), the HO₂ measurements in some of the previous studies mentioned may have suffered from the RO₂ interference discussed on page 3, resulting in reported HO₂ measurements that may be greater than the actual HO₂ concentrations. This potential interference would enhance the model-measurement discrepancies reported in these studies. This should be clarified in the discussion on page 12 of the manuscript.

Answers:

We added a paragraph on Page 12 Line 13 “HO₂ measurements in previous field campaigns could have suffered from interferences from specific RO₂ species, so that the reported observed-to-model ratios could have been even larger in these campaigns.”