

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.

1.1 Comments: *Interferences in the OH detection, OH chemical modulation tests: Was the propane concentration varied in the field? From lines 265 – 267 it is unclear if the variable titration efficiency is a laboratory result or field observation. If it was the latter, how was titration efficiency determined in the field?*

Response: The amount of propane and corresponding titration efficiency (changed to removal efficiency according to Referee #3) was optimized and determined in the field before each titration test. More detail information is provided in the revised manuscript.

Change: We added on Page9 L269: “The knowledge of ϵ is essential for an accurate quantification of potential interferences. The removal efficiency was tested and optimized in the field using the OH calibration device as a radical source. The value of ϵ was found to depend on the flow rates of the added gases (propane and nitrogen). Propane was added as a 5% mixture in nitrogen with a flow rate between 0.02 and 0.2lpm (Liter per minute) which was further diluted in a carrier flow of pure nitrogen (0.04 to 0.5lpm). The dependence of ϵ on the flow rates showed that mixing of the injected propane into the high flow of ambient air was inhomogeneous similar to results reported in Novelli et al. (2014). Because of technical difficulties with the flow regulation, the removal efficiency was re-determined before each ambient titration test. The values obtained for ϵ ranged between 80% and 97% with an accuracy of 10% (1 σ) at fixed nominal propane and nitrogen flows.”

1.2 Comments: *Were laboratory tests conducted to ensure no internal removal of OH in the cell (line 273)?*

Answer: We did kinetic calculation to estimate the impact of propane addition on internal removal of OH in the cell, which show only minor impact as long as the removal efficiency is less than 100%.

Change: We revised the text from Page 10 Line 273 to Line 275: “Kinetic

calculations show that the added propane removes less than 0.3% of internally produced OH. The calculation assumes that the added propane is homogeneously mixed in the sampled air, yielding an expected OH lifetime which is larger than 0.1s and therefore much longer than the residence time (3ms) in the low-pressure detection cell. Therefore, the propane concentrations used in the chemical-modulation tests are not expected to influence possible OH interference signals.”

1.3 Comments: Figure 2: What do the dashed lines correspond to? It is difficult to assess from this figure if there is any diurnal variation in the magnitude of the interference signal? Could the authors comment on any variation observed, e.g. as a function of atmospheric composition? Is this possible unknown interference signal of sufficient magnitude to account for the modelled measured OH discrepancy at $[\text{NO}] < 300\text{pptv}$ (line 479)?

Answer: In Figure 2, the dashed lines separate one set of test from the other. To assess the possible variation of the interference signals, we summarized the conditions during the 6 titration experiments in a new table. We found no evidence that the unaccounted interference correlates with other measured species. The signal appears to be similar with values within the range of $1 \times 10^6 \text{ cm}^{-3}$ in quite different chemical conditions during the campaign. For a large range of NO concentrations, the residual OH determined in the titration tests was similar. 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.”

2. Comments: *Possible RO₂ interference: Fuchs et al. (Review of Scientific Instruments, 2008) report a possible interference in the RO₂ instrument from pernitric acid and methyl peroxy nitrate which have the potential to thermally decompose in RO_x system and be detected as HO₂ and CH₃O₂. Could the authors comment on the impact this interference may have for these field conditions, particularly under the high NO_x conditions experienced in the morning? Could this interference explain the model measured discrepancy in RO₂ at this time? What is the impact of this interference on the ozone production rate calculated from the measured HO₂ and RO₂ concentrations?*

Answer: We calculated the thermal decomposition of the peroxy nitric acid (HO₂NO₂), methyl peroxy nitrate (CH₃O₂NO₂) and PAN as Fuchs et al. (2008) did. Although these species could cause interference and help to explain the underestimation of HO₂ and RO₂, the impact is so small that have only minor impact on our measurements for high NO condition.

Change: We added on Page 11 L338: ‘A bias in the measurement of RO₂ may be caused in polluted air by peroxy radicals, which are produced in the low-pressure converter of the RO₂ instrument by thermal decomposition of peroxy nitric acid (HO₂NO₂), methyl peroxy nitrate (CH₃O₂NO₂) and PAN (Fuchs et al., 2008). In the atmosphere, HO₂NO₂ and CH₃O₂NO₂ are in a fast thermal equilibrium with HO₂ and CH₃O₂, respectively, together with NO₂. The possible interference scales with NO₂, which was highest during the Wangdu campaign in the morning (median value of 15 ppbv; cf. Fig. 6). For this condition, according to model calculations by Fuchs et al. (2008), HO₂NO₂ and CH₃O₂NO₂ are expected to produce interferences of +2.6 % and +9 % for the detected HO₂ and CH₃O₂ radicals, respectively. Since HO₂ and CH₃O₂ contributed about 50 % (measured) and 10 % (modelled) to the total RO_x in the morning, the estimated

interference for measured RO_2 is only +2 %. The interference from PAN decomposition in the instrument was calculated by Fuchs et al. (2008) to be 0.1 pptv per ppbv of PAN. Since PAN concentrations modelled for the Wangdu campaign are less than 1 ppbv, also from this compound no significant interference is expected. Another bias may be due to the perturbation of the reactor chemistry from high ambient NO concentrations (Fuchs et al., 2008). For the measurements in the RO_x and HO_2^* mode, the corresponding interferences are estimated to be less than +1 % and +3 %, respectively, at 15 ppbv NO.'

3. Comments: *Model measurement comparison of RO_2 : The manuscript focusses on the differences observed between measured and modelled RO_2 in the morning, but in figure 5 the model under-predicts RO_2 and $\text{RO}_2^\#$ until 16:00. Some comments should be provided on this under-prediction; the under-prediction in OH reactivity cannot account for this under-prediction beyond 10am. Please extend this commentary to lines 849 in the Conclusion also. Owing to the strong coupling between RO_2 , HO_2 and OH (highlighted in figure 11), how does the model under-prediction of total RO_2 impact the model's ability to predict OH and HO_2 ? Could the model be scaled to reproduce $[\text{RO}_2]$ and then the performance of the model to predict OH and HO_2 re-assessed? There are inconsistencies in the modelled and measured radical ratios (and OH reactivity) that warrant further investigation. Section 3.6 would benefit from a more detailed discussion of the modelled RO_2 species – what are the other $\text{RO}_2^\#$ species in figure 8? Please define 'MO₂' in this figure caption.*

Answer: Considering the uncertainties, RO_2 and $\text{RO}_2^\#$ were significantly underestimated only during the morning (06:00—10:00) hours. To resolve the issue of the model under-estimation of the RO_2 and $\text{RO}_2^\#$, three sensitivity studies were done to investigate the possible impact of a faster recycling (S1), a primary source (S2) and a slower removal rate (S3) of RO_2 . In the revised manuscript, we added the results from two sensitivity tests to the Figure 5 (see following).

Change: In the revised manuscript, we added the sensitivity run with scaled VOCs

(S1) and additional primary source (S2) in Figure 5.

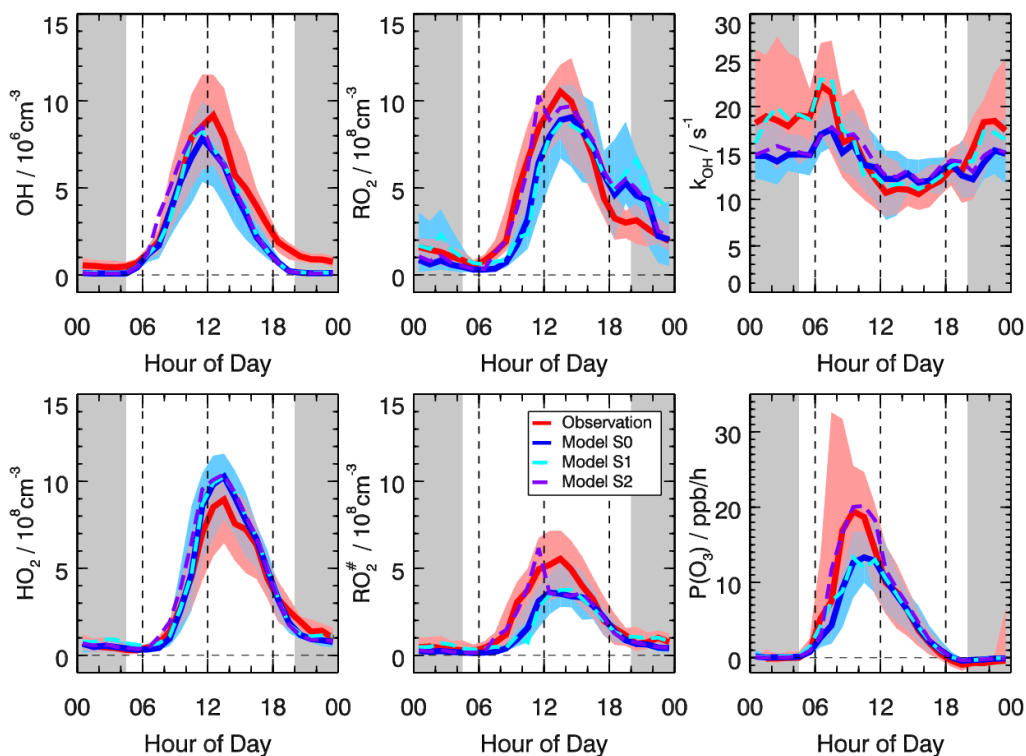


Figure 5 Comparison of hourly median diurnal profiles of OH, HO₂, RO₂, RO₂[#] concentrations and k_{OH} and the ozone production rate P(O₃) (thick lines give median values, colored areas give 25% and 75% percentiles). S0 (blue line) denotes results from the base model run. S1 (cyan, dashed line) shows 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.

We added a sentence at the end of Section 2.4 Page 13 Line 408: “The uncertainty of measurements and modelling needs to be taken into account in the comparison. The uncertainty of radical measurements is mainly determined by the measurement accuracies (OH: ±11%, HO₂: ±16%, RO₂: ±18%). A series of tests based on Monte Carlo simulations show that the uncertainty of the model calculations is approximately 40%.”

We revised the text in Page 17 Line 528 “RO₂ and RO₂[#] were significantly underestimated during the morning (06:00—10:00) hours with an observed-to-modelled ratio of 3 to 5, which is larger than the combined uncertainty (a factor of 2).

Reasons for discrepancies between measured and modelled RO₂ are further analyzed in Section 3.6.”

Page 18 from Line 569 to Line 596, we revised the text “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.

In sensitivity test S2, an additional primary source of RO₂ (OLTP) from terminal alkenes was introduced into the model. A source strength of 2 ppbv h⁻¹ from 06:00 h to 12:00 would be required to achieve a good model-measurement agreement (within 20 %) for both RO₂ and RO₂[#]. The modelled OH and HO₂ concentrations also increase and are slightly overpredicted by about 10% and 20%, respectively. This can still be considered as agreement within the error of measurements and model calculations. After 12:00 the difference between modelled and measured RO₂ becomes smaller than 15%, within the range of the accuracy of RO₂ measurements.

A candidate for an additional primary RO₂ source would be reactions of VOCs with

chlorine atoms, which are produced by photolysis of nitryl chloride (ClNO₂) (Osthoff et al., 2008). ClNO₂ is formed from the heterogeneous reactions of Cl⁻ ions with nitrogen pentoxide (N₂O₅) and accumulates during nighttime. After sunrise, ClNO₂ is expected to be completely photolysed within a few hours. The resulting Cl atoms can abstract H-atoms from saturated hydrocarbons or can add to alkenes. The alkyl radicals produce RO₂ which in case of alkene-derived peroxy radicals carry a chlorine atom. ClNO₂ was measured by a CIMS instrument at the Wangdu field site from 20 June to 8 July (Tham et al., 2016). The concentrations increased during night and reached on average high values of 0.5 ppbv at 08:00 h, followed by a decay to zero until 11:00 h. In their study, Tham et al. (2016) investigated the role of ClNO₂ photolysis on the photochemical formation of RO₂ and ozone during the Wangdu campaign. They used the MCM v3.3 with an additional chlorine chemistry module by Xue et al. (2015). We repeated the study by adding the same chlorine chemistry to our modified RACM2 mechanism and found the same additional formation rates of RO₂ and O₃ as reported by Tham et al. (2016). In our model run, a ClNO₂ source is assumed that leads to a linear increase of ClNO₂ during nighttime to a maximum value of 0.5 ppbv at 08:00 h on every day. After 08:00 h, the modelled source is turned off. ClNO₂ starts to photolyze after 06:00 h with a photolysis frequency that was calculated from the measured actinic flux. A maximum Cl production rate of 0.2 ppbv h⁻¹ is obtained at 08:00 h, yielding an additional RO₂ production with a similar rate. Compared to the additional RO₂ production rate required for model run S2, this is an order of magnitude too small. The mechanism is also not capable to sustain the additional RO₂ production during the whole morning, because ClNO₂ is photolytically depleted within 2 - 3 hours. Even if the modelled source strength is increased to match the highest ClNO₂ mixing ratio of 2 ppbv observed on 21 June (Tham et al., 2016), the additional primary RO₂ production of 0.5 ppbv h⁻¹ is still not sufficient. Thus, although ClNO₂ photolysis was a relevant radical source, it alone cannot explain the missing source of RO₂ radicals in the morning.

A further model test (S3) was performed, in which the rate of RO₂ removal was artificially reduced by decreasing the reaction rate constants between RO₂ and NO. Such a reduction would be justified, if the rate constant for RO₂+NO would be systematically too large in the model. Another reason could be a systematic measurement error of the NO concentration, or a segregation effect between RO₂ and NO due to inhomogeneous mixing in case of local NO emissions. In order to account for the discrepancy between modelled and measured RO₂ in the morning, the loss rate

would have to be changed by a factor of 4, which seems unrealistically high for each of the above mentioned possibilities. Also, there is no plausible reason why a systematically wrong rate constant or NO measurement error would appear only during morning hours.”

A more detailed discussion of the modelled RO₂ species is added in Sect. 3.6 as suggested. In Line 563 Page 18, we added: “In the group of modelled RO₂[#] species, isoprene peroxy radicals (ISOP) make the largest contribution during daytime. Other modelled RO₂[#] include peroxy radicals from alkenes, aromatics, long-chain (> C₄) hydrocarbons, and MVK and MACR. Among the RO₂ radicals which do not belong into the RO₂[#] group, peroxy radicals of short-chain (<C₅) alkanes are dominating: methyl peroxy radicals (MO₂), ethyl peroxy radicals (ETHP), and peroxy radicals HC₃P from HC₃ (e.g., propane). Acetyl peroxy radicals (ACO₃+RCO₃) are also a substantial fraction of RO₂.”

Minor comments:

Comments: *Line 331: Do the RO₂[#] concentrations determined in the HO₂ and RO₂ cell agree?*

Answer: RO₂[#] is only measured in the RO₂ cell. The HO₂ cell measured HO₂ with a

minimum contribution from $\text{RO}_2^\#$ (see section 2.2.3).

Comments: *Line 358: Please give the typical solar background at noon. Was it necessary to shade the cells?*

Answer: We revised the text in 358: ‘The typical solar background was about 40 cts/s which is a factor of 20 higher than the typical background signals obtained at night. Therefore, the detection limit was reduced by a factor of 5. A shade-ring was installed during the campaigns to shield the cell from direct solar radiation.’

Comments: *Line 527: ‘HO₂ concentrations are well reproduced by the model during the daytime’. From figure 5 it looks like the model has a tendency to over-predict [HO₂] in the afternoon. Could this over-prediction be masking the full magnitude of the model underprediction of OH at this time (as HO₂ is a strong recycling of OH)?*

Answer: In a sensitivity model run, we constrained the HO₂ concentration to the observed values and found the underprediction of OH would be more significant, because the original model predicted slightly higher concentrations of HO₂. The observed-to-modelled ratio of OH would increase to 1.8 in this case. An analysis of the OH budget using only measurements is done in our accompanying paper by Fuchs et al. 2016. This study shows that the OH destruction cannot fully be explained by known production rates in the late afternoon, when NO concentrations are lowest. We revised the text in line 527: “In general, HO₂ concentrations are reproduced by the model during daytime within the combined uncertainties of measurements and model calculations. Nevertheless, the model has a tendency to over-predict HO₂ in the afternoon. If we constrain the model to the observed HO₂ concentrations, the observed-to-modelled OH ratio increases from 1.6 to 1.8 for daytime averaged conditions (04:30–20:00).”

Comments: *Line 593-594: ‘scaling VOC concentrations to match measurements.’ which VOC species were scaled? Does the VOC species chosen influence the modelled [RO₂]?*

Answer: All input VOCs are scaled (see in table 2) to remain the same ratio between

different VOC species. Sensitivity tests showed that the modelled RO₂ is not very sensitive to different specific VOC species since the required change of modeled k_{OH} is relatively small (< 20%). The detailed explanation described above was added in the discussion of the RO₂ underprediction (refer to question 3).

Comments: *Line 595 'can be partly closed.' and also, line 701 'rate better agrees..' please provide the percentage change.*

Answer: More detail information is provided in the text as: “The observed-to-modelled RO₂ ratio is improved from 2.8 to 1.7”

Comments: *Line 720 – 723: This statement seems to be at odds with the model-measurement comparison presented in this manuscript which shows good agreement between modelled and measured HO₂ in the morning but a modelled measurement discrepancy for RO₂. Calculating ozone production from an RO₂ concentration estimated from HO₂ could mask a high morning ozone production rate.*

Answer: The statement is changed to: ‘Total photochemical ozone production rates were directly measured in a sunlit environmental chamber during the SHARP campaign in Houston (Texas) 2009 (Cazorla et al., 2012; Ren et al., 2013). The comparison with ozone production rates determined from measured HO₂ and from modelled HO₂ and RO₂ suggests that the model underestimated both HO₂ and RO₂ at high NO_x in the morning.’

Comments: *Line 769: There is no experimental evidence that HONO formed from the reaction of HO₂.H₂O + NO₂, as postulated by Li et al., (2014), occurs and so shouldn't be speculated on here.*

Answer: We canceled the statement as suggested.

Comments: *Line 770: Could an example of OH+hydrocarbon which does not form HO₂ or RO₂ be provided here.*

Answer: We modified the text in line 770 as “Further radical terminating OH losses include reactions with unsaturated dicarbonyls (DCB1, DCB 2, DCB 3) and acetyl nitrate species (PAN, MPAN, etc) in RACM2.”

Comments: *Line 848: Please provide the equivalent NO required in the previous campaigns for comparison.*

Answer: The equivalent NO required in the previous campaign is 0.8ppbv for PRIDE-PRD2006 and 0.4ppbv for CAREBEIJING2006. We rephrased the text: “...This behaviour is qualitatively in agreement with previous results from two field campaigns in China, in the Pearl River Delta and in the North China Plain, where the required equivalent NO is 800pptv and 400pptv (Lu et al., 2012, 2013).”