

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) Comments: *The authors performed several Interference measurements using an external chemical titration technique. Unfortunately it appears that these interference measurements were not done continuously but were done only on four specific days. However, it is not clear exactly when the tests were done and what the ambient conditions were during each test. Were any tests done when NO was less than 300 pptv, the conditions when the model-measurement discrepancies were the greatest, or was the measured interference similar for all ambient levels of NO? This should be clarified. Adding the times when these tests were done to Figure 3 would provide more information on whether these tests were done under typical ambient conditions for the campaign. Was this interference subtracted from all of the OH measurements?*

Answers: Because the titration device was a prototype, the chemical modulation tests were only performed on four days. The time period and chemical conditions are summarized and showed in a new figure in the revised manuscript. The unexplained residual signal are constant in the range of $1 \times 10^6 \text{ cm}^{-3}$, independent on the ambient NO concentrations.

Referee #1 also had similar questions about the titration experiments. Therefore, we would like to refer to our answer to question 1 of Referee #1 for more detail information.

Change: We added a sentence in Line 431: “Because the test results are not sufficiently accurate to draw firm conclusions about an unknown interference, the OH data in this work was not corrected for a potential interference. Instead, the differences found in Fig. 2 are treated as an additional uncertainty of the OH measurements presented in this paper.”

2) Comments: *On page 17 the authors state that the measured OH concentrations are approximately $1 \times 10^6 \text{ cm}^{-3}$ greater than model predictions during the afternoon when the mixing ratios of NO decrease from 0.3 to 0.1 ppb. This discrepancy appears*

to be consistent with the average measured interference of $1 \times 10^6 \text{ cm}^{-3}$ described on page 14, suggesting that the observed discrepancy with the model could be due to the interference. This possibility should be discussed in more detail.

Answers: If an accounted signal of $1 \times 10^6 \text{ cm}^{-3}$ was subtracted from the measured OH concentration, the observed-to-modelled ratio of OH would be reduced from 1.4 to 1.2 for $\text{NO} < 300 \text{ ppt}$ and from 1.9 to 1.5 for $\text{NO} < 100 \text{ ppt}$.

Change: We added a discussion about the averaged unaccounted signal and model-measurement discrepancy comparison and revised the text from Line 522 to Line 524: “The median diurnal profiles of the measured and modelled OH concentrations agree within their errors of 10% (1σ) and 40%, respectively, from sunrise to midafternoon. When the median NO mixing ratio (cf. Fig. 6) drops gradually from 0.3ppbv to 0.1ppbv in the afternoon, a systematic difference evolves, with measured OH concentrations being approximately $1 \times 10^6 \text{ cm}^{-3}$ higher than the model calculations. The discrepancy is of similar magnitude as the averaged unexplained OH determined in the chemical modulation experiments (Table 2). Thus, the overall agreement for OH would improve, if the unaccounted signal was fully considered as an OH measurement interference. However, the underestimation of OH would persist for low NO conditions if a potential unaccounted signal was subtracted. When NO concentrations are less than 100pptv, the observed-to-modelled OH ratio would be reduced from 1.9 to 1.5, indicating that an OH source would still be missing for low NO conditions.”

3) Comments: *In their measurements of HO_2 , the authors varied the added NO to determine the interference from alkene and aromatic peroxy radicals. However, it is unclear to me how the authors determined the RO_2 conversion efficiencies described on page 11 unless the absolute conversion efficiency for one of the NO flows was determined through calibrations with known concentrations of peroxy radicals. Did the authors perform RO_2 conversion efficiency calibrations similar to that described in Fuchs et al., 2011? This should be clarified.*

Answers: The NO concentration was in all cases lowered to values, at which no significant interferences from RO_2 in the HO_2 detection are expected (p10 l296-299). The NO concentration was varied between two values, in order to check, if this was

the case, because a systematic difference between measurements at the two NO concentrations is expected, if RO₂ was detected together with HO₂. For the majority of measurements, the difference was only a few percent, which means that essentially no RO₂ interferences were present. Nevertheless, a small correction was applied, for which was assumed that the interference from RO₂ was the same at all times. The correction factor was derived from a regression analysis between measurements at different NO concentrations.

Change: We revised the text from Line 307 to Line 311: “The HO₂^{*} ratios were used to derive correction factors for the determination of interference-free HO₂ concentrations. For small NO concentrations as used in this work, we assume that the interference from RO₂[#] is directly proportional to the applied NO concentration. Based on this assumption, we derived HO₂^{*}/HO₂ ratios of 1.02, 1.05, and 1.2 for the addition of 2.5, 5, and 20ppmv NO, respectively. These ratios were then used as correction factors to generate a consistent data set of interference-free HO₂ concentrations from the HO₂^{*} measurements. After all, the correction was small enough that deviations from this assumption would not significantly affect our results.”

4) Comments: *It is not clear how the authors derive the RO₂[#] concentrations and compare it to the model. The measured HO₂^{*} in the ROx channel reflects the conversion of alkene, aromatic, and other RO₂ radicals to HO₂ in the detection cell with a conversion efficiency dependent on the RO₂ radical as described in Fuchs et al. (2011). Subtracting the HO₂ measured in the HO₂ axis gives RO₂[#]. Ideally, the authors should compare this measured value which is the result of various conversion efficiencies to the modeled RO₂[#], where the individual modeled RO₂ concentrations are scaled by their expected conversion efficiencies, which are not necessarily all 0.8. However, it appears that the authors are scaling the measured RO₂[#] by an average conversion efficiency of 0.8 and comparing this value to the modeled concentration of the sum of the interfering RO₂ concentrations. This should be clarified. Have the authors measured the individual RO₂ conversion efficiencies for their instrument?*

Answers: In the current setup, the RO₂[#] concentrations is derived from the HO₂ concentrations detected in the HO₂ cell and the HO₂^{*} concentrations detected in the RO₂ cell applying the expression $RO_2^{\#} = (HO_2^* - HO_2)/0.8$. An averaged relative

detection sensitivity for the $RO_2^\#$ in the RO_2 cell is estimated to be 0.8 according to previous publications (Fuchs et al., 2011; Lu et al., 2012) and dominant VOCs reactivity groups (mainly alkenes and isoprene) in Wangdu. We have performed tests on the RO_2 conversion efficiency for simple alkene, e.g. ethene, propene, for this new instrument and observed similar conversion efficiencies as Fuchs et al. (2011) reported for low NO concentrations in the detection cell. The other RO_2 conversion efficiencies are then extrapolated as done in Lu et al. (2012).

Change: We modified the text in Line 331 as “The concentration measurements of HO_2 (from the HO_2 cell) and of HO_2^* (from the RO_x system) allow to estimate the total concentration of $RO_2^\#$ (Whalley et al., 2013): $RO_2^\# = ([HO_2^*] - [HO_2])/\alpha RO_2^\#$ ”

5) Comments: *The authors state that the underestimation of the RO_2 concentrations by the model during the high NO conditions in the morning is improved when the OH reactivity of the model is increased, but few details are provided. Similar results were found during CalNex by Griffith et al. (JGR, 2016). How much did the modeled RO_2 increase in this scenario? Perhaps the results of this model run could be added to Figures 5 and 9.*

Answers: We have performed sensitivity test to upscale the VOC reactivity, which is shown in the revised Figure 5 as following (S1). In this sensitivity test, the input VOC concentrations are scaled up so that the modelled OH reactivity agree to measurements. The observed-to-modelled RO_2 ratio is improved from 2.8 to 1.7 on average from 06:00 to 09:00. More detail information is given in the revised manuscript as following.

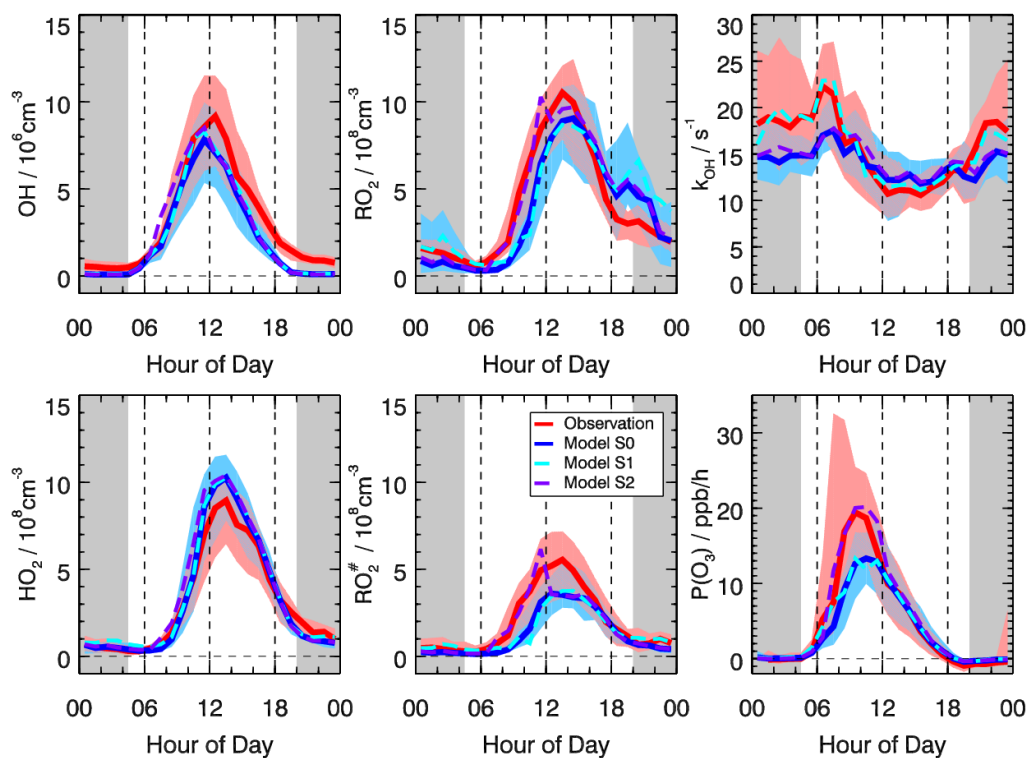


Figure 5 Comparison of hourly median diurnal profiles of OH, HO₂, RO₂, RO₂[#] concentrations and k_{OH} and the ozone production rate P(O₃) (thick lines give median values, colored areas give 25% and 75% percentiles). S0 (blue line) denotes results from the base model run. S1 (cyan, dashed line) shows results, when the VOC concentrations in the model are increased to match the observed OH reactivity. S2 (violet, dashed line) shows results, when an additional primary RO₂ source (2ppbv h⁻¹) is added in the model for the time between 6:00 and 12:00. Grey areas indicate nighttime.

Change: We revised Page 18 from Line 569 to Line 596: “The strong underprediction of the observed RO₂ by more than a factor of 4 in the morning cannot be explained by the measurement errors and interferences discussed in Sections 2.3.4 and 2.3.5. In order to explore potential reasons for this underprediction, several sensitivity tests were performed. First, the impact of a faster OH to RO₂ conversion by an increased amount of VOC was tested (model sensitivity run S1). Second, an additional primary source of RO₂ was introduced into the chemical mechanism (S2). Third, the possibility of a slower removal rate of RO₂ was tested (S3).

The first possibility (S1) is supported by the observation that the modelled OH reactivity in the base run (S0) is smaller than the measured OH reactivity in the morning

until about 09:00. If this missing reactivity is caused by unmeasured VOCs, the true RO₂ production from reactions of VOCs with OH would be larger than the modelled one. To fill this gap, the total concentration of the measured VOCs was increased to match the measured k_{OH} in the time window from 06:00 to 09:00. The relative partitioning of the VOCs was not changed. The model run (S1) with the upscaled VOC reactivity resolves part of the RO₂ discrepancy until 09:00 (Fig. 5). The observed-to-modelled RO₂ ratio is improved from 2.8 to 1.7 without affecting the good model-measurement agreement for OH and HO₂. Further sensitivity tests showed that the modelled RO₂ is not sensitive to the speciation of the additional VOC reactivity, since the required change of k_{OH} is relatively small (< 20%). Because no missing OH reactivity was found after 09:00 h in the morning, the gap between measured and observed RO₂ cannot be explained by unmeasured VOCs later in the morning.

...”

6) Comments: *Similarly, the authors find that the model underestimates the rate of ozone production under high NO conditions due to the underestimation of RO₂ radicals by the model. Similar results were found during CalNex (Brune et al., Faraday Discuss., 2016, 189, 169; Griffith et al., JGR, 2016). Does the underestimation of RO₂ (and therefore P_{O₃}) depend on the measured OH reactivity? Griffith et al. (2016) found that the underestimation of P_{O₃} by the model was higher when the OH reactivity from VOCs was the greatest.*

Answers: In the sensitivity run, in which we scaled VOCs to match measured OH reactivity, also the discrepancy between modelled and calculated ozone production rate is reduced (see revised figure 5).

We tested, if there is a correlation between the underestimation of RO₂ by the model and VOC reactivity. However, no clear relation is observed for this campaign.

Change: We added discussion on ozone production underprediction found in other field campaigns, including CalNex, to show the common feature of model inability to reproduce peroxy radical concentration for high NO_x condition. The text is added to the end of Section 3.8: “Other HO_x field studies have also found that models underpredict the observed ozone production rate in urban atmospheres (Martinez et al., 2003; Ren et al., 2003; Kanaya et al., 2008; Mao et al., 2010; Kanaya et al., 2012; Ren

et al., 2013; Brune et al., 2016; Griffith et al., 2016). In these studies, the observed production rates were determined from measured HO₂ concentrations only, without the contribution of RO₂ for which measurements were not available. In general, the ozone production from HO₂ was underpredicted by chemical models at NO mixing ratios greater than 1 ppbv, reaching a factor of about 10 between 10 ppbv and 100 ppbv NO. In campaigns before 2011, unrecognized interferences from RO₂[#] species may have contributed to the deviation between measurement and model results. The interference, however, is expected to account for less than a factor of 2, because HO₂ and RO₂ concentrations are approximately equal (Cantrell et al., 2003; Mihelcic et al., 2003) and RO₂[#] is only a fraction of the total RO₂ (e.g., Fig. 5). This expectation has been confirmed in recent studies, where the interference was taken into account and the significant underprediction of the ozone production from HO₂ still persists (Ren et al., 2013; Brune et al., 2016; Griffith et al., 2016). During the CalNex-LA 2010 campaign in Pasadena (California), part of the discrepancy could be explained by unmeasured VOCs, which were recognized as missing OH reactivity (Griffith et al., 2016). Another major reason for the HO₂ underprediction could be an incomplete understanding of the HO₂ chemistry at high NO_x concentrations (Ren et al., 2013; Brune et al., 2016; Griffith et al., 2016). ”