

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.

Note: All the comments to change grammar and wordings suggested by the reviewer were changed accordingly. We appreciate the detail correction.

**Comments:** *Line 14. It is a bit confusing to say the RO<sub>2</sub> is in good agreement, but then to say that RO<sub>2</sub> is underestimated by a large amount in the morning. Suggest changing this text to make the points clearer.*

**Answers:** We changed the text Line 11: "...If additional OH recycling equivalent to 100 pptv NO is assumed, the model is capable of reproducing the observed OH, HO<sub>2</sub> and RO<sub>2</sub> concentrations for conditions of high VOC and low NO<sub>x</sub> concentrations. For HO<sub>2</sub>, good agreement is found between modelled and observed concentrations at day and night. In case of RO<sub>2</sub>, the agreement between model calculations and measurements is good in the late afternoon when NO concentrations are below 0.3ppbv. A significant model underprediction of RO<sub>2</sub> by a factor 3 to 5 is found in the morning at NO concentrations higher than 1ppbv, which can be explained by a missing RO<sub>2</sub> source of 2 ppbv h<sup>-1</sup>."

**Comments:** *Line 45. Do the values of 0.8 and 0.4 ppbv refer to average or median values required? If so, state this.*

**Answers:** We changed the text Line 45: "An equivalent of 0.8 ppbv and 0.4 ppbv of NO was required in PRD and Beijing on average, respectively."

**Comments:** *Line 109. Note that peroxy radicals will also shift the NO to NO<sub>2</sub> ratio as the air travels down the sample line.*

**Answers:** We can in principle apply the inlet correction of the peroxy radicals to the NO<sub>x</sub> measurement, since we have ambient measurements of peroxy radicals. However, because the peroxy radicals are highly reactive, they are expected to be

easily lost in the inlet. Their contribution to the shift of NO to NO<sub>2</sub> is in general small compared to that of O<sub>3</sub>. Therefore, a correction would not significantly change results.

We added a statement in Line 110: 'The effect of changes of the NO to NO<sub>2</sub> ratio by peroxy radicals is negligible due to their small concentrations and their high loss rate in the inlet line.'

**Comments:** *Table 1. All of the various techniques when multiple instruments were measuring are not given. Suggest making the list complete.*

**Answers:** We extended Table 1 to include all the techniques (e.g. for NO<sub>x</sub>, HONO, etc).

**Comments:** *Line 120. This discussion of HONO measurements is good, but given the potential uncertainties in such observations, it might be good to do a more detailed comparison, perhaps including a figure comparing all six measurements.*

**Answers:** A detailed comparison of the different HONO measurements is beyond the scope of this publication and will be the topic of a separate publication. Differences in the HONO measurements do not change results of our analysis here and are taken into account as additional uncertainty.

**Comments:** Line 130. An instrument with higher sensitivity is more sensitive. This is a common confusion. Suggest changing to “are generally better,”

**Answers:** We revised the text Line 128 – 136: “HONO measurements from the FZJ-LOPAP instrument are used as model constraint, because it showed the best detection limit and temporal coverage during the campaign. Results of model calculations only change less than 10%, if either measurements by the PKU LOPAP or NOAA CEAS are used as constraint. The other CEAS HONO instruments measured only during a few days. The GAC HONO measurement is known to be affected by interferences from ambient NO<sub>2</sub> and was therefore not used here.”

**Comments:** *Line 220. It says that the correction is small compared to ambient OH, but this depends on the conditions. Near sunrise and sunset (or at night), this could be a large correction.*

**Answers:** We revised the text: ‘A correction is applied that is small compared to ambient OH concentrations during daytime.’

**Comments:** *Line 225. It says that there was no interference from ozonolysis of simple alkenes, but what about larger, more complex alkenes (non-biogenic) that could be present?*

**Answers:** This statement summarizes results reported in Fuchs et al. (2016). The result was that ozonolysis reactions in general (most likely including also non-biogenic alkenes) are not causing significant interferences in this type of LIF instrument for atmospheric concentrations. GC measurements also suggest that the majority of alkenes were small alkene species (ethene, propene) during this campaign. The effort to investigate interferences in the OH detection will be certainly continued in the future.

**Comments:** *Line 257. This reviewer does not like the use of “titration” in this context. The authors can do as they choose, but suggest using “removal” or “conversion” efficiency rather than titration. Also suggest removing both commas on this line.*

**Answers:** We changed this to “removal efficiency”.

**Comments:** *Line 271-272. The issue of mixing reagents into a flow containing HOx radicals at ambient pressure has been solved by others, particularly those make CIMS-based HOx measurements (e.g. Mauldin et al.).*

**Answers:** As stated in the text, the system was a first attempt to apply this technique in the field and needs technical improvement in the future.

**Comments:** *Line 277. It states that the titration unit caused a 5% difference in OH sensitivity. Was this applied to the data collected while it was present?*

**Answers:** Measurements with the titration system were not used as ambient OH measurements, but only to test, if there were interferences in the detection. Therefore, a change of the sensitivity only affects the quantification of a potential interference. As stated in the text, this calculation has a large uncertainty, so that a 5% change in sensitivity would be negligible.

**Comments:** *Line 307. It states that it is assumed that the contribution of RO<sub>2</sub><sup>#</sup> scales with added NO. Is this justified by lab studies? How are the correction factors given in lines 309-310 applied? ( $HO_2 = HO_2^*/CF$  ?)*

**Answers:** The RO<sub>2</sub> conversion efficiency clearly increases with increasing NO concentration because a reaction of RO<sub>2</sub> with NO is required to form HO<sub>2</sub>. This dependence was also shown in laboratory studies (Fuchs et al. 2011.).

We have performed tests on the RO<sub>2</sub> 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 conversion efficiency was about 10%. The other RO<sub>2</sub> conversion efficiencies are then extrapolated as done in Lu et al. (2012).

We revised the text from Line 296 to Line 299 on page 10: “A significant reduction of the relative interference from RO<sub>2</sub> can be achieved by using a smaller amount of added NO. Although less NO will cause a smaller HO<sub>2</sub> conversion efficiency, possible interferences from RO<sub>2</sub> will be even more strongly reduced because RO<sub>2</sub> conversion to OH requires one more reaction step with NO. For this reason, the NO concentration used for the conversion of HO<sub>2</sub> during this campaign was chosen to be significantly smaller ( $\leq 20$  ppmv) than in previous field campaigns (500ppmv) (Lu et al., 2012, 2013). At this low concentration, it is expected that interferences from RO<sub>2</sub> become almost negligible (Fuchs et al., 2011).”

We revised the text from Line 307 to 311 on Page 11: “The HO<sub>2</sub><sup>\*</sup> ratios were used to derive correction factors for the determination of interference-free HO<sub>2</sub>

concentrations. For small NO concentrations as used in this work, we assume that the interference from RO<sub>2</sub><sup>#</sup> is directly proportional to the applied NO concentration. Based on this assumption, we derived HO<sub>2</sub><sup>\*</sup>/HO<sub>2</sub> 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 HO<sub>2</sub> concentrations from the HO<sub>2</sub><sup>\*</sup> measurements. After all, the correction was small enough that deviations from this assumption would not significantly affect our results.”

**Comments:** *Lines 334-337. Are the ambient data corrected for the artifacts as described?*

**Answers:** The background signals from the NO addition are subtracted from the HO<sub>2</sub> and RO<sub>2</sub> measurements. Artifacts caused by NO<sub>3</sub> are not subtracted from RO<sub>x</sub> measurements since there was no measurement available. The model gives an average concentration of about 10 pptv which only would cause an interference that would be equivalent to  $1 \times 10^7 \text{ cm}^{-3}$  RO<sub>2</sub> which is similar to the detection limit of the RO<sub>x</sub> measurement.

We added a statement in Line 337: “Measurements were corrected for the NO background signal, but no correction was applied for potential interferences from NO<sub>3</sub>, because no NO<sub>3</sub> measurement was available. However, model calculations (see below) suggest that there was no significant interference from NO<sub>3</sub> for conditions of this campaign.”

**Comments:** *Line 358. Based on the discussion, the detection limit at noon is about  $1.5 \times 10^6$ . Is this a systematic or random effect of the solar light leakage? Can the data be corrected for this? Is this included in the overall measurement uncertainties?*

**Answers:** Sunlight is entering the measurement cell through the orifice through which ambient air is sampled into the fluorescence cell. The signal is subtracted from the total photon count rate as described Line 206-210. The detection limit is higher in the presence of sunlight because of the higher total count rate, which is only partly due to

OH fluorescence in this case. Therefore, the statistical noise (shot noise) of the OH measurement is increased.

Line 363. Do the authors believe that RACM 2 is a suitable mechanism to study detailed HOx radical chemistry? Why not use the explicit MCM mechanism, modified as you did to include updated isoprene chemistry? Perhaps add some discussion as to why the RACM 2 mechanism was selected.

**Answers:** We applied MCM and RACM in previous, similar studies and found no difference of model results for radicals (Lu et al. 2012). The likely reason for this is that the RACM mechanism is designed for ozone prediction, which is connected to the radical recycling mechanism. An explicit mechanism that includes all VOC intermediates is not required in this case. For the same reason we modified the isoprene mechanism in RACM since this impacts OH recycling.

We added in Line 368: "Previous model studies of radical chemistry showed that predictions of radical concentrations by the RACM are similar to results by explicit mechanisms like the Master Chemical Mechanism (Lu et al. 2012)."

**Comments:** *Line 389. When saying that the OH reactivity can "be well explained", suggest adding a quantitative value to the degree of agreement (within 22% or whatever).*

**Answers:** The sentence was changed to "Slightly more than 60% of the OH reactivity can be explained by the measured concentrations of CO, NOx and hydrocarbons during daytime. More than 90% of the OH reactivity can be explained, if also measured oxygenated VOC species are included (Fuchs et al., 2016b)."

**Comments:** *Line 398. What species are being referred to as "these species"? Suggest a bit more text to make it clear.*

**Answers:** Namely, most aldehydes are running free in the model. Added a sentence: "In order to avoid unrealistic accumulation of oxygenated VOC species (mostly aldehydes), ...".

**Comments:** One question: why didn't the peroxy radical concentrations also increase during this time period?

**Answers:** The peroxy radical concentrations were suppressed by higher NO concentrations on this day.

**Comments:** *Lines 485-494. It appears to me that the NO<sub>3</sub> interference is sufficient to explain some or all of the nighttime signal observed.*

**Answers:** Test with a similar design LIF instrument shows that NO<sub>3</sub> could cause an OH interference. In chamber experiment, 1ppbv of NO<sub>3</sub> yielded a signal that is equivalent to an OH concentration of  $1 \times 10^7 \text{ cm}^{-3}$  (Fuchs et al. 2016). A NO<sub>3</sub> concentration of 10 pptv that is suggested by model calculations for conditions of this campaign would cause an interference that would be equivalent to an OH concentration of  $1 \times 10^5 \text{ cm}^{-3}$ , which is similar to the detection limit.

The statement 'Using NO<sub>3</sub> concentrations from the model (average. 10 pptv), the expected interference would be less than  $1 \times 10^6 \text{ cm}^{-3}$  for this campaign.' was changed to: '... the expected interference would be  $1 \times 10^5 \text{ cm}^{-3}$  for this campaign, 5 times less than the averaged nighttime OH measurement.'

**Comments:** *Lines 495-503. Suggest a discussion and perhaps a figure showing the major contributors to the OH reactivity.*

**Answers:** The OH reactivity contribution is presented in a separate paper by Fuchs et al. The focus for this paper is to analyze the HOx chemistry and thus the OH contribution is discussed in more detail in the accompanying paper.

**Comments:** *Lines 515-516. Suggest rewording this sentence. One suggestion would be to separate the data into two equal groups rather than have this long discussion about why the two groups are not equal in size.*

**Answers:** We have divided the data into two groups and analyzed them separately.

Though the chemical conditions were slightly different, we found similar results from model-measurement comparison of radicals for the two periods. Therefore, we combined these two periods and present campaign averaged diurnal profiles.

We simplified the sentence and tried to make it more readable: “As described in Section 3.3, chemical conditions were slightly different before and after 20 June. We found similar results of model-measurement comparisons for radicals from the two periods. Therefore, the following interpretation and discussion will focus on campaign averaged diurnal profiles. ”

**Comments:** Line 522. The median measure-model difference discussed is of the order of the various artifacts and interferences. Have the data been corrected for all of them before doing this comparison? If so, suggest stating this somewhere.

**Answers:** OH data is corrected for the well-known and characterized ozone interferences and no significant interference from NO<sub>3</sub> is expected as described in section 2.3.1.

The interference tests described in 3.1 were only occasionally performed and gave only an upper limit for potential additional interferences that would not change the results of our analysis of daytime OH. No correction of data is justified from these tests. Because reviewer #2 raised the same question, please refer also to the answer there.

**Comments:** *Line 523. It is not clear what is meant by “At the same time”. Suggest rewording to make this clearer.*

**Answers:** The sentence is changed to “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).”



**Comments:** *Line 563. Is there any evidence of organic nitrites contributing to the enhancement of peroxy radicals in the morning? Photolysis of such species, if they exist, could contribute to the difference seen.*

**Answers:** We have no measurements of organic nitrites during this campaign. We tested including an artificial external source of RO<sub>2</sub>, which could be originating from photolytic reactions. To reproduce the observed RO<sub>2</sub>, 2 ppb/h of additional RO<sub>2</sub> production is required.

**Comments:** *Line 592. It states that the production rate of RO<sub>2</sub> could be underestimated, but one should also consider that the loss rate of RO<sub>2</sub> could be overestimated somehow.*

**Answers:** We also analyzed the destruction of RO<sub>2</sub> in the morning, which is dominated by the reaction with NO. The overestimation of the RO<sub>2</sub> destruction rate could be due to 1) systematic lower NO measurements; 2) segregation between NO and RO<sub>2</sub>; 3) an error of lumped reaction rate constants. A sensitivity run testing the effect of this uncertainty shows that the modelled and measured RO<sub>2</sub> would agree if the reaction rate constant of RO<sub>2</sub>+NO was smaller by a factor of 4. Such large change cannot be easily explained.

**Comments:** *Line 594. It states that VOC concentrations are scaled to match measurements. Which measurements? Are they the VOCs or kOH?*

**Answers:** The VOC concentrations are scaled to match measured OH reactivity. We revised the text: “To fill this gap, the total concentration of the measured VOCs was increased to match the measured k<sub>OH</sub> 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 RO<sub>2</sub> discrepancy until 09:00 (Fig. 5).”

**Comments:** *Line 600. Suggest “...concentrations that are used as constraints.” A thought on nighttime chemistry: if there is NO<sub>3</sub> present, then the NO concentration*

*should be very small unless the NO<sub>3</sub> production rate is very large. This is because of the rapid reaction between NO and NO<sub>3</sub>. This could help with the modeling of nighttime chemistry.*

**Answers:** We had no NO<sub>3</sub> measurement in this campaign. The observed NO was usually below detection limit of the instrument (60pptv) during nighttime. In this case, the modelled RO<sub>2</sub> is high and highly variable. We tested another model scenario that forces the NO to be higher than 60pptv to limit accumulation of RO<sub>2</sub>, which reduces the observed-to-modelled ratio 1.2 during the night.

**Comments:** Lines 758-769. Suggest including Ye et al in the discussion of HONO budgets.

**Answers:** We added a sentence in Line 769. "... and photolysis of particulate nitrate is proposed to be of potential importance for the tropospheric HONO production (Ye et al., 2016)."

**Comments:** Line 770. Suggest giving an example of a reaction of OH with VOCs that do not lead to peroxy radicals.

**Answers:** We modified the text in line 770: "Further radical terminating OH losses include reactions with unsaturated dicarbonyls (DCB1, DCB2, DCB3) and acetyl nitrate species (PAN, MPAN, etc) in RACM2."

**Comments:** Line 832. Yes, the interference would be minor compared to the daytime maximum, but it could be very important at sunrise and sunset.

**Answers:** The statement was modified accordingly.

**Comments:** References. The papers on HOx measurements are very Euro-centric. Suggest adding some papers from US HOx measurement groups.

**Answers:** More results from the HOx groups outside Europe were added such as Griffith et al., 2013, 2016; Mauldin et al., 1999; Kim et al., 2014; Brune et al., 2016,

Kanaya et al., 2008, 2012.

**Comments:** *Figure 1. The colors for SN2 and SOH are very similar. Suggest changing one of them to a very different color.*

**Answers:** Changed accordingly.

**Comments:** *Figures 3, 4, 5, 6, 8, and 10. Is the gray period meant to signify nighttime? If so, the authors should check this carefully. It appears that there are photolysis processes (such as O<sub>3</sub>) that occur after sunset (see Figure 10).*

**Answers:** The gray area indicates nighttime. For Figure 10 there is a typo error in the data analysis routine, we have now revised this.