

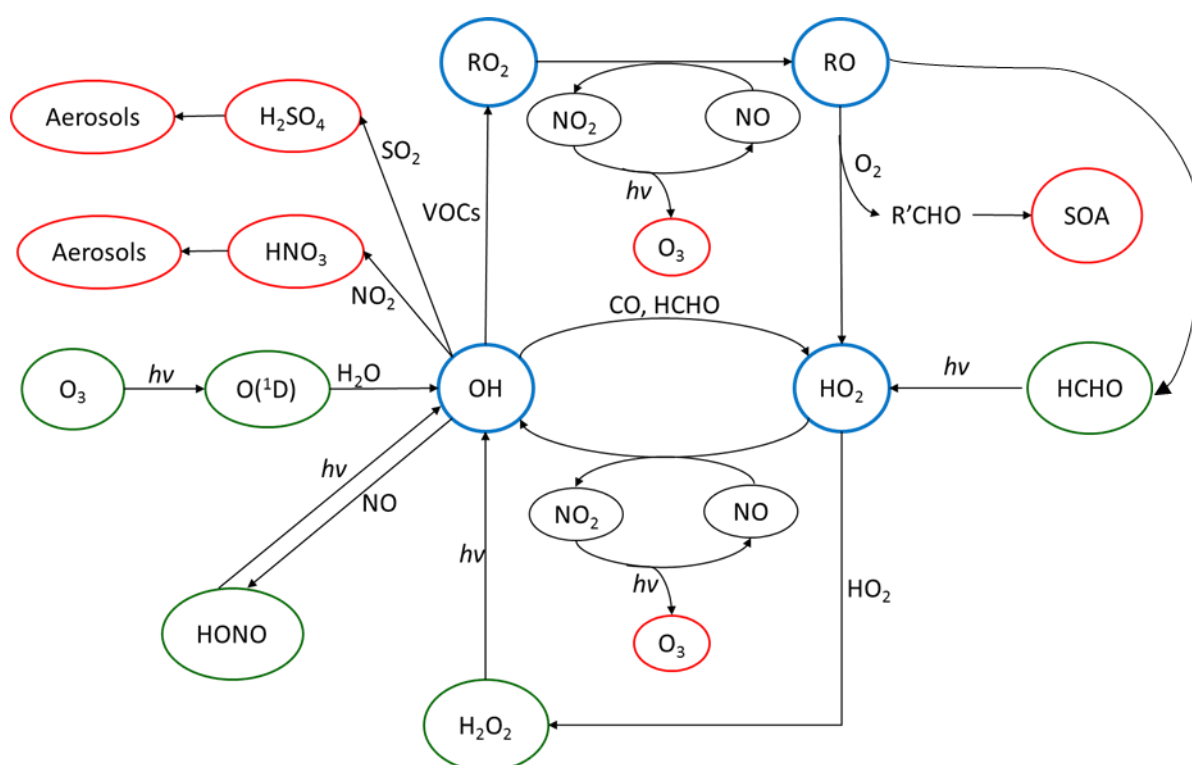
Reviewer 1.

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.

Figure 1: I fully appreciate the challenge in creating efficient and accurate diagrams such as Figure 1 to portray the chemistry of radical cycling. The species in green are described as primary routes for radical formation. I agree with the way that ozone is portrayed given that its role as an initiator as well as a product of the chemistry is shown. Both HONO and HCHO need to be better explained as they are also chemical products. Maybe a line from RO to CH₂O acknowledging that CH₂O is coming from oxidation (likely most of it) although some is also directly emitted. For HONO, its origin is still not well understood, so maybe this should be acknowledged in the caption by noting that it's abundance cannot be fully explained by formation via OH+NO. In the literature, CH₂O and H₂O₂ are typically described as being responsible for “secondary” radical production rather than “primary” radical sources. While there may be a large primary source of CH₂O in this particular environment, the same is not true for H₂O₂. One potential solution is to avoid the whole use of the word “primary” and simply say that the “green circles represent species that contribute to radical formation.”

A line between RO to HCHO has been added, and as suggested by the reviewer the caption has been changed so that the green circles represent species that contribute to radical formation.

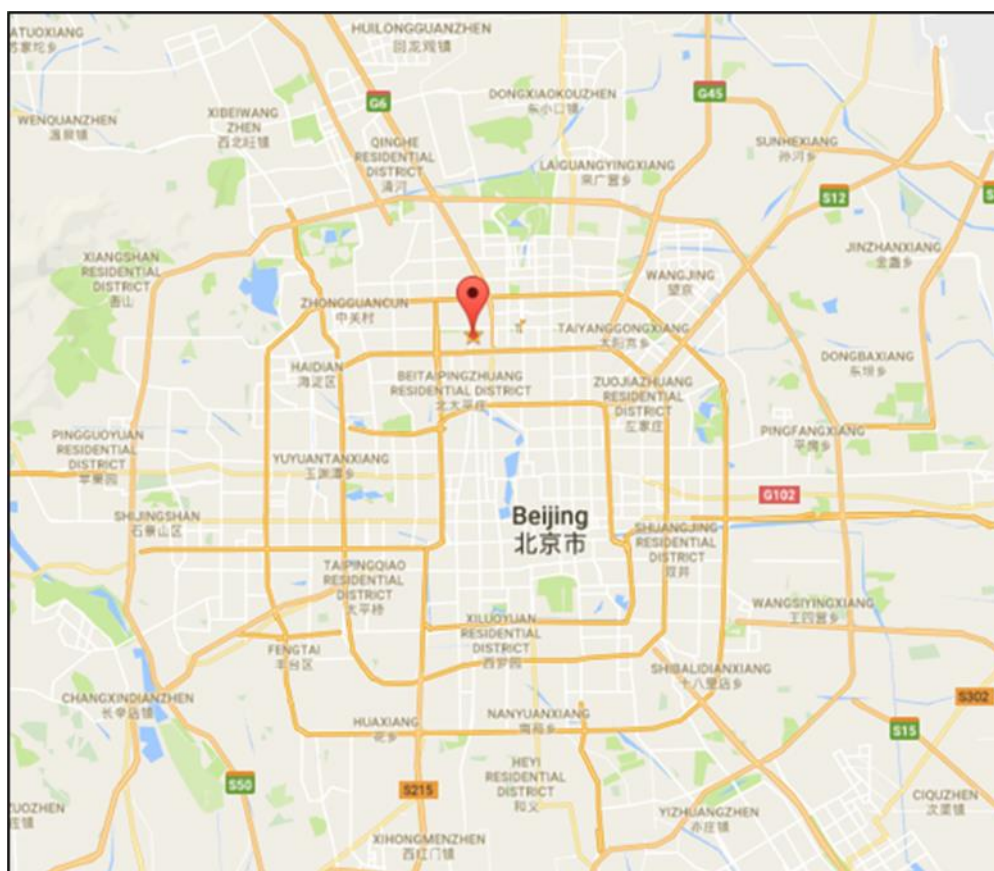
Updated figure below:



Updated/Modified caption: Figure 1. “The tropospheric photochemical cycle, with the green circles representing species acting as routes for radical formation, the blue circles representing the radical species themselves and the red circles representing the formation of secondary pollutants. The cycle does not show any heterogeneous source (e.g. heterogeneous production of HONO) or loss processes for the radical species. It should be noted the measured HONO abundance cannot be explained by the reaction of OH + NO alone”

Is there a significance to the two additional yellow stars in Figure 2?

No. In order to avoid confusion these have been removed from figure. 2 Please see updated figure 2 below:



Typo on line 277: O2 should be O3

This has been fixed.

The mention of an AIRPRO project first comes up on line 160. It is mentioned again in the caption of Figure 3, then in Table 4, and again on line 473. Otherwise, all other references in the text, figures, and tables are to APHH. Only in the summary (line 754) do the authors finally say the “APHH AIRPRO campaign”. Is AIRPRO an acronym? If so, it is undefined. Is it even necessary to mention AIRPRO? If so, it is crucial to make a clear distinction between what is meant by APHH versus AIRPRO.

We have removed AIRPRO from the paper so that the campaign is just called the APHH campaign.

On line 226, the authors note that the model was constrained by HCHO, but this species is not shown in Figure 4. This may be because it had minimal influence on radical production, but it is also a key outcome from VOC oxidation. While I am not surprised that it is small compared to HONO, I am somewhat surprised that it doesn't seem to be important compared to photolysis of other carbonyl species and alkene ozonolysis. I would like to see HCHO added to Figure 4.

HCHO has been added to Figure 4. See updated figure and caption below:

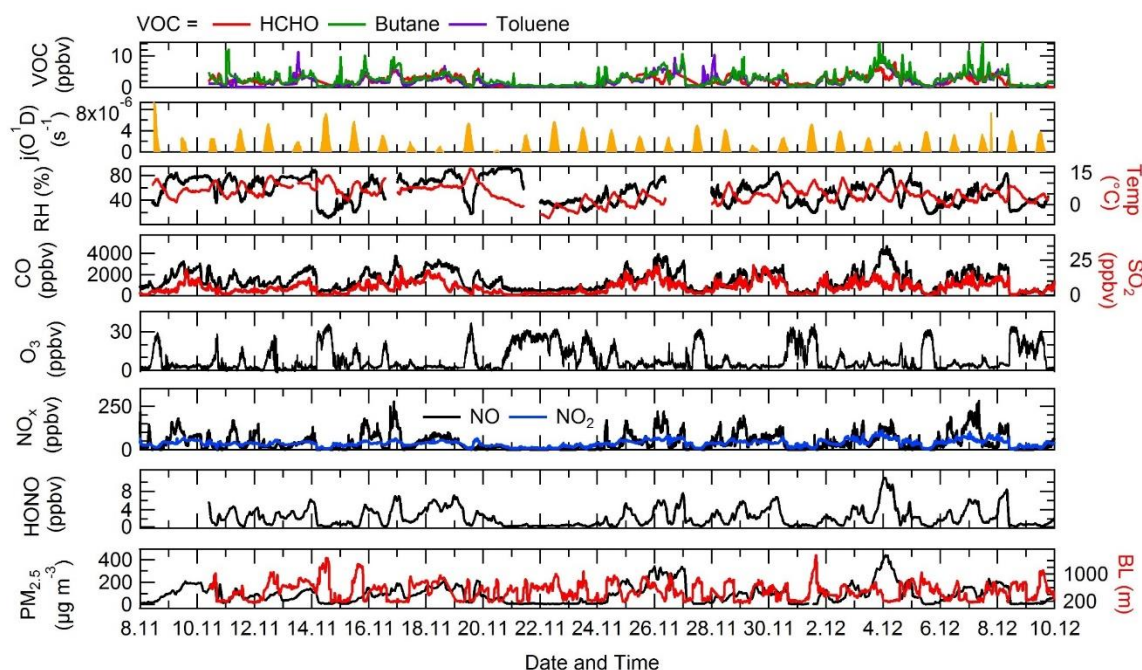


Figure 4. Time-series of $j(\text{O}^1\text{D})$, relative humidity (RH), temperature (Temp), CO, SO₂, O₃, NO_x, HONO, boundary layer (BL), PM_{2.5}, HCHO, butane and toluene from the 8th of November to 10th December 2016 at Institute of Atmospheric Physics (IAP), Beijing.

As shown in Figure.9 the photolysis of HCHO contribute ~2% to the primary formation of RO_x.

There is no comment about using PAN as a constraint, so was it predicted by the model? How well does it compare? Could it be a radical source at the surface?

PAN was not measured during the winter APHH campaign (only during the summer campaign) thus no comparison could be made between modelled and measured values. Indeed, it may be a radical source at the surface, however, the analysis of production and termination of radicals shown in Figure 9 shows a net-formation of PAN – suggesting that PAN is acting as an overall net RO₂ sink.

Figure 4 would also be improved if a few more things were added. For instance, a couple of VOCs (an alkene and an aromatic would be good). Also, there was a ceilometer at the site. Could mixing height be added to the figure? I expect it would be quite relevant to some of the variability marking the haze periods. While this information does not alter the outcome of the paper, it provides valuable additional context.

HCHO, butane, toluene and boundary layer height have all been added to Figure 4 (see response above for updated version of the Figure.4 and caption), and a short discussion about this has been added.

Modified text related to figure.4:

“The median diel variation in $j(\text{O}^1\text{D})$, relative humidity (RH), temperature, CO, SO₂, O₃, NO, NO₂, HONO, PM_{2.5}, boundary layer height (BL), HCHO, butane and toluene is shown in Figure 4.”

“The VOC concentration (HCHO, toluene and butane) track pollution events and each other very well; the mole fraction of the VOCs varied between 0.2 - 11.3 ppbv.”

The average diel profile of boundary layer height has also been added to Figure 5, replacing the SO₂ panel, both for inside and outside of haze, along with a short discussion.

Updated version of Figure.5 with the updated caption:

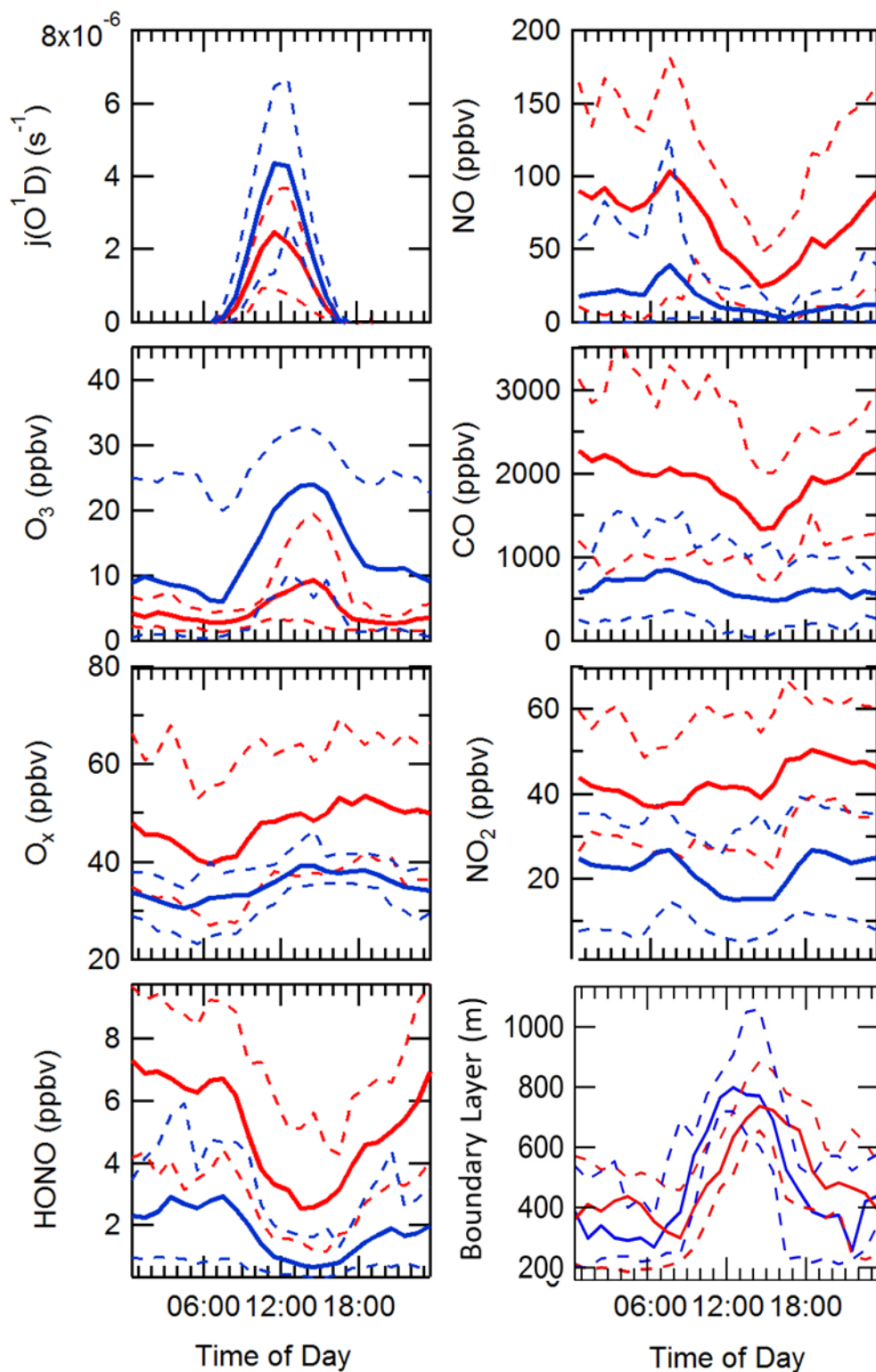


Figure 5. Comparison of the median average diel variation for $j(\text{O}^1\text{D})$ (s^{-1}), NO (ppbv), O_3 (ppbv), CO (ppbv), O_x (ppbv), NO_2 (ppbv), HONO (ppbv) and boundary layer height (m) inside and outside haze events; denoted by solid red and blue lines, respectively. The dashed lines represent the interquartile range for the respective species and pollution period.

Modified text relating to Figure 5:

“The boundary layer height (BLH) shows a similar diurnal variation inside and outside of haze, although the maximum BLH in haze is shifted to 14:30 compared to 12:30 outside of haze. The maximum and minimum BLH is similar inside and outside of haze and shows that containment is not the only driving force for pollution periods.”

Figure 4: Extra tick marks at irregular intervals on the CO axis appear to be an error.

These have been corrected on Figure 4 (see response above which shows an updated Figure.4).

Figure 5: The panel for J(O¹D) shows a small blip after dark for the red curve. I assume that this is an error. If not, what does it signify?

We apologise, this was an error and has been corrected in Figure 5 (see above).

Figure 5: Are the solid lines medians? Would it be better to call the dashed lines the interquartile range rather than confidence intervals? These are after all being used to exhibit real ambient variability in the two populations of data being compared.

The solid lines are indeed the median values and we have changed the caption from confidence intervals to interquartile range.

Modified text: “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) in 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.”

Some information on mixing depth would also be helpful in the discussion of figure 5. For instance, how important is containment in explaining the high values during the haze periods in addition to wind direction?

A panel showing the boundary layer height inside and outside of the haze has been added to figure 5 replacing the SO₂ panel (see response above), and shows that containment is not a large factor for explaining the high values observed during haze periods.

Modified text: “The boundary layer height (BLH) shows a similar diurnal variation inside and outside of haze, although the maximum BLH in haze is shifted to 14:30 compared to 12:30 outside of haze. The maximum and minimum BLH is similar inside and outside of haze and shows that containment is not the only driving force for pollution periods.”

Line 338: “OH reactivity is discussed further in Section 2.5” (this is a typo that needs to be corrected)

This has been fixed in the revised MS.

Lines 339-341: “Figure 6 shows the steady state calculation for OH between 2/12/2016 to 8/12/2016 where it is compared with the measured OH concentrations. These days were chosen as full data coverage for HONO, NO, j values, radical and k(OH) measurements were available.” Referring back to figure 4, it does not appear that HONO measurements are available from 2/12-5/12. Have I missed something? HONO is accounted for in calculations for each day in Figure 6, but this does not seem to track what I see in Figure 4. For instance, the lowest NO_x and highest ozone occurs on 5/12, so why does HONO make its greatest contribution on that day? I can’t make sense of it.

The HONO dataset shown in Figure 4 was from one HONO instrument only and the HONO used in the steady-state calculation was the HONO concentration recommended by Crilley et al. (2019) based on measurements by several instruments during the campaign, and represents a more complete dataset. The HONO shown in Figure 4 has now been updated to those recommended by Crilley et al. (2019), and are the values that have been used in the steady-state calculation and MCM model. Low NO_x would lead to reduction in recycling from HO₂ + NO, which is the largest source of OH production, and

hence on 5/12 at the lowest NO_x, this makes HONO the largest contributor to the rate of OH production. Figure 4 has been updated with the correct HONO dataset, see response above for the updated version of Figure 4 along with the updated caption.

Crilly, L. R., Kramer, L. J., Ouyang, B., Duan, J., Zhang, W., Tong, S., Ge, M., Tang, K., Qin, M., Xie, P., Shaw, M. D., Lewis, A. C., Mehra, A., Bannan, T. J., Worrall, S. D., Priestley, M., Bacak, A., Coe, H., Allan, J., Percival, C. J., Popoola, O. A. M., Jones, R. L., and Bloss, W. J.: Intercomparison of nitrous acid (HONO) measurement techniques in a megacity (Beijing), *Atmos. Meas. Tech.*, 12, 6449–6463, <https://doi.org/10.5194/amt-12-6449-2019>, 2019.

Lines 343-346: Further discussion of Figure 6 states that “The agreement highlights that the OH budget can be determined by field measurements of the parameters necessary to quantify its rate of production and loss, and is closed to within 10%, well within the 26% error on the OH measurements themselves.” I would agree that this plays out in the aggregate, but there is always value in looking at gradients that occur in the time series, and there is a significant discrepancy on 4/12 that falls well outside the 26% error that at least deserves mention if not some investigation or deeper explanation. Even 3/23 exhibits a shift in agreement after the peak that might be able to provide insight. Why does HO₂+NO drop so much faster than measured OH on that day? This period on 3/23 requires substantial additional OH sources to make sense.

The steady-state Figure 6 has been revised and has been generated using kOH values from optimised fitting of the OH decays (consideration of the start and end of the decay fit), as used in the MCM modelling comparison. See below for updated version of Figure 6. The diel profile has been separated into haze and non-haze periods as recommended by reviewer 3.

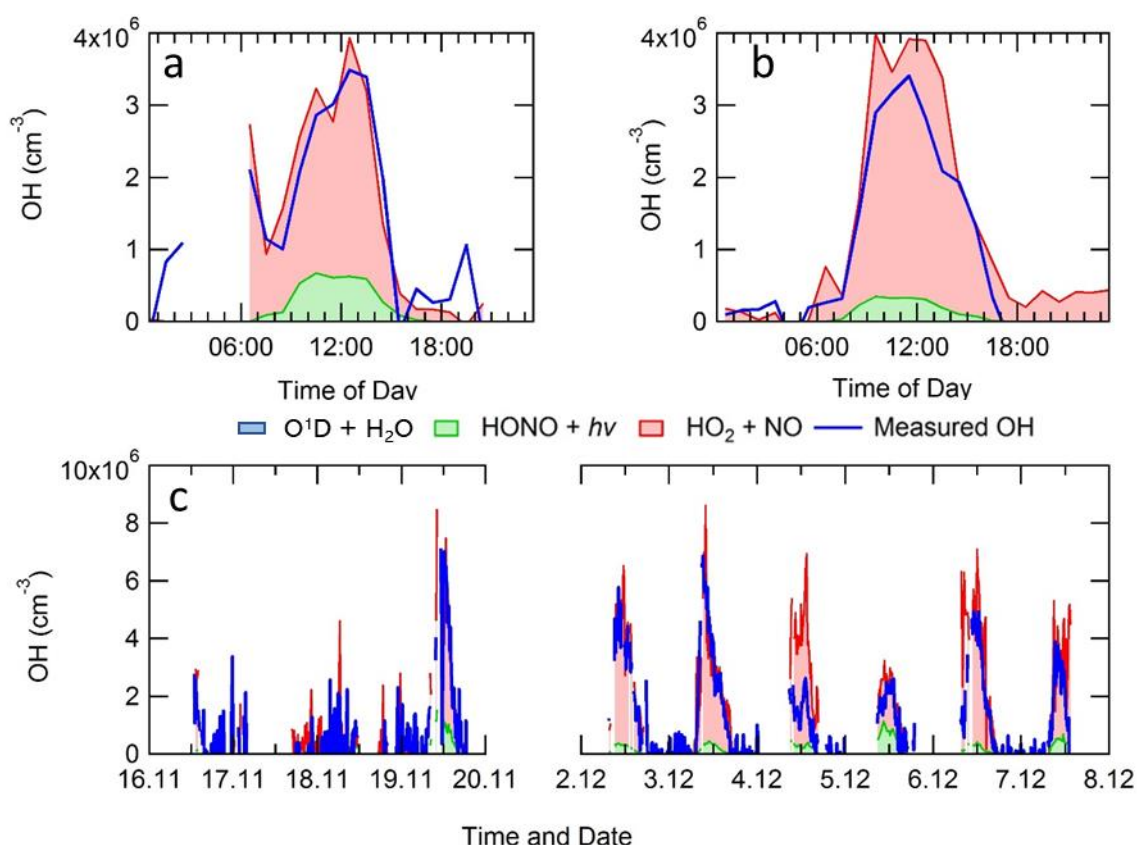


Figure 6. Average diel profile for observed and steady state calculated OH concentrations for: (a) non-haze, and (b) haze periods. Panel (c) shows a comparison time-series for the steady state calculation of OH and measured OH. The OH generated by O¹D+H₂O, although included in the key, is too small to be visible.

Figure S7 below shows that if the measured or modelled kOH is used on the 03/12 the PSS and measured OH agree within error. Although we saw no evidence of OH recycling in the kOH decay curves (no bimolecular behaviour – see response to reviewer 2), the measured kOH was lower than the modelled on the 04/12 and the use of the measured kOH may have caused the PSS to overestimate OH on this day. However, using the modelled kOH in the PSS calculation does reproduce the PSS calculated OH using the measured kOH and the PSS stills overpredicts the OH by a factor of ~ 2.4 . The large overprediction by the PSS suggests the differences between the PSS and measured OH on the 04/12/2016 stems from measurement problems and could be derived from issues with the OH, HO₂, HONO or NO measurements on this day. On the 3/12, the HO₂ + NO drop is driven by a decrease in NO, however the PSS and measured OH do agree within the error on the OH measurements.

The text in the MS has been modified: “Although on the 04/12/2016 the PSS overpredicts the measured OH by a factor of ~ 2.5 , the differences between the PSS and measured OH could be due to a variety of reason including errors in OH, HO₂, NO, kOH and HONO measurements and NO segregation across the site. A further discussion for the PSS for the 04/12 can be found in the supplementary section S1.6.”

The information added to the Supplementary Information is as follows:

“S1.6 In-depth comparison of measured OH and OH calculated from the PSS on the 04/12 using measured and modelled OH reactivity.

On the 04/12/2016 the PSS calculation for OH is overpredicted by ~ 2.5 and the modelled OH reactivity is higher than the measured OH reactivity by an average of $\sim 14 \text{ s}^{-1}$. The modelled OH reactivity was used in the PSS calculation for OH and a comparison between the PSS calculation using measured and modelled kOH and measured OH is shown in Figure S7. Figure S7 shows that whilst using the modelled OH reactivity does reduce the calculated PSS OH, the PSS using modelled kOH still overpredicts the measured OH by a factor of ~ 2.4 . The large overprediction by the PSS suggests the differences between the PSS and measured OH on the 04/12/2016 stems from measurement problems and could be derived from issues with the OH, HO₂, HONO or NO measurements on this day.

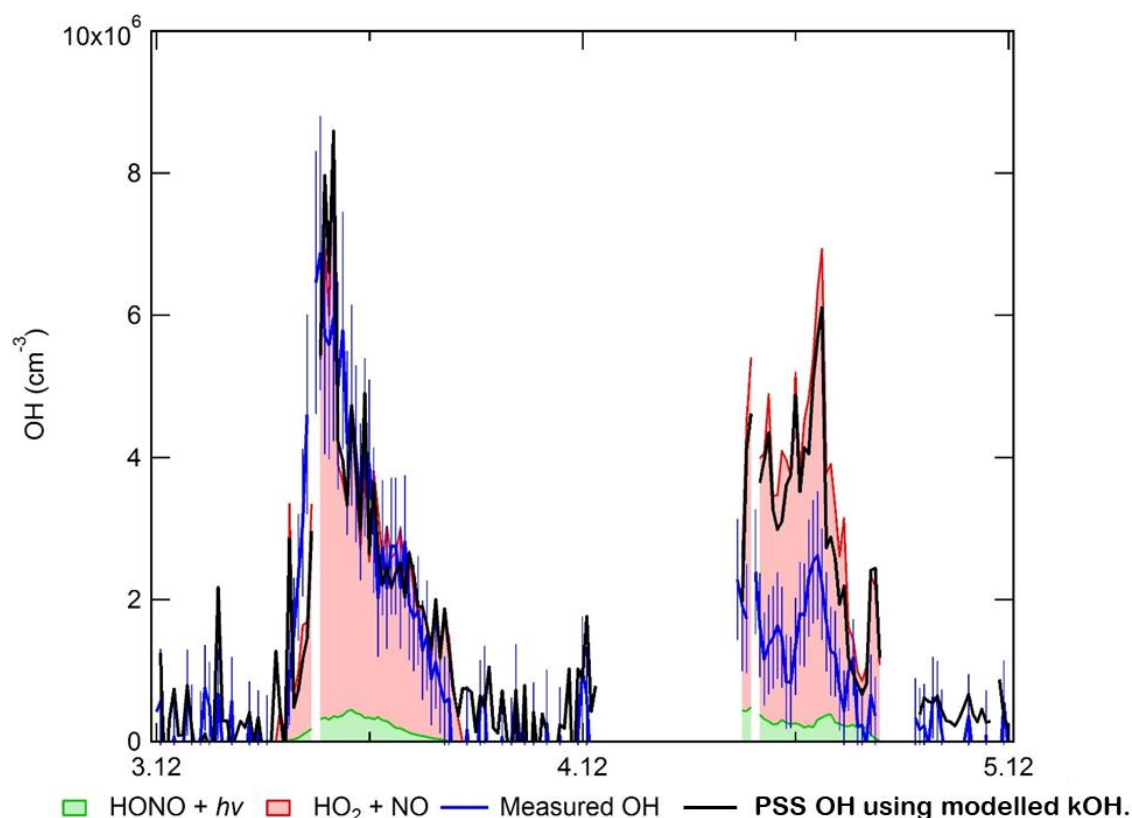


Figure S7. Comparison of measured OH (with errors, blue bars) with OH calculated from a photostationary steady-state (PSS) calculation using measured OH reactivity. The contributions towards OH production from HONO + hv (green) and HO₂ + NO (red) are shown, as well as the OH calculated using the PSS but with modelled OH reactivity (black)."

Lines 364-366: Authors state, "As seen in Figure 7, the measured daily maximum for the radical species varied day-to-day over the range 1 to 8 x 10⁶ cm⁻³, 0.7 to 1.5 x 10⁸ cm⁻³ and 1 to 2.5 x 10⁸ cm⁻³ for OH, HO₂ and sum of RO₂ respectively." I am again being nitpicky, but precision in your language is important, and I again feel like I am not looking at the same figure that is being described. For instance, which day shows peak OH at 1x10⁶? The lowest I see is ~2.5x10⁶. For HO₂, every day after 2/12 shows peak values well below the stated 0.7x10⁸. Similarly, for RO₂ I see several days peaking at values less than the stated 1x10⁸. These imprecisions lower confidence in the other values you mention regarding over and underprediction of OH, HO₂, and RO₂ that cannot be deduced as easily from the figure

These inconsistencies have been corrected and the precision in the wording tightened up, and the other values have been checked for accuracy. Originally, we used some values from the first measurement period during 17/12 – 19/12 but then discounted these as no measurements were available at midday for OH. For HO₂, we apologise, the power was given incorrectly, the last day peak is at 0.7 x 10⁷. The other values have been checked and are correct.

New range of concentrations: OH – 2.3 – 8 x 10⁶ cm⁻³, HO₂ – 0.07 – 1.5 x 10⁸, RO₂ – 0.8 – 2 x 10⁸

Modified wording, "As seen in Figure 7, the measured daily maximum for the radical species varied day-to-day over the range 2.5 to 8 x 10⁶ cm⁻³, 0.07 to 1.5 x 10⁸ cm⁻³ and 0.8 to 2 x 10⁸ cm⁻³ for OH, HO₂ and sum of RO₂ respectively."

In the caption for Figure 7, it is stated that the lines in panel (d) are from the model, but this seems unlikely. Is this a typo?

Yes. This has now been corrected in the caption.

Lines 407-410: The authors state, “The ability of the model to reproduce (to within ~10%) both the OH reactivity and the OH concentration when constrained to measured HO₂ (in MCM-cHO₂), but not to reproduce RO₂ radicals (whether constrained or not to HO₂) is suggestive of an incomplete representation of the chemistry of RO₂ radicals in the winter Beijing environment.” This is somewhat of a throwaway statement. Under the extreme NO_x conditions, both OH and its lifetime have very little dependence on RO₂. Given the dominance of HO₂+NO as a source of OH (80-90%) it is somewhat of a foregone conclusion that the constrained version of the model corrects the OH discrepancy. It is simply the lack of RO₂ in the model that indicates missing RO₂ chemistry. The bigger problem is explaining the HO₂, which is partly derived from RO₂. Are there any other notable changes when HO₂ is constrained?

We feel this is still an important statement to make as it also highlights that the OH and HO₂ measurements are self-consistent. MCM-cHO₂ also increases the RO₂ concentration by a factor of ~3.5 compared to MCM-base, but the RO₂ is still underpredicted by a factor ~7. We have added statement to the paper to make these points as follows.

Modified text: “MCM-cHO₂ also increases the RO₂ concentration by ~3.5 compared to MCM-base, but the RO₂ is still underpredicted by a factor ~7.”

We agree with the referee that this highlights missing RO₂ chemistry and this is discussed later in the paper.

At this point, it has already been established that the OH abundance is fully consistent with the observed HO₂, based on both the photostationary state equation and the MCM-cHO₂ model calculations. The latter calculations further demonstrate that the improved representation of OH does almost nothing to close the gap with RO₂ observations (figure 8). For this reason, defining RO_x as OH+HO₂+RO+RO₂ does not provide any additional insight. Both production and loss is dominated by OH reactions, which is not where you are looking to solve the problem. If radical production is dominated by HONO photolysis to produce OH and getting OH correct in the model does nothing to rectify RO₂, I don’t understand how this helps. It is just another way of showing the same thing that you have already shown in Figures 6 and 8. Also, when OH+NO dominates radical loss in the haze period, it isn’t really a termination, but more akin to a null cycle for radicals since it will photolyze to return to OH on a short timescale. If you removed this cycling, and only accounted for HONO from other sources, the figure would be more accurate. Nevertheless, the dominance of OH reactions prevents this figure from advancing beyond what has already been demonstrated.

Figure.9 highlights that most of the RO₂ in the model derives from OH sources, and highlights the need for additional primary RO₂ sources, this has clarified this in the paper using the statement below:

Modified text, line 508-509: “Figure 9. Shows that almost all of the RO₂ species in the model are derived from OH sources highlighting the need for additional primary RO₂ sources in the model.”

We have also removed the cycling between OH + NO and HONO photolysis as suggested by the referee so now termination is not shown through the OH + NO pathway, and Figure.9 now only accounts for the HONO from other sources. The percentages for termination and production in the paper and Table 5 (which have been removed to the Supplementary Information) have also been updated.

Modified text: “As shown in Figure 9, primary production of new radicals (radicals defined as RO_x = OH + HO₂ + RO + RO₂) via initiation reactions was dominated by the photolysis of HONO (72%, averaged over the campaign), with a small contribution from the photolysis of HCHO (2%), photolysis of carbonyl species (9%) and ozonolysis of alkenes (16%).”

Modified text: “A comparison between the primary production routes observed during the APHH and previous urban winter campaigns can be found in supplementary section S1.2.”

Modified text: “OH + NO₂ contributes up to 94% and 65% in haze and non-haze, respectively. Figure 9 shows that during non-haze conditions contribution to termination from the net formation of PAN (~35%) becomes important; but under haze conditions less than 6% of RO_x termination comes from the net formation of PAN.”

Updated version of Figure:

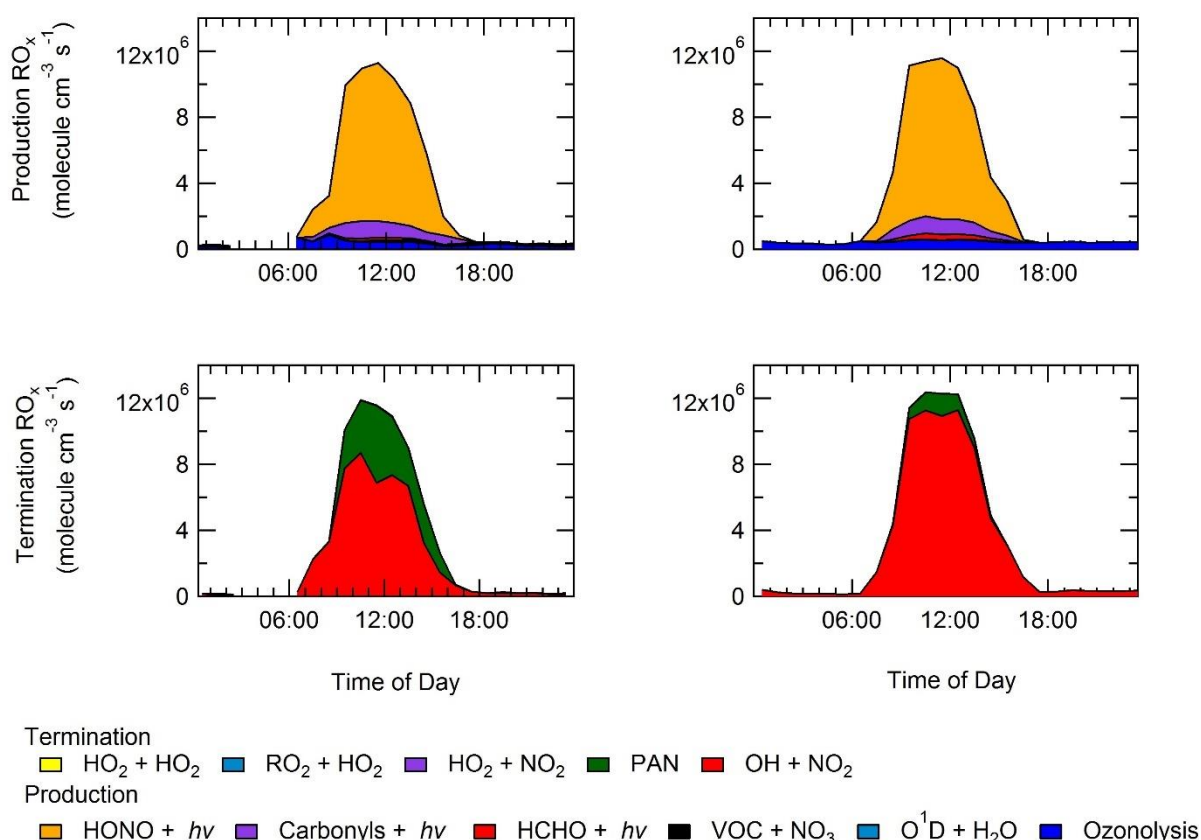


Figure 9. Rates of primary production (top panel) and termination (bottom panel) for RO_x radicals (defined as OH + HO₂ + RO + RO₂) calculated for MCM-base model separated into haze (right) and non-haze (left) periods. The definition of haze is when PM_{2.5} exceeds 75 μm⁻³. The production from: O¹D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

The updated table and discussion have been moved in supplementary section S1.2 as follows:

“S1.2 Primary radical production and comparison with previous campaigns.

As summarised in S4 Table 1, several other winter-time campaigns have highlighted the importance of HONO, including the PUMA campaign (Emmerson et al., 2005) in Birmingham; the IMPACT campaign in Tokyo (Kanaya et al., 2007); the NACHTT campaign in Boulder (Kim et al., 2014) and the PMTACS-NY campaign in New York (Ren et al., 2006). These campaigns showed 36.2, 19, 80.4, and 46 % contribution to primary production of RO_x from HONO. However, it should be noted that HONO was not measured during the PUMA campaign, so the percentage contribution to the primary production of radicals should be considered a lower limit as it is based upon modelled HONO (where only the reaction of OH + NO was considered), which is often an underestimate (Lee et al., 2015). As shown in Table 5, the Birmingham, Tokyo, New York and Suburban Beijing campaigns all show a high contribution towards RO_x production from ozonolysis, 63, 35, 42 and 28%, respectively, only the campaign in Boulder (5%) showed little contribution, which is similar to the observations made during

APHH campaign. The Boulder campaign is the only one that showed a significant contribution (14.9 %) to primary radical production from the reaction of $O(^1D) + H_2O$, whilst other winter campaigns show a contribution of less than 1%. The higher contribution from photolysis of O_3 during the Boulder campaign may be due to the campaign taking place in late February (spring) and, as shown in Table 1, photolysis rates, water vapour and temperature were all higher.

	PUMA, Birmingham, UK	IMPACT, Tokyo, Japan	NACHTT, Boulder, USA	PMTACS- NY, New York, USA	BEST-ONE, Suburban Beijing, China	APHH, Central Beijing, China	PKU, Central Beijing, China
Date	Jan – Feb 2000	Jan – Feb, 2004	Late Feb 2011	Jan – Feb, 2001	Jan – March 2016	Nov -Dec, 2016	Jan-Feb, 2017
OH (cm^{-3})	$\sim 1.7 \times 10^6$	$\sim 1.6 \times 10^6$	$\sim 2.7 \times 10^6$	$\sim 1.4 \times 10^6$	3×10^6	3×10^6	1.4×10^6
O_3 (ppbv)	37	20	40	20	30	15	10
$j(O^1D)$ (s^{-1})	$\sim 1 \times 10^{-5}$	$\sim 2.8 \times 10^{-5}$	$\sim 1 \times 10^{-5}$	$\sim 5 \times 10^{-6}$	7×10^{-6}	$\sim 3 \times 10^{-6}$	-
$j(O_3)$ (%)	0.6	<1	14.7	1.1	<1	<1	<1
$j(HONO)$ (%)	36.2 ^[1]	19	80.4	65.5	46	72	86
Ozonolysis (%)	63.2	35	4.9	42.4	28	16	6
$j(\text{Carbonyls})$ (%)	22	23	-	-	9	9	7% ^[2]
$j(HCHO)$ (%)	6	10	-	6	9	2	
Reference	Emmerson et al. (2005)	Kanaya et al. (2007)	Kim et al. (2014)	Ren et al. (2006)	Tan et al. (2018)	This work.	Ma et al. (2019)

Table S1. Summary of some previous measurements of OH, HO_2 and RO_2 that have taken place during the winter, and a summary of the major primary radical sources during these campaigns. All values are the noon average for each campaign. [1] This should be considered a lower limit due to no HONO measurements being made during the campaign. [2] Primary production from the sum of $j(\text{Carbonyls})$ and $j(HCHO)$."

The comparisons given in Table 5 are fine and do not require figure 4, but they are also somewhat of a distraction as you have already determined that the OH can be explained. As a reader, I am expecting you to advance more quickly to the clear questions regarding RO_2 established at the end of section 3.

We agree, and so this table and the comparison/discussion with previous campaigns (other than the discussion in the text for BEST-ONE and PKU campaigns) have been moved into the supplementary material. See response above.

Line 462: "As summarized in Table 2" should be "Table 5"

This line is no longer in the paper as it has been moved into the supplementary material, see response above and is now "As summarised in S4 Table 1".

Line 467: "campaign" is misspelled

This has been corrected.

Table 4 and 5: “NCITT” should be “NACHTT”

Corrected in both tables.

Line 539: “as shown in Figure 10” should be “Figure 11”

This has been corrected.

Line 541: “and can almost be reproduced by the model at NO concentrations above 100 ppbv.” I do not think this a valuable statement as there is no expectation that the model is getting such an answer for the right reason. Instead, what you are seeing is that NO_x reactions effectively suppress complex RO₂ concentrations at only a few ppbv in the model, while it appears that in the observations such suppression does not occur until NO_x is well above 100 ppbv

We agree and this statement has now been removed from the paper.

Line 545: “degredation” is misspelled and should be “degradation”

This has been corrected.

Section 4.3: It is not clear to me why this section is necessary to the paper. Everything to this point has been about trying to understand the model discrepancies with radical chemistry, especially at high NO_x. At this point, I would expect some discussion of what might be pursued in the future to reconcile the problem. The foray into what these oxidants are doing in terms of aerosol formation feels like it belongs in another paper. I would shorten what is already a lengthy manuscript and remove this section.

We still feel that it is an important outcome of higher than expected concentrations of oxidants, namely that the rate of secondary aerosol production is also higher than expected. However, we agree about trying to shorten the manuscript and so have moved this section to the supplementary information, with just a sentence to signpost this in the main paper.

Signposting text in main text: “A discussion on the impact of similar OH concentration inside and outside of haze on the oxidation of SO₂ and NO₂ can be found in the supplementary section S1.3.”

Section added to the supplementary information shown below:

“S1.3 NO₂ and SO₂ oxidation during haze events

Secondary oxidation products, such as nitric acid and sulphuric acid, which partition to the aerosol phase, are major contributors towards the formation of secondary particulate matter (Huang et al., 2014). The OH measurements enable calculation of the rate of SO₂ and NO₂ oxidation *via* reaction with OH, to form gas-phase species HNO₃ and H₂SO₄. Figure 4 shows that on average 1.5 ppbv/h and 0.03 ppbv/h of gas-phase NO₂ and SO₂ are oxidised to form acidic species, and that the oxidation increases in these haze periods caused by comparable OH concentration in and out of haze and, as shown in Figure 4, an increase in local NO₂ and SO₂ concentrations. NO_x can also be lost in the atmosphere by the formation of N₂O₅ (Evans, 2005) and subsequent hydrolysis, but this is unimportant in Beijing during winter due to the low levels of O₃. The reaction of OH + SO₂ in the gas-phase is the rate-determining step in the formation SO₄²⁻, so the H₂SO₄ formed in the gas-phase will partition in the aerosol phase (Barth et al., 2000). H₂SO₄ is effectively a non-volatile gas at atmospheric temperatures, and H₂SO₄ condensation onto pre-existing particles is an irreversible kinetic process (Zaveri et al., 2008). Whilst HNO₃ is a semivolatile species and the gas-particle partitioning is highly sensitive to meteorological conditions including: temperature, RH, particle size distribution, pH and particle

composition. If the relative humidity is lower than the deliquescence relative humidity (RH_d), then the HNO_3 that is formed in the gas phase reacts with NH_3 to form ammonium nitrate aerosol (NH_4NO_3):



If the ambient RH exceeds the RH_d then HNO_3 and NH_3 dissolve into the aqueous phase (aq):

To take into account the reversible process, knowledge of the RH_d that marks the transition between the solid and the aqueous phase, and the equilibrium constant, K_p , for the two phase is required (Ackermann et al., 1998). The MADE module (modal aerosol dynamics model for europe) uses these thermodynamic parameters as given by (Mozurkewich, 1993), resulting in:

$$\ln\left(\frac{RH_d}{100}\right) = \frac{618.3}{T} - 2.551 \quad S E1$$

for RH_d and:

$$\ln(K_p) = 118.87 - \frac{24084}{T} - 6.025 \ln(T) \quad S E2$$

for K_p . SE1 and SE2 shows that nitrate formation is favoured thermodynamically at low temperatures and high relative humidities (Ge et al., 2017). Previous measurements of SO_4^{2-} and NO_3^- made in wintertime Beijing suggests that photochemistry is important in the formation of nitrate aerosol, but not the formation of sulphate (Ge et al., 2017; Sun et al., 2013).

Figure S4 also shows that the gas-phase oxidation of NO_2 increases under haze conditions, showing that nitrate formation is driven by photochemistry in haze events despite the lower photolysis rates. Similar conclusions have been made in Lu et al. (2019) from measurements during the BEST-ONE campaign; with SO_4^{2-} aerosol predominantly driven by aqueous-phase chemistry whilst the production of NO_3^- aerosol from gas-phase oxidation of NO_2 with OH is important. The maximum production rate of HNO_3 observed during the BEST-ONE campaign is the same as the one calculated for the APHH campaign (3 ppbv hr^{-1}). The BEST-ONE campaign assumed all the gas-phase HNO_3 formed partitioned into the aerosol-phase due to the high relative humidity observed during the campaign.

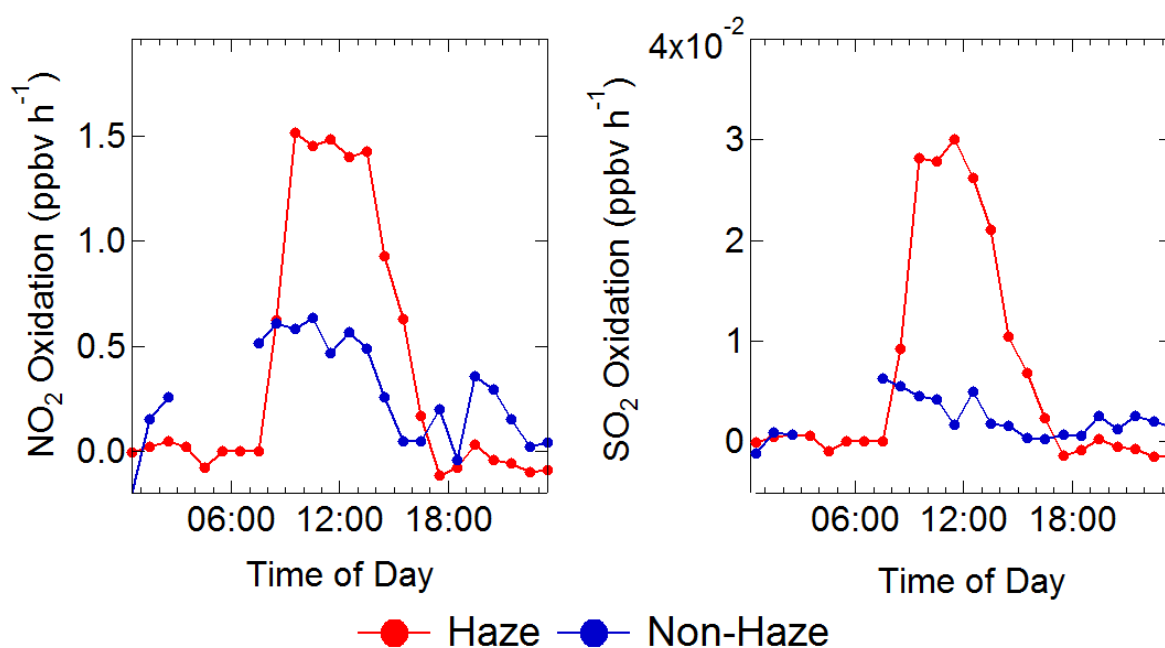


Figure S4 Average diel profiles of the rate of oxidation of NO₂ (left) and SO₂ (right) via reaction with OH in non-haze (blue) and haze (red) conditions.

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Section 4.4: This section focusing on ozone production only makes sense to include if it attempts to reconcile to calculated rate of production with what is observed. Ozone itself is on the order of only 1-30 ppbv and Ox fluctuations are on the order of 10-15 ppbv per day based on what is shown in Figure 5. Thus, a formation rate of 71 ppbv/hr on average would need to be offset by an equally large NO_x sink via NO₂+OH. Also, with such low ozone, it would seem that radicals play an outsized role in NO_x cycling between NO and NO₂. Has there been any analysis of NO/NO₂ and its consistency with the observed ozone and radical abundances?

We feel that the inclusion of the ozone production rate is important as it highlights how this missing RO₂ chemistry impacts the models ability to predict *in situ* ozone formation.

The Leighton ratio calculated from the measured ozone, NO and NO₂ concentrations from the campaign is generally below 1 indicating that the ratio of NO/NO₂ are not in steady-state during the winter campaign and so it is not possible to estimate a peroxy radical concentration from this.

Also, a comparison between measured O₃ and ozone production rate is difficult as the changes in measured ozone will be controlled by transport and dilution which the box model does not take into account. In the case of this work the ozone concentration is likely reduced by mixing with O₃ depleted air – such as air from the nearby large roads in Beijing. Here we are showing that the instantaneous rate of ozone production is underestimated by the model compared with measured levels of HO₂ and RO₂ are used.

Line 765: “2.7.0” please fix this typo

Fixed