

Anonymous Referee #2

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We would like to thank the reviewer for comments and suggestion which helped us to improve the manuscript. The reviewer comments are given below together with our responses and changes made to the manuscript.

Main comments

1. While the measurements and analysis presented appear robust, the paper concludes that there is a significant discrepancy in quantitative understanding – but without assessing potential causes for this. I find this a little unsatisfactory – I would like the authors to add some suggestions – both related to measurement methods, model limitations and potential new chemical understanding – which could resolve these. These may include suggestions for future work to move the situation forwards.

Answers:

We added a paragraph on Page 13 Line 26 following the discussion of the role of Chlorine chemistry: “The underestimation of RO₂ concentrations in the model occurred mainly during the pollution episodes when the measurement site was influenced by air mass transported from the Beijing central area or by local emissions. Since ClNO₂ and molecular chlorine were not measured in this campaign, their possible role in the production of RO_x is difficult to quantify. High N₂O₅ concentrations were observed in this campaign with values up to 10 ppbv during the pollution episodes (Wang et al., 2017a) and also aerosol chlorine was abundant (up to 7 µg/m³) to facilitate the production of ClNO₂. Therefore, the ClNO₂ has the potential to explain, at least part of the missing RO₂ source. However, the production rate of ClNO₂ depends on the N₂O₅ aerosol uptake coefficient and the ClNO₂ yield, both of which can be highly variable (Tham et al., (2018)). Therefore, measurements of chlorine chemistry related species would be essential to evaluate its effect on the OH-HO₂-RO₂ radical system, but they are not available here.”

In the summary, we added a sentence on Page 15 Line 37 “Although the chlorine chemistry has the potential to partly explain the missing radical source, its effect on radical concentrations could not be quantified due to the lack of ClNO₂ measurements. In the future, the measurements of chlorine-related species (e.g. ClNO₂, Cl₂) would be helpful to gain more insights what the contributions of ClNO₂ are to the radical sources and to the formation of secondary pollution. ”

2. Is the site location representative of Beijing? Huairou is on the northern perimeter of Beijing, adjacent to the higher ground to the north and outside of much of the city development. Is the chemical environment then representative of “downtown” Beijing, in the city centre. The authors should confirm this (e.g. through comparison of basic AQ metrics), and I would like them to reflect the presentation of their location as different from (e.g.) the CARE campaigns etc in the text, and potentially the manuscript title

Answers:

We added the measurement of CO, NO₂, O₃, SO₂, and PM_{2.5} obtained at 12 stations in Beijing downtown as well as the measurement at the campaign site in the supplement (Figure S1). We found a consistent trend in these measurements.

We added on Page 3 Line 10 “As shown in Fig. S1, the concentrations of CO, NO₂, SO₂, and PM_{2.5} observed at the site showed good correlations with the measurements conducted in the city center (12 EPA stations), although the concentrations were in the lower range during pollution episodes. However, the city center measurements showed higher peak values with large variability, which were mainly caused by local emission. This demonstrates that the measurement site is a representative for conditions in the Beijing with minor influence by local emission. In contrast, a previous field campaign that included OH-HO₂-RO₂ radicals measurements were performed at a rural site in Wangdu in summer 2014 (Tan et al., 2017). The Wangdu site was located in the middle of the North China Plain, about 200 km southwest of Beijing. The site was mainly influenced by regional transportation of air pollutants from anthropogenic emissions (Fuchs et al., 2017).”

3. Accumulating evidence is pointing to Cl chemistry being important for radical formation; CINO₂ observations were not made during this campaign – what is the sensitivity of the conclusions to the assumed CINO₂ / Cl atom levels – how might this (and the NO_x-dependence of the availability of Cl vs inorganic reservoir formation) affect the radical budgets?

Answers:

Please refer to the answer to the first comment.

Other Comments

p. 1 Line 34 – “series of control provisions” give dates to increase the relevance of the paper in future years

Answers:

We revised the sentence as “After a series of air pollution control provisions have been implemented by the Chinese government in the last 15 years to improve the air quality in China.”

P2 L1 – national trends need a reference

Answers:

We added a reference from Kan et al. (2012).

Kan, H., Chen, R., and Tong, S.: Ambient air pollution, climate change, and population health in China, *Environ Int*, 42, 10-19, <https://doi.org/10.1016/j.envint.2011.03.003>, 2012.

P2 L7 “attack”?

Answers:

We revised the word as “initiate the oxidation of”.

P2 L12 “guarantees” is a bold word to use – what about species with slow OH reaction (eg CH₄)

Answers:

We revised the word as “facilitate”.

P2 L14 O₃ photolysis is not the dominant source of HO_x in the BL, outside of remote marine environments – as shown by eg fig 9 of this paper

Answers:

We changed the sentence as “In wintertime, the radical chemistry is less active than in summertime because the solar radiation is weaker due to the higher solar zenith angle. For example, one of the important OH primary sources, photolysis of ozone, is strongly reduced by the smaller photolysis rate and the lower water vapor abundances at low temperatures during wintertime.”

P2 L 18 “general expectation” – what about previous measurements of OH

Answers:

We changed the sentence as “... The significant difference between OH concentrations in summer- and wintertime indicates that the radical chemistry only plays a minor role in winter. Especially during particle pollution events, the dimming effect of aerosol will further attenuate the solar radiation and thus lowering the radical chemistry activity.”

P2 L25+ Needs reference to Hofzumahaus et al. Science paper

Answers:

Reference is added.

P3 L10 Compare NO_x PM etc with central Beijing to justify site description as “Beijing”

Answers:

Please refer to answer to main comments 2.

P5 L10+ The description of the checks of OH-chem vs OH-wave is good and reassuring, but more detail on the RO₂ and HO₂ method and particularly the uncertainties in these would be useful

Answers:

We expanded the description of HO₂ measurements on Page 3: “HO₂ was converted to OH by NO addition below the sample nozzle in a second fluorescence cell that had otherwise the same design as the OH cell. The contribution of OH is subtracted using the measurement in the OH channel and OH sensitivity in the HO₂ channel. It is known that the measurement of HO₂ by chemical conversion can introduce interference from specific RO₂ radicals (Fuchs et al., 2011; Whalley et al., 2013; M. Lew et al., 2018). The best way to reduce the interference is to decrease the NO mixing ratio in the HO₂ cell (Fuchs et al., 2011; Whalley et al., 2013; Whalley et al., 2017; Tan et al., 2017). In this study, the NO addition was reduced to minimize the RO₂ interference without losing too much of the HO₂ conversion. The NO concentration was switched every two minutes between the additions of 0.5 standard millilitres per minute (sccm) and of 2 sccm from a mixture of 1% NO in N₂. This yields a nominal mixing ratio of 2.5 ppmv and 10 ppmv of NO in a sample flow of 1 SLM and Especially flow of 1 SLM. No significant difference was found for the two HO₂ data sets showing that the HO₂ measurements were interference-free.”

We expanded the description of RO₂ measurements on Page 4: “RO₂ measurements with the LIF instrument require the conversion of RO₂ to OH. This was done in two steps. In a reaction flow tube (pressure 25 hPa, volume 2.8 L, sample flow 7.5 SLM) high concentrations of CO (1100 ppm) and NO (0.7 ppmv) were added to convert RO_x to HO₂ (Fuchs et al., 2008). CO was added to suppress the conversion from HO₂ to OH to avoid wall losses of OH radicals in the reactor. The HO₂ radicals were transferred to the fluorescence cell through a nozzle pinhole with a diameter of 4.0 mm. The fluorescence cell was operated at 4 hPa like the other fluorescence cells. The HO₂ radicals were finally converted to OH radicals using a flow of 5 sccm of pure NO yielding a nominal mixing ratio of 1100 ppm NO within a sample flow of 3.5 SLM and an N₂-

sheath flow of 1 SLM. The measurements from the other two fluorescence cells were used to calculate the contributions from OH and HO₂ and subtracted to retrieve the RO₂ measurements.”

P6 L5 Does the LOPAP discrepancy correlate with other factors – eg aerosol nitrite levels ?

Answers:

Unfortunately, the aerosol nitrite was not measured in this campaign. We tried to correlate the discrepancy between the two LOPAP measurements with measured parameters but could not identify a parameter that correlates with the observed differences in the two measurements. Since the cause of the LOPAP discrepancy is not clear yet, the discrepancy adds to the uncertainty of the measurement.

P6 L30 How did the model constraint work. Was the model simply updated to the observed levels every 15 mins?– does this introduce noise into the output concentrations. What about spin-up time to simulate intermediate species.

Answers:

We added a few sentences on Page 6 Line 33: “The model was operated in a time-dependence mode with 5-min time resolution for which measurements used as constraints updated the model values. 2 days spin-up time was used to initiate the model.”

P7 L14 Give values for the thresholds used to define the pollution regimes

Answers:

We changed the sentence in Page 7 Line 14-16 as “The measured OH reactivity was used to separate polluted from clean periods by a threshold value of $k_{OH} = 15 \text{ s}^{-1}$ (daily average). This corresponds also to CO mixing ratios higher than 1ppmv and PM_{2.5} higher than 50µg/m³ since these parameters were highly correlated.”

P9 L12 jO¹D and jNO₂ should not be correlated given the different adsorption spectra and quantum yield wavelength dependence for O₃-O¹D and NO₂ photolysis. See discussion in Rohrer & Berresheim, Nature 2006 and other HO_x measurement / j correlation analyses eg Smith et al. ACP 2006 P9

Answers:

Although the absorption spectra and quantum yield wavelength dependence for O₃-O¹D and NO₂ photolysis are different, the relative good correlation between j(O¹D) and j(NO₂) was found in this campaign ($R^2=0.87$). Two kinds of correlation can be found. (1) If the photolysis frequencies are changed by clouds, they are linearly correlated. (2) If they are changed by different solar zenith angles, they have a square root dependence. The actual exponent varies between 0.5 and 1, depending on the on the local meteorological conditions during a certain campaign at a certain location.

L38 – can you expand on the “NO measurement artefact” ?

Answers:

It is not really an artefact but just because NO concentration was below detection limit (60 pptv). If NO is below LOD, the measurement will show a large variability which resulted in a large fluctuation in the model. Therefore, we cancel the word artefact here.

We changed the sentence in Page 10 Line 1-6 to “...which could be the result of a NO measurement below the detection limit. The observed NO concentrations were often below the limit of detection of the NO_x instrument (60 pptv), which did not allow precise measurements due to the fluctuation of the background signal. Besides, it also led to large variability in the modelled NO₃ and result in overprediction in the nighttime RO₂ (Tan et al., 2017). On the other hand, a small bias ...”

P11 L18 reword

Answers:

We changed the sentence to “During the summertime in Wangdu, the contribution from alkene ozonolysis was only 15% (Fig. 9). However, the absolute rate was 0.47 ppbv/h, larger than what was observed in Huairou/Beijing in wintertime (0.16 ppbv/h).”

P13 L33 – Need to be clear that the observations and model only determine the local chemical ozone production rate, while a wider view (Eularian or trajectory) is needed to compare with O3 levels (ie accounting for advection). Also relevant to Fig 12b.

Answers:

We changed the sentence as “This indicates that the O_x was produced by local photochemical reactions and/or was transported from the upwind areas. The change of the O_x concentration is caused by both chemical production/destruction and physical processes (advection, vertical mixing, deposition and so on). Therefore, it is important to note that the large local production rate is not necessarily observed in the measured, local O_x concentration. In this study, we compared the chemical production rate and the O_x concentration change to illustrate whether chemical production can support the O_x concentration increase.”

Modelling – how significant were modelled VOC degradation products in terms of increasing the OH reactivity, compared with the measured (parent) VOCs?

Answers:

We changed the sentence in Page 10 Line 11-16 as “The model was capable to reproduce the directly observed OH reactivity within 10% during all episodes (Fig. 7). This calculation includes the reactivity from observed VOCs (about 73-83% of the observed k_{OH}) and the estimated contributions from OVOCs calculated by the model (17-27%). The speciation of the total OH reactivity showed that the major OH reactants were NO_x and CO. On average, CO and NO_x contributed 23% and 37% to the total OH reactivity, respectively. 18% of the observed reactivity can attribute to measured VOC species. In comparison, the model generated species contributed 22% to the total reactivity. For the polluted episodes, the average OH reactivity increased from 10 to 26 s⁻¹ with a significant increase in the relative contributions from the inorganic compounds (from 52% to 63%).”

[P15 L35 – see main comment above](#)

Answers:

Please refers to the answer to main comments 1 and 3.