

Reviewer 2.

We thank the reviewer for their careful reading of the manuscript. We address each of the comments in turn below, with the comments first given in bold, followed by the response in normal type, followed by any changes made to the manuscript.

I agree with reviewer one on the possibility of shortening the paper which, at the current status, feels more as a description of the observation (with some model run) but does not really try and push for suggesting possible explanations for the finding or even looking in explanations given in the past (segregation for example or Cl₂ chemistry) to check if they would help the situation in this campaign.

As outlined in the responses to Reviewer 1, we have now shortened the manuscript by either shortening or completely removing Tables, Figures and Sections, and moving these to the Supplementary Material.

Unfortunately, there were no ClNO₂ measurements during the winter campaign, and hence it was not possible to calculate a time series for Cl atoms formed from photolysis of ClNO₂ and to assess any additional RO₂ radicals generated. Using the model run where an additional RO₂ source was added to reconcile the measurements and the model, a rough calculation has shown that the ClNO₂ concentration would have to be of the order of ~5800 ppbv in order to close the gap between modelled and measured RO₂. Previous measurements of ClNO₂ in suburban Beijing has shown a peak of ~2.9 ppbv (Wang et al. 2017) which is ~3 orders of magnitude smaller than the ClNO₂ concentration required, suggesting other additional primary sources are needed in the model besides Cl chemistry.

Added statement to paper about chlorine chemistry (page 28, line 615 – 619): “Although the ClNO₂ concentration required to bridge the gap between model and measurements would be ~5800 ppbv on average (see supplementary section S1.8 for details). Previous measurements in China in suburban Beijing have shown ClNO₂ peaking at 2.9 ppbv (Wang et al. 2017), however, and suggests other additional primary source are needed in the model besides Cl chemistry.”

This section has been added into the supplementary material:

“

S1.8 ClNO₂ and Cl concentration required to bridge the gap between measured and modelled total RO₂

Unfortunately, there were no ClNO₂ measurements during the winter campaign, and hence it was not possible to calculate a time series for Cl atoms formed from photolysis of ClNO₂ and to assess any additional RO₂ radicals generated. Using the model run where additional RO₂ source was added to reconcile the measurements and the model a rough calculation has shown that the ClNO₂ concentration would have to be on average ~5800 ppbv in order to close the gap between modelled and measured RO₂. Figure S10 shows the average diel of the calculated ClNO₂ and Cl concentration with peak at 1.4×10^4 ppbv and 1.6×10^6 molecule cm⁻³, respectively. The ClNO₂ and Cl concentration have been calculated using SE3 – SE5:

$$P'RO_2 = k_{VOC+Cl}[VOC][Cl] \quad \text{S E3}$$

$$[Cl] = \frac{P'RO_2}{k_{VOC+Cl}[VOC][Cl]} \quad \text{S E4}$$

$$[ClNO_2] = \frac{k_{VOC+Cl}[VOC][Cl]}{jClNO_2} \quad \text{S E5}$$

where $k_{\text{VOC}+\text{Cl}}$ is a generic rate constant to represents the reaction of all VOCs with Cl which in this case is $4 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$, [VOC] is the sum of the measured VOC concentration for the campaign and $\text{P}'\text{RO}_2$ is the calculated additional RO_2 used in MCM-PRO2 (see main paper section 4.2 for more details). The ClNO_2 required to bridge the gap between measured and modelled of RO_2 is ~ 3 orders of magnitude greater than the peak ClNO_2 concentration measured in suburban Beijing (2.9 ppbv) by Wang et al. (2018) suggesting that other additional primary source are needed in the model besides Cl chemistry .

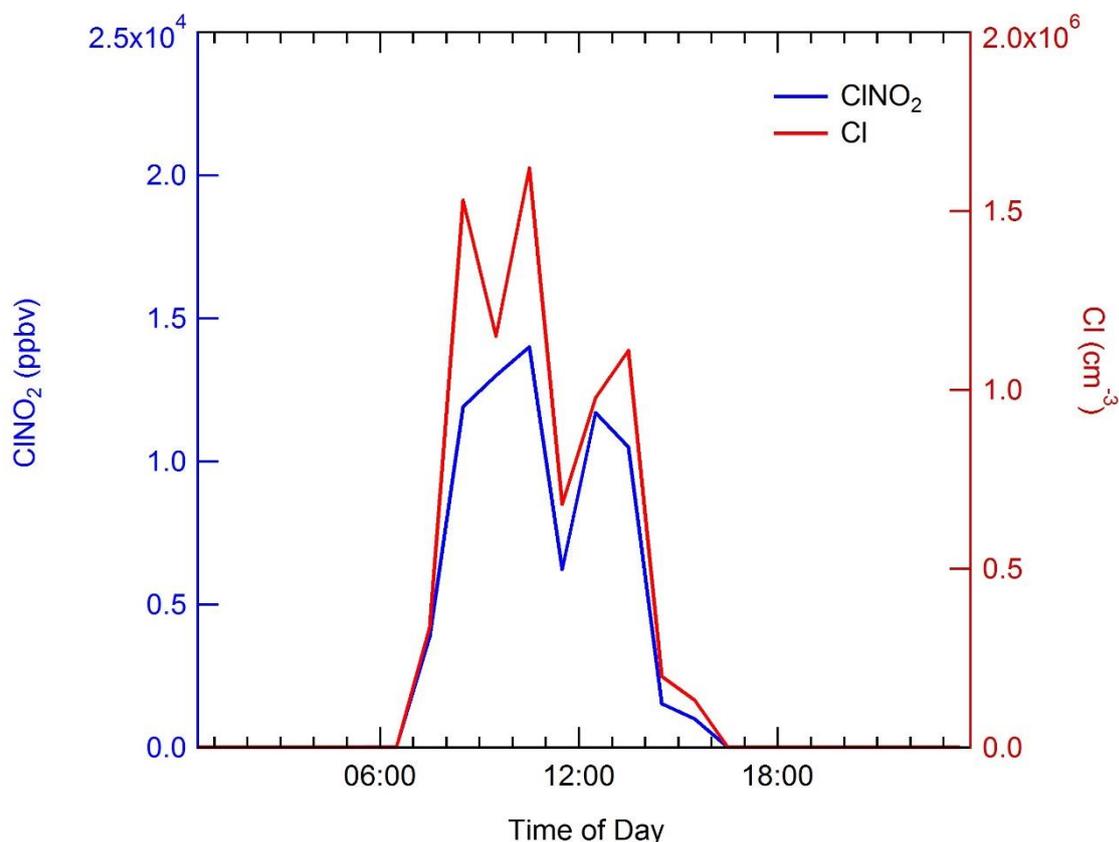


Figure S10 Average diel of the ClNO_2 and Cl atom concentration required to bridge the gap between measured and modelled RO_2 . The ClNO_2 and Cl concentrations have been calculated from the additional primary source of RO_2 added to the MCM-PRO2 model run, see section 4.2 in the main paper for more details.

“

Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., Wang, W., Tham, Y.J., Wang, Z., Yang, L. and Chen, J., 2017. Observations of N_2O_5 and ClNO_2 at a polluted urban surface site in North China: High N_2O_5 uptake coefficients and low ClNO_2 product yields. *Atmospheric environment*, 156, pp.125-134.

Regarding segregation, there were several instruments for NO measurements located at different positions around the field-site and there were no obvious differences between the measurements, and so we feel that NO segregation between the instruments cannot account for the differences between the measured and modelled RO_2 . We have made a statement in the text (page 25, line 563-564) regarding this: “. There were several instruments for NO measurements located around the site and no differences in concentrations were observed, hence no evidence of any obvious segregation”

I would suggest trying and making better use of the complex and simple RO_2 concentrations. Measurement of RO_2 or scarce to start with and here several time the measurement of simple and complex RO_2 separately is brought up but then the data is not really used. Even when mentioning

that there seems to be a better agreement between the measurement of simple RO₂ and model results at high NO (which, by the way, I do not agree with), the discussion stops there and there is no additional use of the data. Why not checking for example if the RO₂ measurement is consistent with the VOC load?

We have now included an additional analysis of the complex and simple RO₂ concentrations, and their agreement with the model (see the next comment below). Regarding whether RO₂ simple and RO₂ complex are consistent with the VOC load, the increase in KOH contribution for VOCs from non-haze to haze periods has been assessed. It shows that the increased contribution to KOH (s⁻¹) from VOCs going from non-haze to haze is a factor of: ~10 for aromatics, ~8 for alkenes and alkynes, ~6 for alkanes, ~9 for alcohols and ~2 for aldehydes. The large increase in relative contribution to KOH from aromatics, alkenes and alkynes is consistent with the observation of higher complex RO₂ (compared to simple RO₂) during haze periods compared to non-haze periods.

The statement “The increased contribution to KOH (s⁻¹) from VOCs going from non-haze to haze conditions is a factor of: ~10 for aromatics, ~8 for alkenes and alkynes, ~6 for alkanes, ~9 for alcohols and ~2 for aldehydes. The large increase in the relative contribution to KOH from aromatics, alkenes and alkynes is consistent with the observation of higher complex RO₂ (compared to simple RO₂) during haze periods compared to non-haze periods.” has been added to the paper.

The statements: “and can almost be reproduced by the model at NO concentrations above 100 ppbv.” Has been removed from the paper as suggested by reviewer 1.

Does the contribution of simple and complex RO₂ changes with time? During the day? From non-haze to haze periods? I think this type of analysis could maybe also help understanding a little bit more where the large discrepancy between measurement and model results arises from.

The average diel profile of both measured and modelled complex and simple RO₂ inside and outside of haze has been added to Figure 14, and we have added the following text to the paper. “The measured complex RO₂ radical species peak at similar concentrations inside (4.3×10^7 molecule cm⁻³) and outside (4.6×10^7 molecule cm⁻³) of haze. Interestingly, unlike the complex RO₂, the simple RO₂ concentration peaks at a lower concentration inside of haze (3.4×10^7 molecule cm⁻³) compared with outside of haze (5.5×10^7 molecule cm⁻³). The complex RO₂ is underpredicted by the model by a factor of ~48 and ~12 inside and outside of haze, respectively, whilst the simple RO₂ is underpredicted by a factor of ~66 and ~5.7 inside and outside of haze, respectively. The sharp increase for the underprediction of both simple and complex RO₂ inside haze events highlights the need of a large additional primary source of both simple and complex RO₂”.

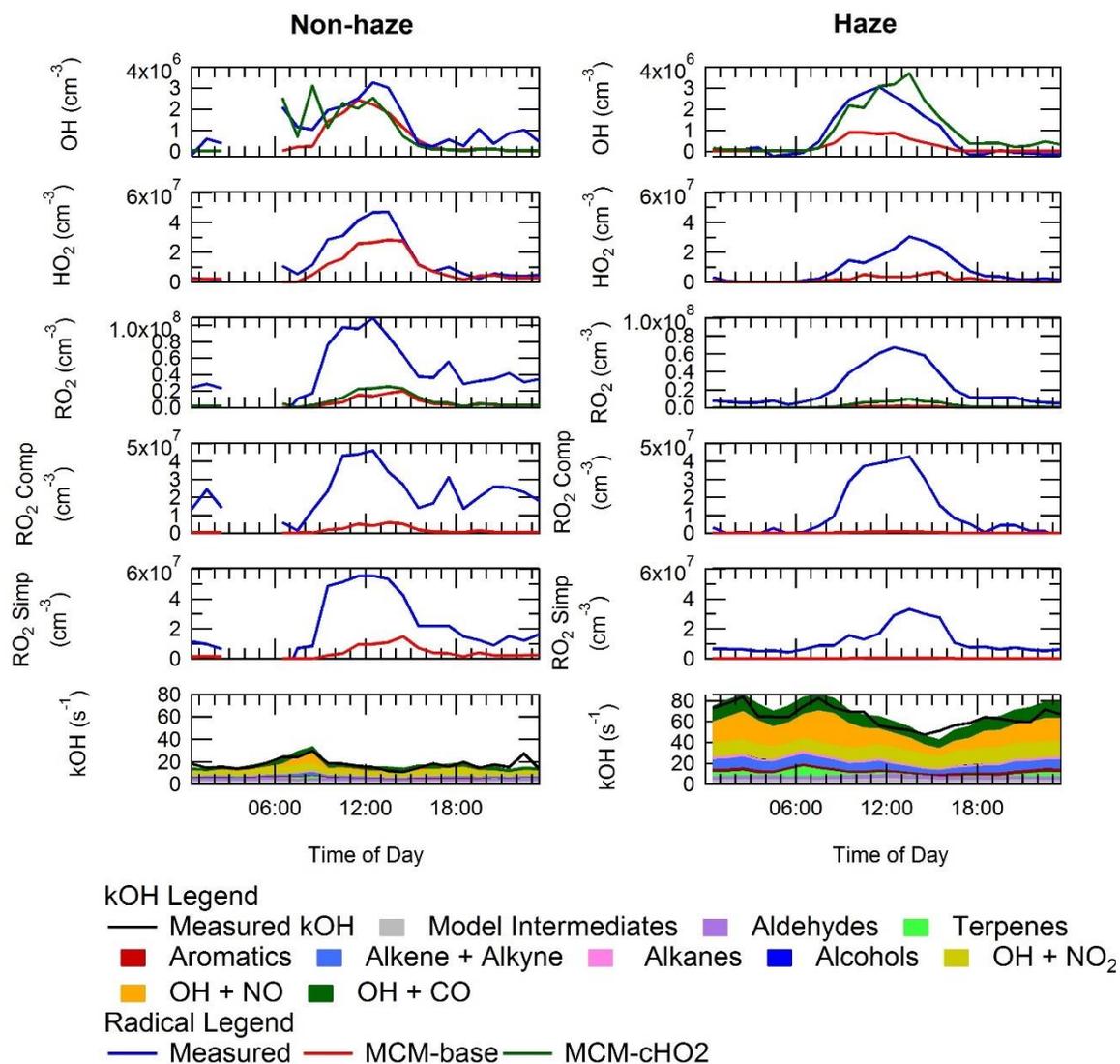


Figure 14. Average diel profiles for measured and modelled OH, HO₂, total RO₂, complex RO₂ (RO₂ comp), simple RO₂ (RO₂ simp) and kOH separated into haze (right) and non-haze (left) periods.

The average diurnal profile of measured and modelled simple and complex RO₂ have been added to Figure.8., and the updated Figure 8. Is shown below:

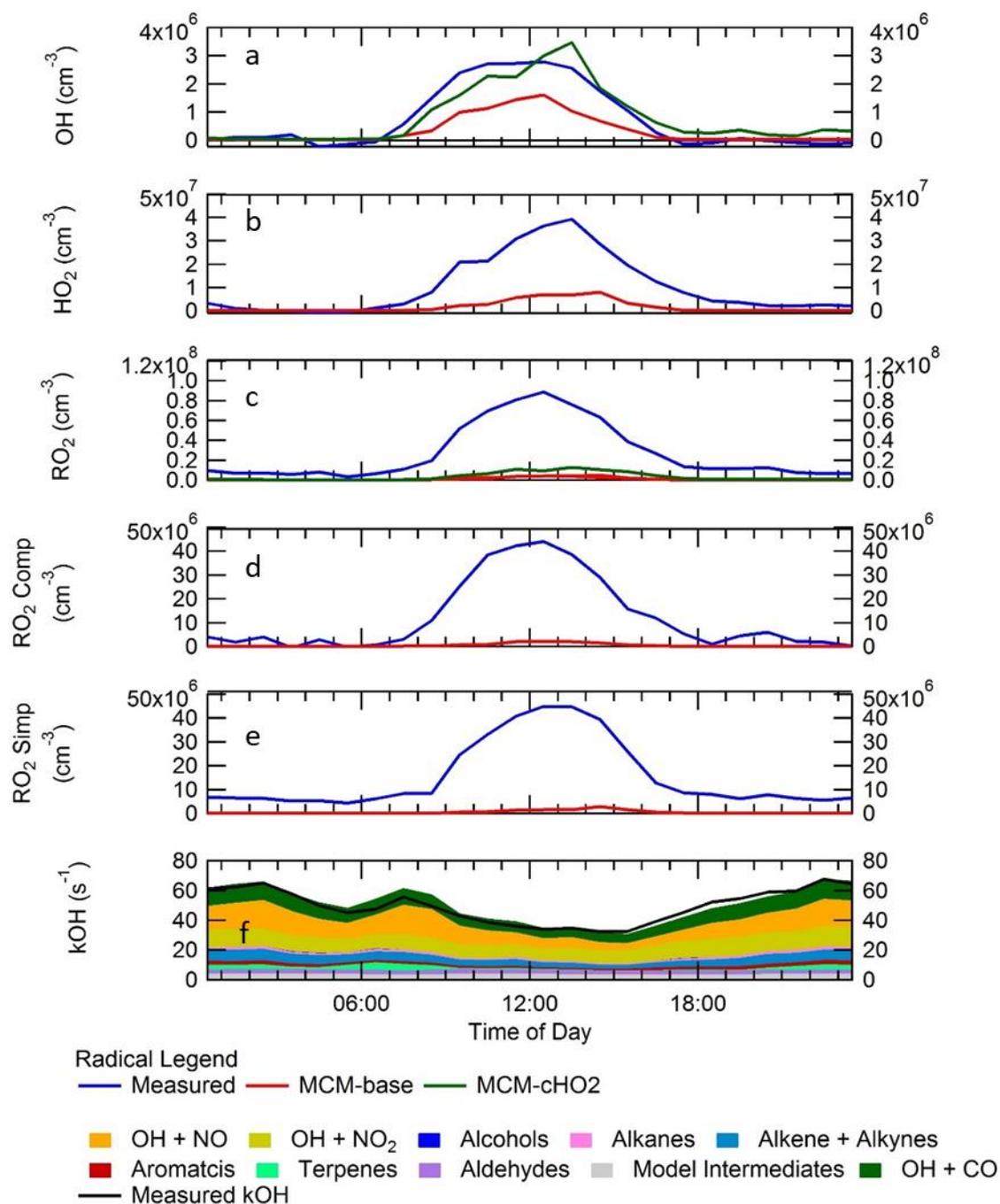


Figure 8. Campaign averaged diel profile of OH (a), HO₂ (b), sum of RO₂ (c), complex RO₂ (d), simple RO₂ (e) for measurements (blue) and box-model calculations: MCM-base (red) and MCM-CHO₂ (green). See text for descriptions of each model scenario. (f) – OH reactivity (s^{-1}) for measurements (black line) and model (stacked plot) with the contribution to reactivity from different measured species and modelled intermediates shown in the key.

Along with a small discussion on the variability during the day. The new text is as follows:

“The complex and simple RO₂ show a very similar diurnal profile both peaking at 12:30 at a concentration of 4.4×10^7 molecule cm^{-3} and 4.5×10^7 molecule cm^{-3} , respectively. The model underpredicts the simple and complex RO₂ at 12:30 by a factor of 30 and 22, respectively. The large underprediction of both simple and complex RO₂ highlights the needs for additional primary sources

forming both simple and complex species in the model. Section 4.2 explores the impact of additional primary source of RO₂ added into the model on OH and HO₂

I am missing a small but useful description of all the measurements used within the model and which instrumentation (with accuracy and precision) was used for the different trace gases. It does not have to go too much in details but there is no mentioning of how NO, which is extremely important for the radicals chemistry, was measured. . .or O₃ or anything.

We have added a Table (Table 2) which describes the methods used for some of the key species which are used to constrain the model. For many of the other species used to constrain the model, details are given in Shi et al 2018, and we have made a clear reference to that paper.

Modified wording “The accuracy and precision of trace gas species can be found in Table 2, details on the HONO measurements used in the modelling scenarios can be found in Crilley et al.(2019). Details for other measurements can be found in Shi et al.(2018)”

The following table has been added to the manuscript:

Instrument	Technique	2 σ Uncertainty / %	2 σ Precision/ ppbv
O ₃ , TEi49i	UV absorption	4.04	0.28 ¹
NO, TEi42i-TL	Chemiluminescence via reaction with O ₃	4.58	0.03 ¹
SO ₂ , TEi43i	UV fluorescence	3.12	0.03 ¹
NO ₂ , CAPS, T500U	Cavity enhanced absorption spectroscopy	5.72	0.04 ¹
HONO	LOPAP x2, BBCEAS x 2, ToF-CIMS and SIFT-MS	9 – 22%	0.025 – 0.130

Table 2. Instruments and techniques used to measure key model constraints. 2 σ uncertainties for the measured trace gas species used in the modelling scenarios are quoted. ¹Precision is given for 15-minute averaging time. For details of the HONO measurements please see Crilley et al.(2019).

In addition to this, there is no description of how the OH reactivity was measured and how much of a deviation from the mono-exponential decay could be expected for values of NO reaching up to 250 ppbv. What is the accuracy of the kOH measured at high NO? Could this represent a lower limit? This should be discuss appropriately and it could add an additional explanation of why the model is largely underestimating the RO₂ and HO₂ concentrations (lack of some primary VOCs).

The kOH decays show no biexponential behaviour suggesting that recycling from HO₂ + NO was not observed and all decays were fitted with a single exponential decay. Details of the OH reactivity instrument have been added to the instrumental details section, and relevant citations are given. The total uncertainty in the ambient measurements of OH reactivity is ~ 6% (Stone et al. 2016). The new text describing the method is as follows:

“OH reactivity measurements were made using the laser flash photolysis pump-probe technique and the instrument is described in detail in Stone et al. (2016). Ambient air was drawn into the reaction cell (85 cm in length, 5 cm in diameter) at 12 SLM. Humidified ultra-high purity air (Messer, Air Grade Zero 2) passed a low-pressure Hg lamp at 0.5 SLM to generate ~ 50 ppbv of O₃ which was mixed with the ambient air. The O₃ was photolyzed at 266 nm to generate a uniform OH concentration across the reaction cell. The change in the OH radical concentration from pseudo-first-order loss with species present in ambient air was monitored by sampling the air from the reaction cell into a FAGE detection cell at ~1.5 Torr. The 308 nm probe laser (same as the FAGE laser describe above) was passed across the gas flow in the FAGE cell to excite OH radicals, and then detected the fluorescence signal at ~ 308

nm detected by a gated channel photomultiplier tube. The OH decay profile owing to reactions with species in ambient air was detected in real time. The decay profile was averaged for 5-mins and fitted with a first-order rate equation to find the rate coefficient describing the loss of OH (k_{loss}), with k_{OH} determined by subtracting the physical loss of OH (k_{phys}). The OH reactivity data were fitted with a mono-exponential decay function as no bi-exponential behaviour was observed, even at the highest NO concentrations, and hence there was no evidence for recycling from $\text{HO}_2 + \text{NO}$ impacting on the retrieved values. The total uncertainty in the ambient measurements of OH reactivity is $\sim 6\%$ (Stone et al. 2016).”

Page2 line46: “. . .quality are of serious concern. . .”

This has been fixed

Page2 line49: “. . . of the world fastest. . .”

This has been fixed.

Page2 line51: I would drop the number after the comma and round the percentages

We agree and this has been done.

Page2 line 59: NO_x, SO₂ and VOCs have not been defined

We have now defined these, and added the following text:

“The reaction of OH with primary pollutant emissions (particularly NO_x (NO+NO₂), SO₂ and VOCs (volatile organic carbon)) can form secondary pollutants such as HNO₃, H₂SO₄ and secondary oxygenated organic compounds (OVOCs).”

Chapter 2.1 More information on the specific of the campaign site would be beneficial. Was the site on the street? On a platform? On the roof of the building? What was the distance between different instruments? I understand there is a specific paper on the topic but just two lines with a little bit information would suffice.

We have added a brief description of the field site as follows:

“The instruments were housed in containers and located on the ground at the IAP site on a grassed area, the distance between the Leeds and York container (VOC and trace gas measurements) was ~ 3 m.”

Chapter 2.2.2 Here as well more details on the sensitivity towards the different RO₂ is needed. The different concentrations of RO₂ are used later on to justify some of the conclusions on the discrepancies between model and measurements so it is important to mention how well know is the separation in two classes of RO₂ and which sensitivity is applied for which classes.

A more detailed description of the ROxLIF instrument has been added which explains how the two different classes of RO₂ are measured and discusses what the sensitivity towards different RO₂ is and how this is determined.

The new text is as follows:

“The ROxLIF flow reactor (83 cm in length, 6.4 cm in diameter) was coupled to the second FAGE detection cell to allow for detection of RO₂ (total, complex and simple) using the method outlined by Fuchs et al. (2008). The flow reactor was held at ~ 30 Torr and drew ~ 7.5 SLM through a 1 mm pinhole ID (in-diameter). The flow reactor was operated in two mode: in the first (HO_x mode) 125 sccm of CO (Messer, 10% in N₂) was mixed with ambient air close to the pinhole to convert OH to HO₂. In the second (RO_x mode), 25 sccm of NO in N₂ (Messer, 500 ppmv) was also added to the CO flow to convert RO₂ into OH. The CO present during RO_x mode rapidly converts the OH formed into HO₂. The air from

the RO_xLIF flow reactor was drawn (5 SLM) into the FAGE fluorescence cell (held at ~1.5 Torr) and NO (Messer, 99.9%) was injected into the fluorescence cell to convert HO₂ to OH. In HO_x mode a measure of OH + HO₂ + cRO₂ (complex RO₂) was obtained; whilst RO_x measured OH + HO₂ + ΣRO₂. sRO₂ (simple RO₂) concentration was determined by subtracting the concentration of cRO₂, HO₂ and OH from RO_x.

In previous laboratory experiments the sensitivity of the instrument to a range of different RO₂ was investigated and can be found in Whalley et al.(2018). Similar sensitivities were determined for a range of RO₂ species that were tested and agreed well with model-determined sensitivities. For comparison of the modelled RO₂ to the observed RO₂-total, RO₂-complex and RO₂-simple, the RO_xLIF instrument sensitivity towards each RO₂ species in the model was determined by running a model first under the RO_xLIF reactor and then the RO_xLIF FAGE cell conditions (NO concentrations and residence times) to determine the conversion efficiency of each modelled RO₂ species to HO₂. “

Page8 line212: Is there really no difference between the accuracy of OH, HO2 and RO2 accounting that HO2 requires conversion into OH and RO2 requires a minimum of 2 NO steps?

Although detection of OH is direct, detection of HO₂ is via conversion to OH via addition of NO, and RO₂ is via conversion to HO₂, and then the HO₂ is converted to OH in the FAGE (requiring two steps as the reviewer points out), because the instruments are calibrated separately using known concentrations of OH, HO₂ and RO₂, the accuracy of the measurement is the same as this depends on the calibration accuracy. The latter is controlled mainly by the accuracy in determining the product of the lamp intensity, the water vapour (in air) and photolysis time (which makes OH and HO₂), which is determined using chemical actinometry. Other factors such as absorption cross-sections, rate coefficients and quantum yields to make OH and HO₂, and the conversion efficiency of OH to the relevant RO₂ (which is quantitative) have very low uncertainties. In addition, the flow of NO is very reproducible.

Page9 line 239: What is the concentration of H2 to 500 ppbv included in the model needed for?

H₂ can react with OH and thus constitutes part of the OH reactivity, although a very minor contribution, and is also a source of HO₂. However, the inclusion of H₂ does not change the modelled reactivity or HO₂ (< 0.1%) much but is included in the model for completeness, as is normally the case in field studies of radicals and comparison with models.

Page 9 line241: What was the time resolution of the GC data?

The time resolution for the GC data was 1 hr and has been interpolated at 15 min intervals for the model. A sentence about this has been added to the paper as follows:

“ The time resolution for the GC-FID data was 1 hr and has been interpolated to 15-min for the model input.”

Page 11 line290: Is the diel variation shown the mean or the median of the data?

It is the median and this has been added to the caption of Figure 5.

“Comparison of the median average diel variation for j(O¹D) (s⁻¹), NO (ppbv), O₃ (ppbv), CO (ppbv), O_x (ppbv), NO₂ (ppbv), HONO (ppbv) and boundary layer height (m) inside and outside haze events; denoted by solid red and blue lines, respectively. The dashed lines represent the interquartile range for the respective species and pollution period.”

Page 11 line300: O3 does not react with high levels of NO but with a high concentration of NO

Thanks, this has been fixed.

Page 21 Section 4.1: I assume that here only the results from the model are shown but this is not clear from reading the text.

Yes, only the results from the model are shown here, and text to make this clear has been added to caption of Figure 9.

“Figure 9. Rates of primary production (top panel) and termination (bottom panel) for RO_x radicals (defined as OH + HO₂ + RO + RO₂) calculated for MCM-base model separated into haze (right) and non-haze (left) periods. The definition of haze is when PM_{2.5} exceeds 75 μm⁻³. The production from: O¹D + H₂O and VOC + NO₃ and the termination reactions: RO₂ + HO₂, HO₂ + HO₂, HO₂ + NO₂, are shown in the key, although many are not visible and contributed <1% of the total production and termination.”

Page 24 Lines 516-521: Has the possibility of segregation of air been investigated and ruled out or why this is mentioned here but there is no discussion on how this could have had an impact on this specific site? It could be worth discussing if this could help bringing measurements and model results in agreement.

As noted in the response to reviewer 1, various NO measurements were made at ground level around the site via multiple instruments and which might have pointed to any segregation of NO owing to local point source. A sentence has been added to paper as follows:

“There were several instruments for NO measurements located around the site and no differences in concentrations were observed, hence no evidence of any obvious segregation.”

Page 24 line 539: Assuming that figure 10 is actually figure 11 (where in the caption of the figure the model line is the red one (?)), I do not agree with the statement in the paper that the model can reproduce the simple RO₂ measured for NO above 100 ppbv. Actually, there is overlap between the model and the measured RO₂ 95th percentile for the complex RO₂. In all honesty, I am not sure this plot tells us much as the model equally predicts pretty much zero RO₂ expected at NO above 10 ppbv for both type of RO₂. Although I agree that the simple RO₂ have been studied more carefully, what would be the difference in rate with NO to justify the observed concentration of RO₂ or what type of different chemistry for the most complex RO₂ would be needed? There is no discussion in this study about it and some suggestions of what is feasible are needed.

We apologise, Figure 10 is indeed Figure 11 and this has been amended in the text.

Please see the response to Reviewer 1 regarding the model behaviour for the various types of RO₂ at high NO, where there is an amended statement that the model could reproduce simple RO₂ at high NO.

This plot (Figure. 11) is important as it shows that the missing source of RO₂ must form both complex and simple RO₂, as the underprediction of both increases with increasing NO.

The effect on decreasing the kRO₂ + NO has been investigated and shows that decreasing the rate constant by a factor ~ 10 cannot reconcile the modelled RO₂ with the measured at high NO (still underpredicted by a factor of 10). Also, whilst the modelled RO₂ is improved by decreasing the rate constant, the increased RO₂ in the model is not recycled into HO₂ and OH and the model underpredictions for these radical species remains. A discussion for these results has been added into the supplementary in section S1.7, and is as follows:

“S1.7 The effects of the kRO₂ + NO rate constant on the modelled radical species

Other than CH₃O₂ and C₂H₅O₂, rate constants for the reaction of many other RO₂ + NO is based on structure activity relationships (SARs) in the MCM and is lumped to kRO₂NO and kAPNO (<http://mcm.leeds.ac.uk/MCM/>). The lumped rate constants kRO₂NO and kAPNO were both decreased by a factor of 2 and 10 to investigate the effects on modelled OH, HO₂ and RO₂. The model where the rate constant for RO₂ + NO was decreased by a factor of 2 is titled MCM-kRO₂-2, whilst the model where the rate constant was decreased by a factor of 10 is titled MCM-kRO₂NO-10.

The comparison of measured values with modelled values (MCM-base, MCM-kRO2-2 and MCM-kRO2-10) is shown in Figure S8. Figure S8 shows that on certain days (e.g. 19/11, 5/12 and 9/12) when the model (MCM-base) could not reproduce the measured values of RO₂ the discrepancy between the measurements and the MCM-kRO2NO-10 model is almost reconciled. On these days the MCM-kRO2NO-10 does not really change the OH or HO₂ concentration from the base model. On all days the MCM-base underpredicts the RO₂ concentration, and MCM-kRO2NO-10 does decrease the gap between measurements and modelled, compared to MCM-base. MCM-kRO2NO-2 does not significantly increase the total RO₂ concentration from MCM-base, unlike MCM-kRO2NO-10. Since changing the rates of RO₂ + NO will be very dependent on the NO concentration, the ratio of measured:modelled radical concentration has been binned against the log of NO for MCM-base, MCM-kRO2NO-2 and MCM-kRO2NO-10 in Figure S9. Figure S9 shows similar results to the timeseries where at the lower concentration of NO (19/11, 5/12 and 9/12) the MCM-kRO2NO-10 can reproduce the RO₂ concentration. The results at higher [NO] show that decreasing the rate of RO₂ + NO improves the agreement between measured:modelled RO₂, especially for MCM-kRO2NO-10, but the observed RO₂ concentration is still underpredicted beyond 30 ppbv.

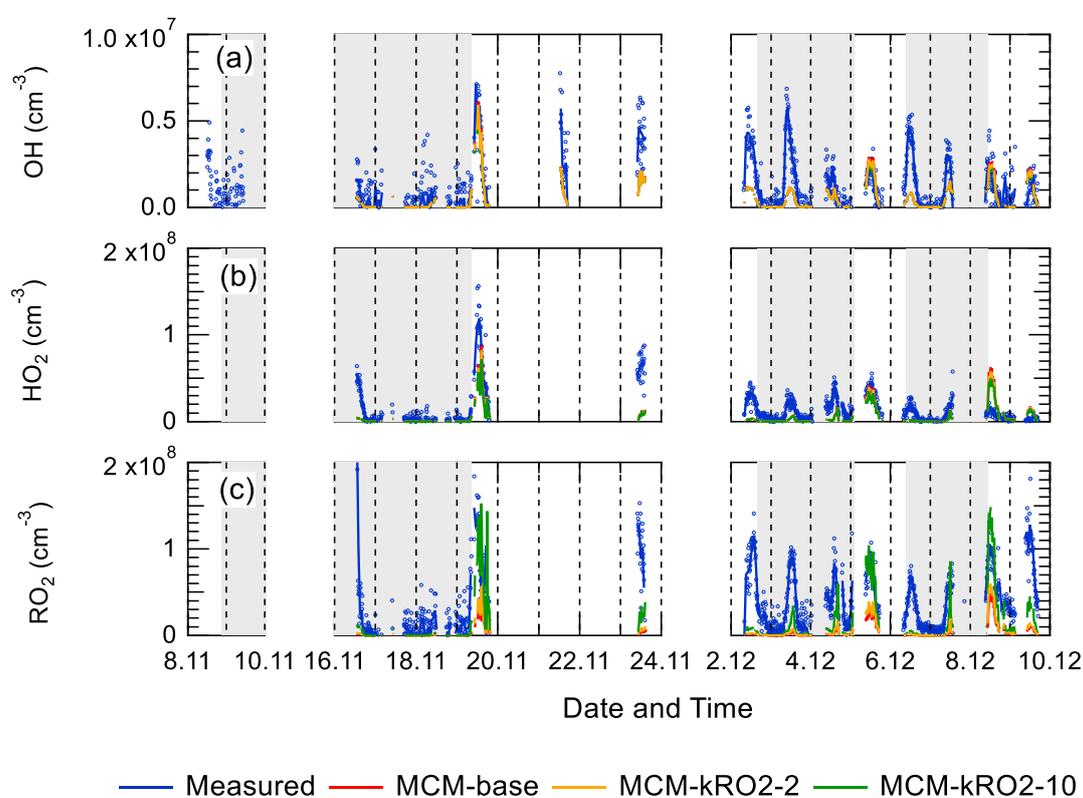


Figure S8. (a) Time-series comparison of measured values of OH with modelled OH concentrations from MCM-base, MCM-kRO23NO-2 and MCM-kRO2-10. (b) Time-series comparison of measured values of HO₂ with modelled HO₂ concentrations from MCM-base, MCM-kRO23NO-2 and MCM-kRO2-10. (c) Time-series comparison of measured values of total RO₂ with modelled total RO₂ concentrations from MCM-base, MCM-kRO23NO-2 and MCM-kRO2-10. The data sets are 15-minutes averaged.

The fact that the OH and HO₂ modelled concentrations do not change significantly for the models with reduced RO₂ + NO rate constant highlights that the enhanced RO₂ radicals (in MCM-kRO2-10) are not recycling into HO₂ or OH, even though the agreement for the RO₂ concentration is improved for these models (MCM-kRO2NO-2 and MCM-kRO2NO-10). The lack of RO₂ recycling highlights that the RO₂ and RO radicals are terminating rather than propagating in the model.

This work highlights alternative chemistry and solutions must be applied for the two different NO regimes observed during the Beijing wintertime campaign. At high [NO] (above 10 ppbv) further reductions in the RO₂+NO rate constant would be required to reconcile the model with observations. However, at NO mixing ratios below 10 ppbv, further reductions in the RO₂+NO rate constant would lead to the model overpredicting the RO₂ concentration.

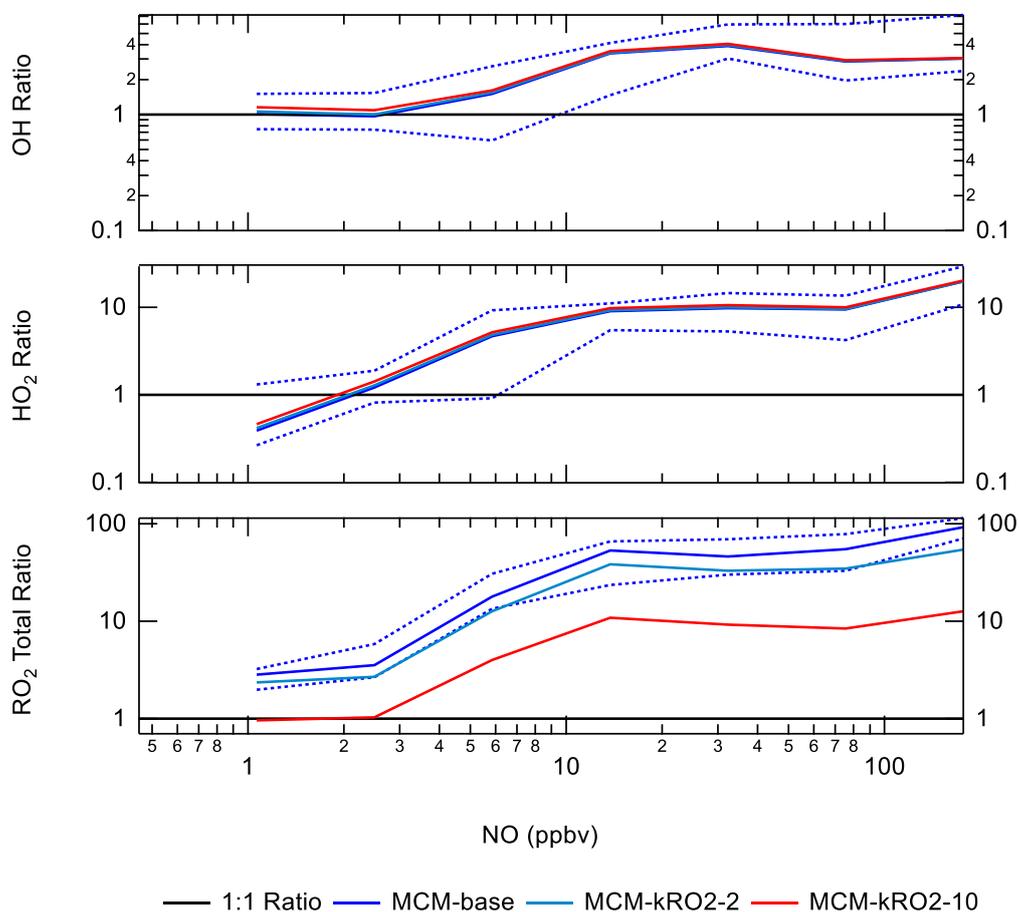


Figure S9. The ratio of measurement/model for OH (a), HO₂ (b) and RO₂ (c) across various NO concentrations for daytime values only ($j(\text{O}^1\text{D}) > 1 \times 10^{-6} \text{ s}^{-1}$). Light blue represents for results from MCM-kRO2NO-2, dark blue represents results from MCM-base and red represents results from MCM-kRO2NO-10.

“

A reference in the paper to this section has been added “The effect on reducing the RO₂ has been investigated and is shown in S1.7 in the supplementary material. The results show that reducing the rate constant by a factor ~ 10 does improved the modelled to measurements agreement by a factor of 8.3 for total RO₂. However, RO₂ is still underpredicted by a factor of ~ 12 at the highest NO. Also the increased RO₂ in the model does not recycle into HO₂ or OH efficiently. This work highlights that uncertainties in the rate constant for RO₂ + NO for different RO₂ cannot be the only explanation for the underprediction of RO₂ in the model.”

Page 27 line 570-573: What would be the concentration of CL2 and/or ClNO2 needed to justify such a production of RO2? This could tell us if it could be possible at all.

Unfortunately, there were no ClNO₂ measurements during the winter campaign, and hence it was not possible to calculate a time series for Cl atoms formed from photolysis of ClNO₂ and to assess any

additional RO₂ radicals generated. Using the model run where an additional RO₂ source was added to reconcile the measurements and the model a rough calculation has shown that the ClNO₂ concentration would have to be of the order of ~5800 ppbv in order to close the gap between modelled and measured RO₂. Previous measurements of ClNO₂ in suburban Beijing has shown a peak of ~2.9 ppbv (Wang et al. 2017) which is ~3 orders of magnitude smaller than the ClNO₂ concentration required, suggesting other additional primary sources are needed in the model besides Cl chemistry.

Added statement to paper about chlorine chemistry (page 28, line 615 – 619): “Although the ClNO₂ concentration required to bridge the gap between model and measurements would be ~5800 ppbv on average (see supplementary section S1.8 for details). Previous measurements in China in suburban Beijing have shown ClNO₂ peaking at 2.9 ppbv (Wang et al. 2017), however, and suggests other additional primary source are needed in the model besides Cl chemistry.”

This section has been added into the supplementary material:

“

S1.8 ClNO₂ and Cl concentration required to bridge the gap between measured and modelled total RO₂

Unfortunately, there were no ClNO₂ measurements during the winter campaign, and hence it was not possible to calculate a time series for Cl atoms formed from photolysis of ClNO₂ and to assess any additional RO₂ radicals generated. Using the model run where additional RO₂ source was added to reconcile the measurements and the model a rough calculation has shown that the ClNO₂ concentration would have to be on average ~5800 ppbv in order to close the gap between modelled and measured RO₂. Figure S10 shows the average diel of the calculated ClNO₂ and Cl concentration with peak at 1.4×10^4 ppbv and 1.6×10^6 molecule cm⁻³, respectively. The ClNO₂ and Cl concentration have been calculated using SE3 – SE5:

$$P'RO_2 = k_{VOC+Cl}[VOC][Cl] \quad \text{S E3}$$

$$[Cl] = \frac{P'RO_2}{k_{VOC+Cl}[VOC][Cl]} \quad \text{S E4}$$

$$[ClNO_2] = \frac{k_{VOC+Cl}[VOC][Cl]}{jClNO_2} \quad \text{S E5}$$

where k_{VOC+Cl} is a generic rate constant that represents the reaction of all VOCs with Cl which in this case is 4×10^{-12} molecule⁻¹ cm³ s⁻¹, [VOC] is the sum of the measured VOC concentration for the campaign and P'RO₂ is the calculated additional RO₂ used in MCM-PRO2 (see main paper section 4.2 for more details). The ClNO₂ required to bridge the gap between measured and modelled of RO₂ is ~3 orders of magnitude greater than the peak ClNO₂ concentration measured in suburban Beijing (2.9 ppbv) by Wang et al. (2018) suggesting that other additional primary source are needed in the model besides Cl chemistry.

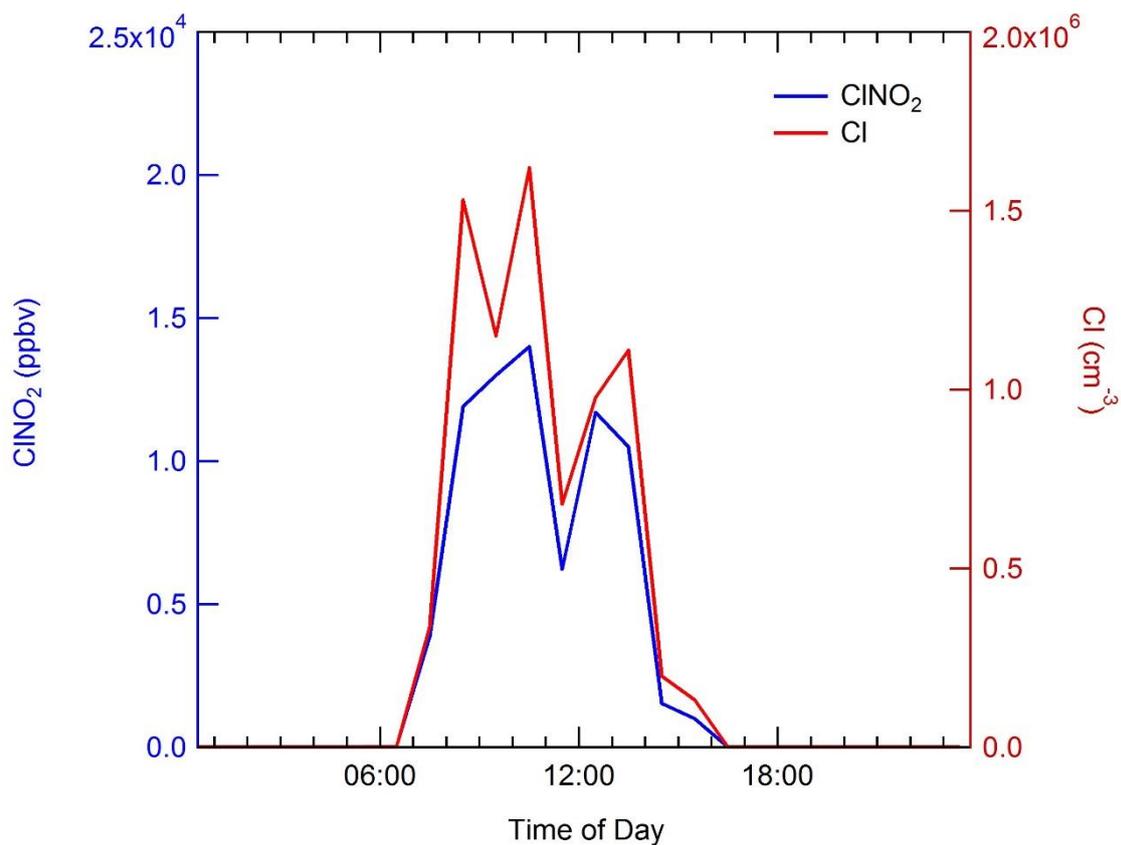


Figure S10 Average diel of the ClNO₂ and Cl atom concentration required to bridge the gap between measured and modelled RO₂. The ClNO₂ and Cl concentrations have been calculated from the additional primary source of RO₂ added to the MCM-PRO2 model run, see section 4.2 in the main paper for more details.

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Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., Wang, W., Tham, Y.J., Wang, Z., Yang, L. and Chen, J., 2017. Observations of N₂O₅ and ClNO₂ at a polluted urban surface site in North China: High N₂O₅ uptake coefficients and low ClNO₂ product yields. *Atmospheric environment*, 156, pp.125-134.