

Interactive comment on “Elevated levels of OH observed in haze events during wintertime in central Beijing” by Eloise J. Slater et al.

Anonymous Referee #1

Received and published: 8 June 2020

Modeling and analysis of wintertime radical measurements (OH, HO₂, RO₂, and OH reactivity) in the highly polluted environment of Beijing offer unique conditions for testing our understanding of radical chemistry and its response to extreme values for precursor concentrations and radical recycling rates. The authors have undertaken a detailed analysis incorporating observational and model-based evidence that builds on a growing body of evidence that radical chemistry is not well understood under such conditions. In its current form, the paper could be shortened quite a bit and contains a bit of sloppiness that feels like a thesis is being repurposed into a manuscript. This work certainly needs to be published and the detailed comments offered below are intended to help improve the communication of these important results. One important omission is the lack of a short discussion on what should come next as this problem has been

C1

observed across several studies and calls for a new approach if it is to be solved.

Detailed comments:

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 its 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.”

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

Typo on line 277: O₂ should be O₃

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.

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

C2

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.

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?

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.

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

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?

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.

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?

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

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

C3

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.

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.

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 × 10⁶ cm⁻³, 0.7 to 1.5 × 10⁸ cm⁻³ and 1 to 2.5 × 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 1 × 10⁶? The lowest I see is ~2.5 × 10⁶. For HO₂, every day after 2/12 shows peak values well below the stated 0.7 × 10⁸. Similarly, for RO₂ I see several days peaking at values less than the stated 1 × 10⁸. 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.

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?

Lines 407-410: The authors state, "The ability of the model to reproduce (to within

C4

~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?

The discussion leading off section 4 feels like a step backward. 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.

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 ex-

C5

plained. As a reader, I am expecting you to advance more quickly to the clear questions regarding RO₂ established at the end of section 3.

Line 462: “As summarized in Table 2” should be “Table 5”

Line 467: “campaign” is misspelled

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

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

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.

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

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.

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 ppb/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

C6

with the observed ozone and radical abundances?

Line 765: "2.7.0" please fix this typo

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-362>, 2020.