Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #3

Received and published: 27 June 2020

This paper presents wintertime measurements of OH, HO2, and RO2 radicals and OH reactivity in Beijing in November and December 2016 as part of the Air Pollution and Human Health in Chinese Megacities" (APHH) campaign. The measurements are separated into "haze" and "non-haze" events based on PM2.5 concentrations, RH, and visibility. The radical concentrations and OH reactivity were modeled using a 0D model based on the Master Chemical Mechanism (MCM) constrained by measured concentrations of HONO, HCHO, O3, NOx, and VOCs, and included several modifications to the model scenarios.

Similar to other winter measurements, the authors find that the measured radical concentrations were higher than expected based on the reduced photolysis rates leading to reduced rates of traditional ROx production reactions. The authors find that the

base MCM model underpredicted the concentration of OH, HO2, and RO2 radicals, especially during haze events and under high mixing ratios of NOx. It was found that the steady-state OH radical budget can be closed with HO2, HONO, and k(OH) measurements, suggesting that the measured OH concentrations are consistent with the measured HO2 concentrations, and the underestimation of radicals is due to a missing source of RO2 radicals. The high radical concentrations and total OH reactivity measured during winter haze events suggests that radical propagation and chemical processing are rapid even during the winter. The underestimation of radicals by the model, and in particular the underestimation of peroxy radicals, suggests that models are significantly underestimating the rate of ozone production during winter haze events.

The results are of interest to the atmospheric chemistry community, and the paper is worthy of eventual publication in ACP. It is quite long, and there appear to be several inconsistencies throughout (see minor comments), and there are several sections/tables that probably could be moved to the Supplement. For example, the discussion of NO2 and SO2 oxidation in relation to aerosols in section 4.3, as well as Table 6 in section 4.2 could probably be moved to the Supplement. However, the paper would benefit from some additional experimental details and clarifications described below.

Main comments:

1) While the title and main conclusions of the paper refer to wintertime haze events, the main modeling of the results summarized in Figure 8 appears to include both haze and non-haze events, while the brief discussion in section 4.3 separates the model analysis to haze and non-haze events, with Figure 14 showing the base model agreement worse under haze events. While the model appears to underestimate the measured RO2 concentration similarly for both events, the agreement of the predicted OH and HO2 concentrations with the measurements is better for the non-haze events. It appears from Figure 7 that the number of haze and non-haze events were roughly equal. As a result, it is not clear whether some of the main conclusions of the paper would be

applicable to the haze events. It would be useful to illustrate in Figure 6, 8, and 13 how the different models in Table 1 are able to reproduce the radical measurements for haze and non-haze events. Is the estimation of the missing source different for the haze and non-haze events? Are the model results/conclusions different for the different events? While they may not be significant, any differences between the events should be discussed in more detail.

2) The authors should clarify their definition of OHwave and OHchem on pages 6-7. The current description suggests that OHchem is the on-line background measurement including interferences, while OHwave is the off-line background measurement. However, Figure 3 compares the measured OH concentration determined using chemical modulation (signal – OHchem background) with that determined by spectral modulation (signal – OHwave background), not a comparison of the background signal measured by both methods.

3) Related to this, the authors state that the spectral modulation measurements were also corrected for laser-generated OH from ozone photolysis + H2O (page 7). Based on the Woodward-Massey et al. (2020) paper, it appears that the interference was calculated based on laboratory measurements of the interference as a function of ozone, water and laser power. This should be clarified. Since this interference would be measured by chemical modulation, a comparison of the measured interference with that calculated would provide additional confidence in the OHChem measurement as well as the accuracy of the interference estimate.

4) There is little discussion of the HO2, HO2*, and RO2 experimental measurement conditions, except that it appears that the conditions were similar to that in the ClearfLo study. The paper would benefit from a brief discussion of the experimental conditions employed in this study. It appears that only a single NO flow was used in the HOx detection cell for these measurements, in contrast to the use of two NO flows used to measure HO2 and HO2* (RO2i) during ClearfLo (Whalley et al., 2018). Instead it appears that HO2* was measured using the ROxLIF detection cell. While it is stated

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that the ROxLIF method is described "in detail below" (page 5), the paper again references Whalley et al. (2018) instead of providing details. Given the high concentrations of NOx in this study, how did the authors account for potential interferences from the decomposition of HO2NO2 and CH3O2NO2? More details on the experimental measurements are needed. In addition the authors should clarify how the simple RO2 and complex RO2 were derived from the measurements. It appears that complex RO2 was obtained from the difference between the HO2* ROxLIF measurements and the FAGE HO2 measurements, while the simple RO2 were obtained from the difference between the ROxLIF RO2 and HO2*measurements. Much of this information could go into the Supplement.

5) Similarly, there is no discussion of the experimental method used to measure total OH reactivity. From the information given in Figure 7, it appeared that the OH reactivity was calculated based on the measured OH sinks, but it is clear from Figure 8 that total OH reactivity was measured. Is the measured OH reactivity shown in Figure 7? A brief description of the measurement technique should be included. Given the high mixing ratios of NO that were observed, did interference from the HO2+NO reaction impact the OH reactivity measurements?

Minor points:

Abstract: There have been previous measurements of radicals at similar NO levels in Mexico City (Shirley et al., ACP, 2006; Dusanter et al., ACP, 2009).

The caption in Figure 3 states that the gray points represent an acquisition cycle of 6 min, but the legend states that they are 4 min averages.

While the VOC measurements used to constrain their model are given in Table 1, the paper would benefit from additional information on the instruments used to measure the other model constraints. Even though this information may be provided in a separate campaign paper, a table similar to that in Whalley et al. (2018) could be included in the Supplement.

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It appears from Figure 4 that HONO measurements were not available between 2/12 and 5/12, but the steady-state calculations shown in Figure 6 include data between 2/12-8/12 and were chosen "as full data coverage for HONO, NO, j values, radical and k(OH) measurements were available." Was HONO available on all these days?

Page 16 and Table 4: The text and table state that the average OH maximum was 2.7 E6 cm-3, but a value of 3.03 E6 cm-3 is stated on page 18.

Page 19: I am not sure late February/March would be considered mid-summer in Boulder, but rather late winter/early spring.

Figure 9: The authors should clarify whether this is an experimental radical budget or one derived from the model. Given the importance of HONO to radical initiation, how sensitive was the model to the systematic differences in the HONO measurements as described in Crilley et al. (2019)?

Page 26: There appears to be a problem with the signs in Equation 3 (see the corresponding equation in Tan et al. (2018)).

Page 26, line 560: Here it is stated that the P'(ROx) is 1.2 E8 cm-3 s-1, but on page 27 line 575 states that it is 1.01 E8 cm-3 s-1.