

Response to Reviewers of:

Rainforest-like Atmospheric Chemistry in a Polluted Megacity by Newland et al., 2020, submitted to ACP

General Response

We thank the reviewers for giving their time to make insightful comments, helping to clarify and further improve our manuscript. The referees recognise the importance of the results presented, and recommend publication in ACP after some changes.

Formatting: Reviewer #2 makes the point that the formatting is not as expected from an ACP Article. Indeed this is correct. However, this is because we have submitted this manuscript with the intention of it being an ACP Letter, and have followed the formatting guidelines for this format (https://www.atmospheric-chemistry-and-physics.net/about/manuscript_types/acp_letters.html). However, there is currently not a mechanism to submit the manuscript as a Letter, with the designation coming after review. Following discussion with the Copernicus editorial team and ACP editors, it was decided that the comments should be addressed with the intention of the manuscript being published as a Letter, and if subsequently it was considered more appropriate for the manuscript to be an Article, then it would be re-formatted as such.

Overall content and scope: As a Letter, the aim of this manuscript is a tight focus on the key, high impact results. That is, evidence of dramatically changing oxidation pathways during the daytime in the summer in Beijing, highlighting the impact of this observation on VOC oxidation chemistry (note, not specifically isoprene chemistry, we are using the measurement isoprene oxidation products as photochemical markers of the changing chemical pathways throughout the daytime), and the inability of models to capture this diurnal change in the oxidation pathways. Again, the paper is not specifically about Beijing per se, but as we discuss, is likely to be relevant to many megacities, particularly in the (sub)tropics, with emphasis on reducing NO_x emissions but still having a high loading of reactive VOCs. The story told by the measured isoprene oxidation products is corroborated by the auxiliary NO_x and ozone measurements.

What the manuscript is not aiming to do is to describe the VOC composition in Beijing, talk about the role of isoprene chemistry in Beijing, or talk about ozone production in Beijing (although, some of this will be the subject of forthcoming publications). We feel that both reviewers have slightly misunderstood this, which is clearly a reflection on how we have written the manuscript. In light of this we have made several changes to the manuscript to try to make these aims clearer. This has begun with the title which we have altered slightly to better highlight the focus of the paper, changing it from: '*Rainforest-like Atmospheric Chemistry in a Polluted Megacity*' to '*Rainforest-like Atmospheric Oxidation Pathways in a Polluted Megacity*'. We have also made changes to the abstract and the introduction. Both reviewers have suggested changes to extend the paper to a more general discussion of the atmospheric chemistry of Beijing, however, as discussed above we do not feel that this is within the scope of the paper, nor necessary background for the scientific points that are being made. What we have done is to add some background on changing NO_x concentrations in urban environments, and in particular in Beijing, as well as the causes of high ozone episodes in Beijing. We feel that this bears more relevance to the manuscript, rather than a broad discussion on either the VOC mix, or ozone production – neither of which are a focus of this Letter. All changes to the manuscript are in line with the reviewers' comments and suggestions.

Responses to each reviewer are given below. Responses to specific points raised by each reviewer are given separately beneath that point. Reviewers' comments are bold and italic, the authors' comments are inset in plain type.

Anonymous Referee #1

Received and published: 26 March 2020

General Comments

The authors summarize their results in the Abstract: "Despite being in one of the largest megacities in the world, we observe significant formation of gas and aerosol phase oxidation products associated with the low-NO 'rainforest-like' regime during the afternoon. This is caused by a surprisingly low concentration of NO, coupled with high concentrations of VOCs and of the atmospheric oxidant hydroxyl (OH). Box model calculations suggest that during the morning high-NO chemistry predominates (95%) but in the afternoon low-NO chemistry plays a greater role (30%)."

In pristine "Rainforest-like" conditions O₃ production is NO_x limited and OH-reactivity is mainly controlled by isoprene (Wei et al. 2019). O₃ in Beijing is largely driven by transport of highly chemically processed air across densely populated areas of 500 million people in the south (your SI, Parrish et al. 2016). Your selection of "typical" pollution days was made accordingly (your SI). This means that air reaching the measurement point in the afternoon in Beijing contains a large fraction of highly processed VOC originating from more distant urban sources. Many different VOC preferable different alkenes contribute to Ozone formation. The individual contributions most likely will change during the day. Alkyl nitrates are key compounds in controlling tropospheric oxidants and the lifetime of NO_x (Teng et al. 2015). During daylight hours alkyl nitrates are produced via radical chain terminating branch reactions from RO₂ and NO. The other larger branch recycles HO_x and produces O₃. In simple terms: increasing the carbon number increases the alkyl nitrate branch. Diurnal variation of individual alkyl nitrates, which should have been measured with the I-CIMS (Lee et al. 2016), will allow to estimate the contribution of individual alkenes (VOCs) to the O₃ formation (Teng et al., Fig. 8). Even if quantitative alkyl nitrate sensitivities are not available it would show how important isoprene oxidation is over the course of the day.

We agree that the high ozone observed in Beijing is likely largely driven by regional sources (which subsequently titrates out the NO in Beijing itself in the afternoon). However, in this manuscript we are not seeking to identify the drivers of ozone production in Beijing. We do not state anywhere that isoprene is (or is not) important for ozone production. Isoprene oxidation products are being used as tracers of the chemical environment in which they were formed. This point should now be clearer in the manuscript.

While I find the study interesting it does not offer a clear explanation how high afternoon O₃ at rather low NO occur.

Again, this is not the point of the study and we make no attempt to look at the drivers of ozone production.

The title is misleading and has to be changed.

We have now changed the title slightly to: 'Rainforest-like Atmospheric Oxidation Pathways in a Polluted Megacity'. Hopefully this helps to emphasise the point that we make in the abstract, that by 'Rainforest-like' we mean that RO₂, specifically ISOP₂O, are reacting with HO₂ / RO₂ rather than with NO as might be expected in an urban environment. We are not referring to the ozone production regime of a rainforest.

A suit of instruments was simultaneously analyzing the air composition in Beijing. Only signals focusing on isoprene oxidation are chosen and presented in this manuscript. It is not clear why this selection was made. In any case in the present form, it does not give a conclusive picture of summer time chemistry in Beijing.

Lee et al. PNAS 113 (2016) 1516-1521 Teng et al. Atmos. Chem. Phys., 15 (2015) 4297-4316 Wei et al. Atmos. Environ. 206 (2019) 280-292

We make it clear in the abstract and introduction that isoprene oxidation products, of which we have an extensive suite of measurements in both the gas phase and particle phases, are used in order to identify the chemical environment in which they were formed. The conclusions drawn from these measurements are backed up by the measurements of NO, NO₂ and O₃. This then provides not only a description of the changing diurnal profile of the oxidation state of the local Beijing atmosphere, but also provides convincing arguments that we have a reasonable understanding of the production pathways of these products in the ambient environment, as opposed to solely from laboratory studies. The aim of the paper is not to give a comprehensive picture of summertime chemistry in Beijing – the focus is on how the chemical environment changes through the day.

Specific comments

Fig. 2 depicts mean diurnal variation of measured species during the Beijing summer observations. The authors use Fig. 2 to justify their conclusions of changing chemistry from high NO in the morning to low NO in the afternoon. While NO measurements clearly show that. The offered explanation using the diurnal behavior of isoprene oxidation products are less clear. High NO and low NO organosulfate tracers 2-MGA-OS (Fig. 2e) and 2-methyltetreol-OS (Fig. 2f) from the particle phase show almost exactly the same diurnal behavior – a pronounced peak at 15:00 (on one day). - ISOPONO₂ concentrations at 15:00 are still above 100 ppt. (Fig.2c) - Fig. 2d shows a double peak behavior and does not help at all. The PTR-MS signal at m/z 71.05 is not MACR+MVK as indicated in the Figure (see methods discussion later) - NO₂ and OH is not shown.

In the text we currently describe 2-MGA-OS as from a high-NO pathway. In fact the formation of the initial precursor MACR is predominantly from high-NO pathways (ISOP34O₂+NO, ISOPDO₂+NO, nomenclature from MCMv3.3.1 (mcm.york.ac.uk)) but the formation of the direct precursor, MPAN, is from a low-NO, high NO₂ pathway, i.e. during the morning it would be expected that the acyl peroxy radical (MACO₃) would react with NO and hence not lead to MPAN, whereas in the afternoon, with an increased NO₂/NO ratio, and NO₂ high enough to largely outcompete HO₂ (although 2-MGA-OS could also come from the HO₂ pathway via the peracid). Hence both of these isoprene oxidation products that are the precursors to the organosulfates would be expected to peak in the afternoon, as seen. In addition, the organosulfate concentrations are also dependent on the availability of particle sulphate (as seen in Bryant et al., 2020 and mentioned in the paper), which on this particular day increases over the period from 10:30 (1 μg m⁻³) to 20:00 (6.5 μg m⁻³). The diurnals presented for the OS

species are consistent with the chemical pathways described but are controlled by more factors than the gas phase chemistry alone. We have clarified this in the text, replacing the original lines with those below.

“Organosulfate tracers, 2-MGA-OS (Figure 2g), and 2-methyltetrol-OS (Figure 2h), and were measured on 11 June, with low concentrations through the morning, increasing during the afternoon to a peak around 15:00-16:00. Both are tracers for low-NO chemistry, with 2-methyltetrol-OS formed via the low HO₂ IEPOX pathway (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012), while 2-MGA-OS (Lin et al., 2013) is formed from the oxidation of MPAN (Kjaergaard et al., 2012; Nguyen et al., 2015), itself formed from the high-NO isoprene oxidation product MACR, in an environment with a high NO₂/NO ratio, as seen in the afternoon in Beijing, and further oxidation leads to 2-MGA (Surratt et al., 2010; Chan et al., 2010; Nguyen et al., 2015).”

ISOPONO2 concentrations may still be above 100 ppt in the afternoon, but clearly loss exceeds production in the afternoon, in contrast to the morning when production exceeds loss.

Methods

Native speakers (there are a few co-authors) should help to improve especially the methods part.

It is not particularly clear what the reviewer is referring to here. The Methods section has been reviewed by the primary authors (all native speakers), with a few minor alterations to spelling and grammar.

CIMS

Discuss in more detail how the CIMS was calibrated for the isomers IEPOX and ISOPOOH, respectively. The methods description suggests that only IEPOX standards were available. Discuss measurement errors for your conditions. No calibration standards for ISOPONO2 were available. Xiong et al. 2015 found different sensitivity and stability for different ISOPONO2 isomers using I-CIMS. Discuss how this impacts the quality of your ISOPONO2 data. How are isomer specific inlet line losses estimated and corrected?

Xiong et al. Observation of Isoprene Hydroxynitrates in the Southeastern United States and Implications for the Fate of NO_x. Atmos. Chem. Phys. 2015, 15, 11257–11272.

As the reviewer has recognised, only IEPOX was available for calibration of the isoprene oxidation products measured with the CIMS in this study and this is already clearly stated in the text. The most analogous calibration standard to the reported measurements is therefore used here. Studies see a variation in sensitivity to different isomers and composition of course, and this will introduce small errors in the reported concentrations. Studies such as Mohr et al. (Nat. Comm. 10, 1, 2019) however report that there is a strong relationship between the sensitivity for compounds with masses > 200 Da and the collision-limit value sensitivity. Collisional limit value sensitivity was also determined in this study and there was a 14% difference in that sensitivity and the IEPOX sensitivity measured. There is an estimated maximum uncertainty of 20% in the CIMS measurements reported here, based on the variation in the suite of calibrations performed as part of this study. This is noted in the text as a limitation in terms of quantification, however in terms of the quality of the IN and

C5H10O3 time series (the most important factor for the conclusions of the paper) the data presented here is highly robust. Isomer specific line losses are not considered in the analysis of the CIMS measurements.

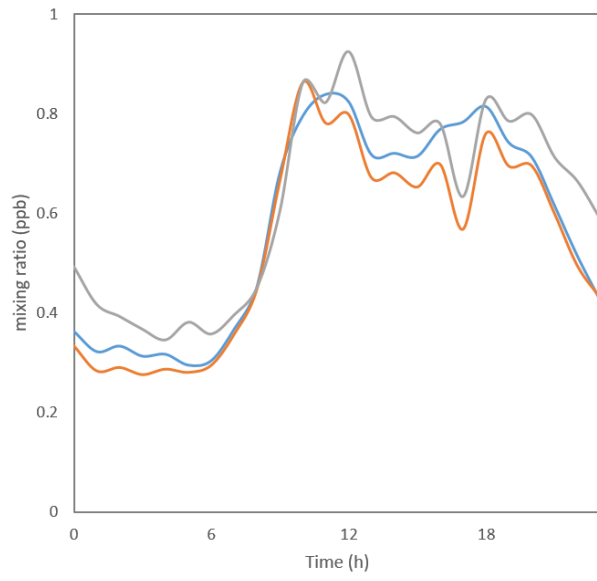
PTR-MS

The PTR-MS instrument description suggests that ambient air containing varying ozone concentrations (low in the morning and very high in the afternoon) is sampled through a 10 L stainless steel container. Your description is not detailed enough to gain the “storage time” in this container. Describe which tests were performed to exclude/estimate production of compounds, which are monitored as 71.05 m/z ions from O3 + VOC reactions in the stainless steel container. How long is the storage time? Such artificial reactions could contribute to the observed “second” peak at 16:00-20:00 which follows the O3 concentration rather than isoprene in Fig. 2d. You mention correctly that ISOPROOH isomers are converted to MVK and MACR on stainless steel surfaces even at room temperature. If the sample air is stored in a stainless steel container for longer than seconds then the signal at mass 71.05 in Fig. 2d by no means can be assigned to MACR+MVK only! Describe what happens to ISOPROOH and IEPOX in your special inlet design.

The PTR-MS sampled air from three locations, as described in the Methods section,

For the first 20 minutes of each hour the PTR-MS sampled from a gradient switching manifold, and for the next 40 minutes the instrument subsampled a common flux inlet line running from the 102m platform on the tower to the container in which the PTR-ToF-MS was housed. Gradient measurements were made from 3, 15, 32, 64 and 102 m...

The data presented in Figure 2 is the 3 m data from the gradient sampling. However, we have added the following figure to the Supplementary Information (Figure S5). This demonstrates that there is very good agreement between the MVK+MACR signal measured in the air sampled from the flux inlet line sampling at 102 m as compared to the gradient sampling at 3 m and 102 m. The flux inlet line was made of PFA tubing and had an estimated 68 s transport time from the inlet to the PTR-MS at ground level, which then directly sampled the air in contrast to the sample being drawn into stainless steel containers for the gradient sampling.



— flux line 102m — gradient 102m — gradient 3m

Anonymous Referee #2

Received and published: 12 March 2020

Overall:

This paper is novel and describes interesting field campaign results in Beijing, China that show through isoprene oxidation tracers that low-NO chemistry is important in the afternoon in Beijing, China. The paper emphasizes the importance that megacities especially those surrounded by vegetation with large biogenic VOC sources and high NO_x levels likely have both low- and high-NO chemistry and modeling tools that are used for policy need to represent both of these pathways accurately.

Although the core of the paper is quite exciting and promising, there are gaps in the paper, which require more description before publication. The paper is well-written, but not well-organized. As described below, expanding on several sections in the main text and moving several sections from the supplement into the main text is needed before final publication.

In general,

The paper in the abstract, conclusions, and throughout, mentions the importance of accurately representing both low- and high-NO chemistry. Most models do represent both of these processes reasonably well at least for isoprene itself. Perhaps, you can expand on what you mean by this further. It may be more important to acknowledge the importance of mixed regimes. The conditions that occur in Beijing in the late afternoon are similar to the regime that occurs in the Southeast U.S. in the afternoon too. In the southeast U.S., isoprene hydroxy nitrates (formed from RO₂ + NO channel) react with OH to form peroxy radicals that then react with HO₂ to form isoprene dihydroxy hydroperoxy nitrates. These products formed from both RO₂ + NO and RO₂ + HO₂ channels are significantly less studied, but important in regimes like you describe here. See references such as :

Xiong et al., 2015, Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NO_x

Lee et al., 2015, Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets.

We agree with the reviewer that the chemical schemes in most regional / global models will represent both high- and low-NO chemistry to some degree, and our statements in the abstract and conclusions were not clear. We have tried now to highlight that it is the inability of models to capture the extreme diurnal cycle of NO observed that will limit the model's ability to correctly predict in-situ ozone production, SOA, etc., even though the chemical scheme within the model may be capable of representing both high and low-NO chemistry.

We agree with the reviewer that the interplay between the high NO and low NO chemical regimes observed during the day can be expected to lead to multifunctional species of which very little is currently known with regards to their atmospheric chemistry.

The format of the paper makes the paper harder to follow and is not similar to what is typically done in ACP. The methods are at the end of the paper instead of in the middle. The methods should be moved after the introduction and before the results.

As discussed above, the manuscript has been formatted as a Letter (see note on formatting in the general response above), unfortunately we were not able to explicitly state this during manuscript submission.

The results section should reference the methods section as needed.

We agree and have now tried to include reference to the methods section where appropriate.

Additionally, substantial information is contained in the supplement with only 3 figures in the main text. Redistributing some of the more pertinent information and figures that are currently in the supplement into the main text would be beneficial. In particular and as described below, the section on GEOS-Chem modeling with Figure S10 and the section describing how you filtered the mean diurnal plots should definitely be in the main text.

Again this is because we have submitted the manuscript formatted as a Letter. We agree that the GEOS-Chem modelling is important to the message of the paper and this has now been included in the main text – see the specific comment below for further details. We have also included the following sentences on the filtering in the main text and directed the reader to the Supplementary Information for further details.

“Data is filtered to only include ‘typical’ chemistry days, these are considered to be when ozone mixing ratios increase through the morning to an afternoon peak of > 70 ppb. Such ‘typical’ days account for 25 of the total of 34 measurement days. Further details of the data filtering is given in Section S1 of the Supplementary Information.”

Additionally, references to the supplement just state “see Supplementary Information”. For information that remains in the supplement after addressing the comment above, please provide more detail either by adding section numbers in the supplement or referring to specific supplementary figures.

We have given the Supplementary Information a clearer structure, a contents page, and now refer to specific sections and figures when referenced in the main text.

Specific comments

Introduction

There are many past papers describing atmospheric chemistry and air pollution in China and Beijing. Some summary of these studies and how this study is similar or different is warranted to put this paper in context. For example, Wang, 2017, Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects summarizes many studies.

We have now included a paragraph on recent NO_x trends in cities worldwide, with a focus on China and Beijing (given below). And also a paragraph on the source of high ozone episodes in Beijing. However, we re-iterate the point that the manuscript is not about the general atmospheric chemistry of Beijing, nor is it about photochemical ozone formation. It is about the diurnal cycle of changing oxidation pathways in Beijing. As such we do not feel that a general background of the VOC mix and atmospheric chemistry of Beijing is needed here.

“In the past twenty years, emissions, and hence atmospheric concentrations, of nitrogen oxides (NO_x) have decreased in urban areas throughout the majority of the developed world. In urban areas this has been due to improvements in vehicle emissions technologies, changes to residential heating, and in many major European cities, due to restrictions on the types of vehicles that are allowed in certain areas at certain times of the day. In China, through the introduction of the “Air Pollution Prevention and Control Action Plan” in 2013 (Zhang et al. 2019) there has been a concerted effort to reduce pollutant emissions. Numerous pollution control measures have been introduced, including improved industrial emissions standards, the promotion of clean fuels instead of coal within the residential sector, improving vehicle emissions standards and taking older vehicles off the road. In Beijing, 900,000 households have converted from using coal to cleaner technologies such as gas or electricity since 2013. These actions have led to a 32 % decrease in NO₂ emissions since 2012 (Liu et al., 2016; Krotkov et al., 2016; Miyazaki et al., 2017). Most significant for NO_x emissions however is the stringent vehicle control measures introduced within the last decade, accounting for 47 % of the total reduction in emissions for the city (Cheng et al. 2019). Such reductions in NO_x emissions are expected to lead to an increased importance of low-NO oxidation pathways for VOCs in urban and suburban areas (e.g. Praske et al., 2018). This will lead to the production of a range of low volatility multi-functionalised products, efficient at producing SOA, which have previously been found only in remote environments removed from anthropogenic influence.

Surface ozone in Beijing has increased through the 1990s and 2000s (Tang et al., 2009). The city regularly experiences daily peaks in the summer-time of over 100 ppb (e.g. Wang et al., 2015). Such high ozone episodes are a function both of chemistry and meteorology, with air masses coming from the mountainous regions to the northwest tending to bring in clean air low in ozone, while air masses coming from the densely populated regions to the south and west bring processed polluted air high in ozone (Wang et al., 2017). A number of modelling studies have concluded that the sources of the ozone during high ozone episodes are a combination of both local production and regional transport (Wang et al., 2017; Liu et al., 2019).“

Page 2 line 66

Please include a reference here that describes the VOC mixture in Beijing. Additionally, you could add the VOC mixture at your sampling location here. How important is isoprene compared to the other VOCs you measure with the DC-GC-FID? How does your VOC mixture compare to other VOC mixtures measured in Beijing or comparable cities in China?

Again, we do not feel that this information is pertinent to this manuscript. Isoprene oxidation products are used here as tracers. The changing diurnal oxidation pathways that are described are relevant to all VOCs. We have highlighted this point in the Discussion with the following comment:

“With the rates of RO₂+NO, and RO₂+HO₂ similar for most peroxy radicals (Orlando and Tyndall, 2012), the chemical regime reported herein is not just relevant to isoprene, but to all

VOCs (see a comparison for butane and toluene in the Supplementary Information Figure S10).”

Figure 2

It would be clearer to the reader to overlay b, c, and d on top of one another and expand these figures horizontally to that of figure a. Also to overlay e and f and also expand this one horizontally to figure a. This way the NO concentration and the region of low NO chemistry can be directly seen in all of the figures.

Adding OH, HO₂, and NO₂ concentration to Figure 2 panel would be beneficial to highlight the low NO/NO₂ ratio mentioned throughout the text and demonstrate how OH and HO₂ change diurnally.

The recommended alterations to Figure 2 have been made. We have aligned all of the plots, and added the NO / NO₂ ratio. OH and HO₂ display diurnal cycles peaking in the middle of the day from 12:00-16:00 as expected and can be found in Bryant et al., 2019 (doi: 10.5194/acp-2019-929).

The Section on “filtering data for mean diurnal plots” in the supplement should either be moved to the main text or summarized in the main text as well as in the Figure 2 caption. Without reading the supplement, the reader would not know that any filtering was done to the data. If possible, please also provide the mean diurnal profile for the same species listed in Figure 2 for the “atypical” days. This way one could contrast how the chemistry differs between a “typical” day where ozone gets above 70 ppb in the afternoon and an “atypical” day, which still occurs 25% of the time, where ozone is lower than 70 ppb. Also provide some discussion on how these products differ on “typical” and “atypical” days.

We have now included the following sentence in the main text, and have highlighted this in the Figure 2 caption:

“Data is filtered to only include ‘typical’ chemistry days, these are considered to be when ozone mixing ratios increase through the morning to an afternoon peak of > 70 ppb. Such ‘typical’ days account for 25 of the total of 34 measurement days. Further details of the filtering is given in Section S1 of the Supplementary Information.”

A mean diurnal of the ‘atypical’ chemistry days would be misleading as they are not all similar, as shown for ozone in Figure S1.

Unfortunately the CIMS data set is shorter than for NO and O₃ (2 June – 18 June), and so only contains three of the ‘atypical’ days. We now show NO, O₃, ISOPONO₂, and IEPOX+ISOPROOH in Figure S1 for the two atypical days 6 June and 10 June, compared to the diurnals of the ‘typical’ chemistry days.

Page 3 line 84

Please include references for these organosulfate tracers. Also you mention 2-MGA- OS is a tracer for high-NO SOA. Technically it is more of a tracer for high-NO and high-NO₂ SOA. On page 3 line 93, you state that 2-MGA-OS is suggestive of both high and low NO chemistry. Please make sure these statements are consistent and include appropriate references.

We agree that the description of 2-MGA as a high-NO product on line 84 is somewhat misleading. We have altered the text accordingly as described in the response to reviewer#1 above, highlighting that 2-MGA-OS requires both high-NO chemistry to form significant amounts of MACR (in the morning), and high-NO₂/low-NO chemistry to form MPAN (into the afternoon). References have been included for the formation of both OS species in the text along with references for the formation of the precursors.

Page 3 line 91

HOMs are mentioned to have been detected at this site. There are potentially products from mixed regimes that could be detected in the late afternoon. For example, other studies have detected isoprene nitrooxy hydroxy hydroperoxides in the late afternoon when NO concentrations drop in the Southeast U.S. (see explanation above in general comments). Can you detect isoprene nitrooxy hydroxy hydroperoxides with your CIMS instrument? It would add a lot to your paper to add this compound to Figure 2 if you can detect it. This would also help to address the general comment, that it's not only about getting low- and high- NO chemistry correct, but representing products from mixed regimes that are not always incorporated into reduced chemical mechanism used in global and regional models.

We thank the reviewers for this suggestion and based on the D'Ambro et al. (ACP., 17, 159, 2017) work from SOAS, the iodide CIMS is sensitive to species such as the groups suggested. The authors here have looked for isoprene nitrooxy dihydroxy hydroperoxide, C₅H₁₁NO₇, formed by first addition of OH to isoprene and reaction of the peroxy radical with NO, then later addition of OH to the remaining double bond and reaction of that peroxy radical with HO₂ in response to this. There are however, in the CIMS data set here, overlapping masses that given the resolving power of the instrument and the < 45 ppm difference between these identified masses it is not possible to confidently report such a measurement requested here. Identifying such compounds is clearly something for future work to focus on, in light of the findings discussed here.

Figure3: It would be beneficial to the reader to add the year for all the campaigns (not just for NYC) as the fno will greatly depend on when the measurements were taken and how much NOx was present.

These labels have been added.

Page 4 line 115: The fact that GEOS-Chem cannot represent this chemistry is important and should not be hidden in the supplement. I recommend moving the description of the GOES-Chem modeling and Figure S10 into the main text or providing significantly more detail here.

The reviewer makes a very good point, the GEOS-Chem modelling really highlights the fact that such models are unable to capture the observed diurnal for NO, and hence will get the oxidation pathways, and hence products, wrong even though the chemical schemes include both the high and low NO chemistry. We have moved all of the GEOS-Chem work from the Supplement, creating a new section in the main text, Section 4, a new section in the Methods, and making Figure S10, Figure 4.

GEOS-chem is a global model, so please rephrase "regional chemical transport model" to include a global model nested over China or some such explanation.

This has been changed.

Figure S10 needs labels for which red or black lines are model versus observations.

These lines have been added to the figure as suggested.

There is recent evidence to suggest that aerosols play an important role in accurately representing ozone in China through loss process of NO_x and HO_x (Li et al., 2019). In your GEOS-chem simulations, do you assume the same aerosol uptake coefficients as this study, and if not could this impact your results in Figure S10?

The same uptake coefficient was used as in the Li et al. (2019) study.

Comparing more compounds (OH, HO₂, isoprene, other VOCs measured by the GC-FID, ISOPROOH + IEPOX, isoprene hydroxy nitrates) with the GEOS-chem results would make your paper much more significant and help better understand how well models are representing the chemistry you describe in Beijing. Can you add this?

A broader discussion on radical budgets in GEOS-Chem over Beijing will be the subject of a forthcoming publication. The point of the modelling here is just to show that nested global models cannot recreate the observed diurnal cycle of NO in Beijing, which appears to be caused by missing processes in our chemical understanding rather than problems with emissions inventories.

If aerosols are important in China for representing O₃-NO_x-HO_x (and in particular the loss of HO₂ to aerosols), how would this impact your results with the box-modeling in Figure 2, which only includes gas-phase chemistry.

This is of course a complex issue, as we mention in the *Discussion and Conclusions*. On the face of it, HO₂ reductions caused by uptake to aerosol might be expected to reduce f_{HO_2} , and hence increase f_{NO} . However, additional feedbacks would also occur, such as the increased ozone associated with reduced HO₂ (Li et al., 2019), which would suppress [NO] and bring the $f_{\text{NO}}/f_{\text{HO}_2}$ ratio back the other way. In short, heterogeneous uptake of HO₂ may be important in certain urban environments, but this importance will be variable on a daily and seasonal basis. The box modelling is a simple representation of the competition between NO and HO₂ for reaction with peroxy radicals, and while an additional HO₂ sink may shift the plot slightly (though maybe not due to the feedbacks mentioned above), it would not change the overall take home message of the plot. Moreover, the recently published experimental study of Tan et al. (2020, ES&T, doi: 10.1021/acs.est.0c00525) conducted in the North China Plain in the summer of 2014 – observed insignificant effects of heterogeneous uptake of HO₂ to aerosol on the radical budget, and hence on ozone formation, in contrast to the modelling of Li et al. (2019).

On page 5 line 137, Jacob et al., 2019 is referenced, but not incorporated in the reference list. Please update this reference or use Li et al., 2019.

This has been corrected in the text to Li et al. (2019).

Page 9 line 274: What was the relative humidity used in the box-model?

A fixed relative humidity of $0.01 * N_A$ was used, i.e. 2.55×10^{17} molecules cm^3 . This is now mentioned in the *Box Modelling* section of the Methods.