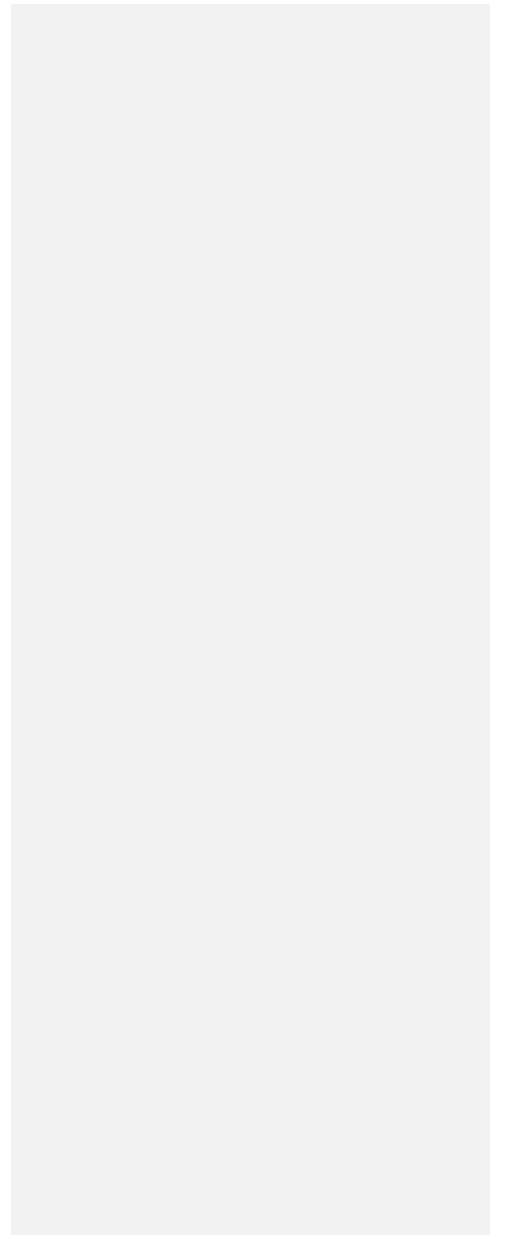5

Response to Reviewers

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Response to Reviewers of:

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

General Response

20 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
25 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
30 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,
35 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 NOx emissions but still having a high
40 loading of reactive VOCs.
The story told by the measured isoprene oxidation products is corroborated by the auxiliary NOx and ozone measurements.

What the manuscript is not aiming to do is to describe the VOC composition in Beijing, talk about the role of
45 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*'
50 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 NOx concentrations in urban environments, and in particular in

2

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 NOx 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 NOx (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 HOx 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.

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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.

95 **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 RO_2, specifically ISOPOO, are reacting with HO_2 / RO_2 rather than with NO as might be expected in an urban environment. We are not referring to the ozone production regime of a rainforest.

100 **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

105
> 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, NO_2 and O_3. This then provides not only a description of the changing diurnal profile of the oxidation state of the local Beijing atmosphere, but also provides
110
> 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.

115 **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
120 *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.*

4

125 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 NO_2 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 NO_2/NO ratio, and NO_2 high enough to largely outcompete HO_2 (although 2-MGA-OS could also come from the

130 HO_2 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

135 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 HO_2 IEPOX

140 *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 NO_2/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)."*

145 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.

150 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

155 *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?*

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160   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

165   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

170   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.

175   **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

180   *in the stainless steel container. How log 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 ISOPOOH 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*

185   *ISOPOOH 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

190   *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.
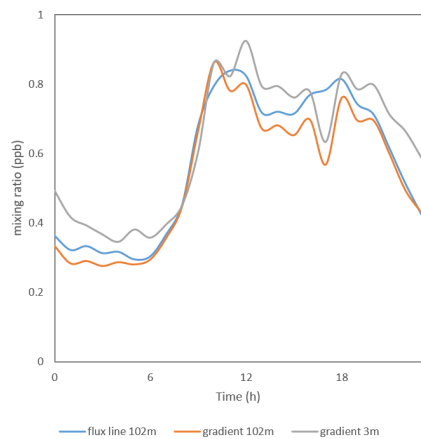
Overall:

This paper is novel and describes interesting field campaign results in Beijing, China that show through isoprene
205 *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 NOx 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
210 *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
215 *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*
220 *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
225 *for the fate of NOx*

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

230 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.

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235   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
240 *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.

245 *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.*

250   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.

255   *"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
260 *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.

265 **Specific comments**

9

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 NO$_2$ 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

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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)."

305

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
310 *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:

315
> *"With the rates of RO_2+NO, and RO_2+HO_2 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
320 *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 / NO_2 ratio. OH and HO_2 display diurnal cycles peaking in the middle of the day from 12:00-16:00
325 > 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
330 *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:

335 *"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
340 for ozone in Figure S1.

Unfortunately the CIMS data set is shorter than for NO and O_3 (2 June – 18 June), and so only contains three of the 'atypical' days. We now show NO, O_3, ISOPONO2, and IEPOX+ISOPOOH 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

345 *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
350 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-NO_2/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

355 *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
360 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
365 from SOAS, the iodide CIMS is sensitive to species such as the groups suggested. The authors here have looked for isoprene nitrooxy **di**hydroxy 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

12

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 NOx and HOx (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, ISOPOOH + 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

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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-NOx-HOx (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, HO_2 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 HO_2 (Li et al., 2019), which would suppress [NO] and bring the f_{NO}/f_{HO_2} ratio back the other way. In short, heterogeneous uptake of HO_2 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 HO_2 for reaction with peroxy radicals, and while an additional HO_2 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 HO_2 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 x 10^{17} molecules cm^3. This is now mentioned in the *Box Modelling* section of the Methods.

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**Marked-up
Manuscript Version**
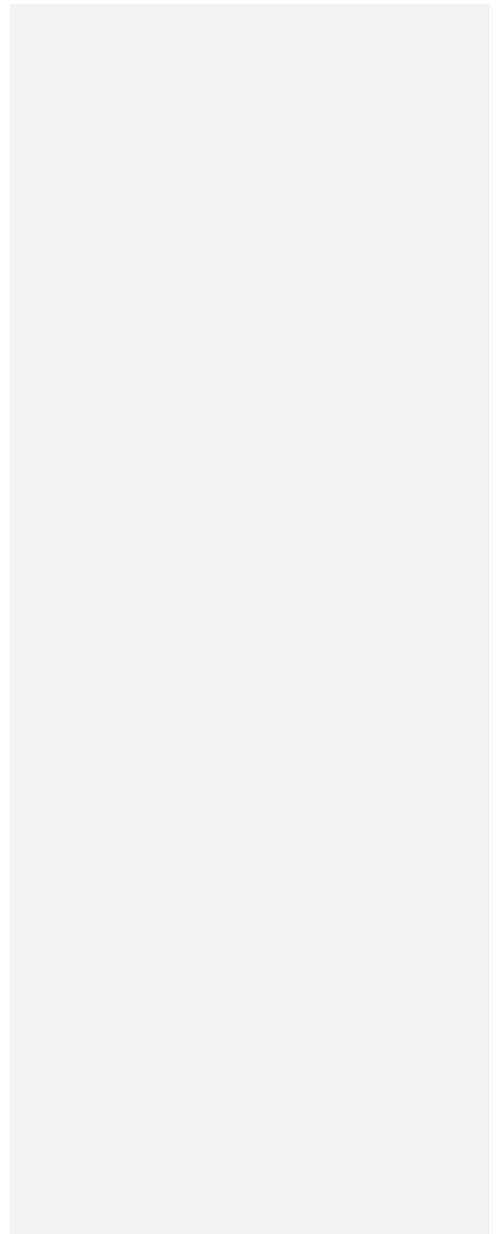
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Rainforest-like Atmospheric <u>Oxidation Pathways</u> in a Polluted Megacity

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Abstract. The impact of volatile organic compound (VOC) emissions to the atmosphere on the production of secondary pollutants, such as ozone and secondary organic aerosol (SOA), is mediated by the 475 concentration of nitric oxide (NO). Polluted urban atmospheres are typically considered to be "high-NO"

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environments, while remote regions such as rainforests, with minimal anthropogenic influences, are considered to be "low-NO". However, our observations from central Beijing show that this simplistic separation of regimes is flawed. 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, caused by extreme suppression of NO concentrations in the afternoon. 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%). Current emissions inventories are applied in the GEOS-Chem model which shows that such models run, when run at the regional scale, fail to accurately predict such an extreme diurnal cycle in the NO concentration. With increasing global emphasis on reducing air pollution, it is crucial for the modelling tools used to develop urban air quality policy to be able to accurately represent such extreme diurnal variations in NO to accurately predict the formation of pollutants such as SOA and ozone.

1 Introduction

The atmosphere in polluted urban areas has a markedly different chemical composition to that in remote regions (e.g. rainforests). This can lead to changes in the chemical oxidation pathways for volatile organic compounds (VOCs), giving rise to the formation of different secondary pollutants. Oxidation by hydroxyl radicals (OH) is the dominant daytime sink for VOCs, leading to the formation of highly reactive peroxy radicals (RO_2). In atmospheres with high concentrations of nitric oxide (NO), emitted by combustion sources such as vehicles, cooking, and energy generation, RO_2 radicals react predominantly with NO (Orlando and Tyndall, 2012). This tends to break the initial VOC down to smaller, more oxidised VOCs, and can also produce organic nitrates ($RONO_2$). This pathway also produces NO_2, the photolysis of which leads to ozone production. In contrast, in low-NO atmospheres RO_2 predominantly react with other RO_2, including hydroperoxyl radicals (HO_2), or can isomerize/auto-oxidise to form different multi-functionalized oxygenated RO_2 (Crounse et al., 2013). These low NO pathways tend to maintain the original carbon skeleton. The large highly oxidised molecules formed can efficiently partition to the aerosol phase to yield secondary organic aerosol (SOA) (Bianchi et al., 2019), which often comprises a large fraction of submicron atmospheric particulate matter (PM) in many regions (Jimenez et al., 2009).

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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 NO_2 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).

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Biogenic sources dominate global emissions of VOCs to the atmosphere, with the highly reactive VOC isoprene (2-methyl-1,3-butadiene) contributing ~70% by mass (Sindelarova et al., 2014). The gas and aerosol phase products of isoprene oxidation have been extensively characterized in the laboratory (Wennberg et al., 2018, and references therein). For isoprene, the low-NO oxidation pathway leads to low volatility products, such as isoprene hydroperoxides (ISOPOOH), that can go on to form significant quantities of SOA via formation of isoprene epoxides (IEPOX) (Figure 1) (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012). The high-NO pathway can also form SOA via the formation of methacrolein (MACR), which can react further to form SOA constituents such as 2-methylglyceric acid (2-MGA) and corresponding oligomers (Kroll et al., 2006; Surratt et al., 2006; 2010; Nguyen et al., 2015) (Figure 1). Other significant contributors to isoprene-SOA formed via the high NO pathway include nitrates (e.g. ISOPONO$_2$) and dinitrates (Schwantes et al., 2019). In this work, a suite of isoprene oxidation products, in both the gas and particle phases, are used as tracers of the changing atmospheric chemical environment through the daytime in Beijing.

2 Results

Beijing is a megacity (population of 21.4 M) with an atmospheric reactive VOC mix with both biogenic and anthropogenic influences (e.g. Li et al., 2020). Mean diurnal cycles of ozone, NO, isoprene, and a range of gas and aerosol phase isoprene oxidation products measured at a city-centre site in summer 2017 (Shi et al., 2019) are shown in Figure 2. Data is filtered to only include 'typical' chemistry days, which are considered to be when the ozone mixing ratio increases 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. Ozone increases throughout the day to a mid-afternoon peak (Figure 2a), driven by the photolysis of NO$_2$, which is rapidly regenerated through the reactions of ozone, RO$_2$ and HO$_2$ with NO. The high level of ozone acts to suppress NO concentrations. Such a diurnal cycle is typical of urban environments (Ren et al., 2003; Whalley et al., 2018). However, ozone is so high in Beijing, with mixing ratios regularly >100 ppbv in the afternoon,

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that on many days NO concentrations fall to < 0.5 ppbv in the afternoon, and on some days to < 0.1 ppbv (see Figure S2).

580 The observed diurnal cycles of 'low-NO' and 'high-NO' isoprene oxidation products (Figure 1) in both the gas and aerosol phases can be explained by the observed diurnal cycle of NO (Figure 2c). The high-NO product isoprene nitrate (ISOPONO$_2$), measured using a Chemical Ionisation Mass Spectrometer (CIMS) – see Methods for further details, is produced through the morning from reaction of isoprene peroxy radicals (ISOPOO) with NO (Figure 2d). During the afternoon, an increasing fraction of ISOPOO

585 begins to react with HO$_2$ or RO$_2$ as the NO concentration drops. This leads to the observed decrease in ISOPONO$_2$, and an increase in the low-NO products IEPOX + ISOPOOH (also measured by CIMS) through the afternoon (Figure 2e). The profile of the high-NO products MACR+MVK, measured by Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) – see Methods for further details, is very similar to that of ISOPONO$_2$ until about 15:00, when they begin to increase, with a second

590 peak observed at around 17:00 (Figure 2f). This latter peak may be an observational artefact as a result of the conversion of ISOPOOH to MACR on metal surfaces within the inlet of the PTR instrument (Rivera-Rios et al., 2014). Isoprene oxidation products can also partition into the particle phase and undergo heterogeneous reactions to form organosulfates, with concentrations driven by a number of additional factors such as particulate sulfate and water vapour concentrations. Organosulfate tracers, 2-MGA-OS

595 (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 HO$_2$ 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

600 product MACR, in an environment with a high NO$_2$/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).

The observed temporal profiles of the isoprene tracer products suggest a chemical cycle switching from a high-NO to a low-NO chemical regime during the day in Beijing. First, isoprene nitrates, formed

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predominantly during the morning (Figure 2d), are characteristic of high-NO chemistry. Second, isoprene hydroperoxides (ISOPOOH) and epoxydiols (IEPOX) (Figure 2eb), formed predominantly during the afternoon, are characteristic of low-NO chemistry, where the reaction of ISOPOO with HO_2 dominates over reaction with NO. The formation of highly oxygenated molecules (HOMs), characteristic of RO_2 isomerisation and auto-oxidation in low NO environments, has also been observed during the afternoon at this site (Brean et al., 2019). Third, the observation of large amounts of 2-methylglyceric acid (2-MGA-OS) (Figure 2g) in the aerosol is suggestive of both high and low NO chemistry having occurred.

3 Box Modelling

The chemical box model DSMACC (Emmerson and Evans, 2009), coupled with the near-explicit oxidation mechanism for isoprene from the Master Chemical Mechanism (MCM v3.3.1) (Jenkin et al., 1997; 2015), was used to assess the sensitivity of the fraction of ISOPOO reacting with NO (f_{NO}) to varying NO concentrations and OH reactivities ($\sum k_{OH+VOC}$ [VOC]). The model was run to steady state at a range of different fixed concentrations of [OH], [NO], and [isoprene], using fixed photolysis rates typical of Beijing daytime (see Section Methods and Section S5 in Supplementary Information). Figure 3 shows that, as expected, f_{NO} increases with increasing NO concentration. It also shows that f_{NO} is not a fixed value for a given concentration of NO, but decreases with the increasing reactivity of the system (the x-axis in Figure 3). The reactivity varies as a function of the VOC mixing ratios, the reactivity of the VOCs, and the OH concentration, i.e. [OH] $\times$ OH reactivity* (Equation E1). Higher reactivity and higher OH concentrations both lead to a higher concentration of peroxy radicals ([HO_2] + $\sum$[RO_2]), reducing f_{NO}. Average measurements of ([OH] $\times$ OH reactivity*) and [NO] for the afternoon (12:00 – 20:00) from a range of different environments are shown in Figure 3 (see also Table S1). The RO_2 chemistry in the rural southeastern US and the Borneo rainforest lies in the low NO regime (i.e. $f_{NO} < 0.5$) for the whole afternoon. In the urban areas of London and New York the chemistry remains in the high NO regime through the whole afternoon. However, in Beijing, the extreme suppression of NO concentrations in the afternoon drives the chemistry from a regime in which > 95 % of the RO_2 is reacting with NO during the morning, to one in which less than 70 % is reacting with NO by mid-afternoon.

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5 Discussion and Conclusions

Modelling was performed with the global chemical transport model GEOS-Chem, with a nested grid at 0.25 x 0.3125 degree resolution over China (see Methods – GEOS-Chem modelling), to investigate the modelled diurnal cycle of NO for Beijing. The results (Figure 4) show that while the model does a good job of recreating the measured ozone and NO_2 profiles, it cannot match the observed [NO] or NO to NO_2 ratio, particularly at sub ppb levels typically observed during the afternoon. Thus the model is unable to capture the formation of low NO products from isoprene and other VOCs in Beijing. The major driver of the low NO concentrations in the model is the high levels of ozone, which titrates out the NO. As such, with the chemistry currently in the model there is very little flexibility available to appreciably change this ratio, i.e. changes to other NO sinks in the model, such as RO_2, through changes to VOC emissions, will have little effect on [NO]. The fact that the GEOS-Chem modelling cannot recreate the extremely low afternoon NO suggests that there may be additional sinks for NO beyond our current chemical understanding. One explanation may be additional NO sinks that recycle OH without producing O_3, as previously proposed for the high VOC-low NO (< 1ppbv) conditions seen in Beijing and other cities (Hofzumahaus et al., 2009; Whalley et al., 2018; Tan et al., 2019). Another explanation may be the presence of high concentrations of other species that can rapidly convert NO to NO_2 e.g. halogen oxides.

Similar mixed NO regimes as observed here for Beijing have been observed previously at a suburban site in the Pearl River Delta (Tan et al., 2019), and in the semi-rural south east US (Xiong et al., 2015), albeit with lower morning NO peaks. Such a mixed regime will lead to a range of low volatility multifunctional products (Xiong et al., 2015; Lee et al., 2016) some of which are only accessible through this regime, which can efficiently partition to the particle phase to contribute to SOA. With the rates of RO_2+NO, and RO_2+HO_2 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).

Our observations from Beijing challenge the commonly accepted view of polluted urban areas as high-NO atmospheric environments in two ways. First, very high ozone (and other sinks) regularly reduces

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afternoon NO to < 1 ppbv, and on some days to < 0.1 ppbv. This leads to the formation of 'low-NO' products in the gas and aerosol phase. Second, the level of NO that is required for 'low-NO chemistry' to occur is not a fixed value, but is dependent on the concentration and reactivity of the VOCs present and

710 the concentration of OH. Hence NO concentrations that represent 'low-NO' conditions in a tropical rainforest, for example, are different to those that represent 'low-NO' conditions in a highly polluted urban environment with elevated VOC/OH reactivity.

Under the conditions observed in Beijing, the production of low-NO SOA and the associated increase in

715 PM is shown to be closely linked to photochemical ozone production. Policies that reduce the afternoon ozone peak might also be expected to reduce the production of these aerosol-phase products. However, such policies must also take account of the complex interactions between NO_x, VOCs, ozone, and PM. For example, reducing NO_x emissions can counter-intuitively lead to increases in ozone, as has occurred in other major cities (Air Quality Expert Group, 2009), while a recent modelling study (Li et al., 2019)

720 has suggested that reducing PM has led to increases in ozone in China, although a recent experimental study (Tan et al., 2020) in the North China Plain saw no effect. With many existing and developing megacities being located in subtropical regions with high emissions of reactive biogenic VOCs, control of which is very difficult, and with continuing reductions in NO_x emissions, such extreme chemical environments as that observed in Beijing can be expected to proliferate. The failure of regional and global

725 models to accurately replicate this chemical regime has wider implications for the prediction of secondary pollutants and hence for determining policies to control air pollution episodes.

Methods

730 The site was located at the Institute of Atmospheric Physics, between the 3rd and 4th ring road. Measurements took place between 17/05/2017 and 24/06/2017. The site is typical of central Beijing, surrounded by residential and commercial properties and is near several busy roads. It is also close to several green spaces, including a tree-lined canal to the south and the Olympic forest park to the north-east. Isoprene mixing ratios were measured by dual channel gas chromatography (DC-GC-FID).

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IEPOX/ISOPOOH were observed using iodide chemical ionisation mass spectrometry. The sum of MACR + MVK was measured using proton transfer mass spectrometry. Particle samples were collected onto filter papers at either 3 hourly or 1 hourly time periods, depending on pollution levels. Filters were extracted and analysed with a high throughput method using ultra high-pressure liquid chromatography coupled to a Q-Exactive Orbitrap mass spectrometer. Nitric oxide, NO, was measured by chemiluminescence with a Thermo Scientific Model 42i NO_x analyser. Nitrogen dioxide, NO_2, was measured using a Teledyne Model T500U Cavity Attenuated Phase Shift (CAPS) spectrometer. Ozone, O_3, was measured using a Thermo Scientific Model 49i UV photometer.

DC-GC-FID

Observations of VOCs were made using a dual-channel GC with flame ionisation detectors. Air was sampled at 30 L min^{-1} at a height of 5m, through a stainless-steel manifold (½" internal diameter). 500 mL subsamples were taken, dried using a glass condensation finger held at -40°C and then pre-concentrated using a Markes Unity2 pre-concentrator on a multi-bed Ozone Precursor adsorbent trap (Markes International Ltd). These samples were then transferred to the GC oven for analysis following methods described by Hopkins et al (2011).

CIMS

A time of fight chemical ionisation mass spectrometer (ToF-CIMS) (Lee et al., 2014; Priestley et al., 2018) using an iodide ionisation system was couple deployed. Experimental set up of the University of Manchester ToF-CIMS has been previously described in Zhou et al. (2019). During the campaign, gas phase backgrounds were established by regularly overflowing the inlet with dry N_2 for 5 continuous minutes every 45 minutes and were applied consecutively. The overflowing of dry N_2 will have a small effect on the sensitivity of the instrument to those compounds whose detection is water dependent. Here we find that due to the very low instrumental background for $C_5H_{10}O_3$ and $C_5H_9NO_4$, the absolute error remains small from this effect (<10 ppt in both reported measurements).

Field calibrations were regularly carried out using known concentration formic acid gas mixtures made in a custom-made gas phase manifold. A range of other species were calibrated for after the campaign,

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and relative calibration factors were derived using the measured formic acid sensitivity during these calibrations, as has been performed previously (Le Breton et al. 2018, Bannan et al. 2015). In addition to this, offline calibrations, prior to and after the field work project, of a wide range of organic acids, HNO_3 and Cl_2 were performed to assess possible large scale sensitivity changes over the measurement period. No significant changes were observed. Offline calibrations after the field work campaign were performed specific to the isoprene oxidation species observed here. IEPOX ($C_5H_{10}O_3$) synthesized by the University of North Carolina, Department of Environmental Sciences & Engineering, was specifically calibrated for. Aliquots of known concentrations of IEPOX ($C_5H_{10}O_3$) were thermally desorbed into a known continuous flow of nitrogen. For $C_5H_9NO_4$ there was no direct calibration source available and concentrations using the calibration factor of $C_5H_{10}O_3$ are presented here.

PTR-MS

A Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS 2000, Ionicon Analytik GmBH, Innsbruck) was deployed at the base of the 325m meteorological tower at the IAP field site. This instrument has been described in detail by Jordan et al. (2009). The PTR-ToF-MS was operated at a measurement frequency of 5 Hz and an E/N ratio (where E represents the electric field strength and N the buffer gas density) in the drift tube of 130 Td. To enable accurate calibration of the mass scale trichlorobenzene was introduced by diffusion into the inlet stream.

The instrument was switched between two inlet systems in an hourly cycle. 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 with air sampled down 0.25 inch O.D. PFA lines and split between a 3 L min^{-1} bypass and 300 ml min^{-1} sample drawn to a 10 L stainless steel container. During the gradient sampling period, the PTR-ToF-MS subsampled for 2 minutes from each container giving an hourly average concentration at each height. In this work, only data from the 3m gradient height is discussed.

Zero air was generated using a platinum catalyst heated to 260 °C and was sampled hourly in the gradient switching cycle. During the field campaign, the instrument was calibrated twice weekly using a 15

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815   component 1 ppmv VOC standard (National Physical Laboratory, Teddington). The calibration gas flow was dynamically diluted into zero air to give a six-point calibration. Data was analysed using PTR-MS Viewer 3.

PM$_{2.5}$ filter sampling and analysis

820   PM$_{2.5}$ filter samples were collected using an ECOTECH HiVol 3000 (Ecotech, Australia) high volume air sampler with a selective PM$_{2.5}$ inlet, with a flow rate of 1.33 m^3 min^{-1}. Filters were baked at 500 ^{o}C for five hours before use. After collection, samples were wrapped in foil and then stored at -20 ^{o}C and shipped to the laboratory. Samples were collected at a height of 8 m, on top of a building in the IAP

825 complex. Hourly samples were taken on 11th June between 08:00 and 17:00, with one further sample taken overnight. The extraction of the organic aerosol from the filter samples was based on the method of Hamilton et al. (2008). Initially, roughly an 8th of the filter was cut up into 1 cm^2 pieces. 4 ml of LC-MS grade H$_2$O was then added to the sample and it was left for two hours. The samples were then sonicated for 30 minutes. Using a 2 ml syringe, the water extract was then pushed through a 0.22μm filter

830 (Millipore) into another sample vial. An additional 1 mL of water was added to the filter sample, then extracted through the filter, to give a combined aqueous extract. This extract was then reduced to dryness using a vacuum solvent evaporator (Biotage, Sweden). The dry sample was then reconstituted in 1 mL 50:50 MeOH:H$_2$O solution, ready for analysis.

   The extracted filter samples and standards were analysed using UPLC-MS^2, using an Ultimate 3000

835 UPLC (Thermo Scientific, USA) coupled to a Q-exactive Orbitrap MS (Thermo Fisher Scientific, USA) with a heated electrospray ionisation (HESI). The UPLC method uses a reverse phase 5 μm, 4.6 x 100mm, Accucore column (Thermo scientifc, UK) held at 40 ^{o}C. The mobile phase consists of LC-MS grade water and 100 % MeOH (Fisher Chemical, USA). The water was acidified using 0.1 % formic acid to improve peak resolution. The injection volume was 2 μl. The solvent gradient was held for a minute at 90:10

840 H$_2$O:MeOH, the gradient then changed linearly to 10:90 H$_2$O:MeOH over 9 minutes, it was then held for 2 minutes at this gradient before returning to 90:10 H$_2$O:MeOH over 2 minutes and then held at 90:10 for the remaining 2 minutes, with a flow rate of 300 μL min^{-1}. The mass spectrometer was operated in

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negative mode using full scan MS^2. The electrospray voltage was 4.00 kV, with capillary and auxiliary gas temperatures of 320 ^{o}C. The scan range was set between 50 - 750 m/z. Organosulfates were quantified using an authentic standard of 2-MGA-OS obtained from J. Surratt using the method described in Bryant et al. (2019).

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OH measurements

The OH radical measurements were made from the roof of the University of Leeds FAGE instrument container at the IAP field site. Two Fluorescence Assay by Gas Expansion (FAGE) detection cells were housed in a weather-proof enclosure at a sampling height of approximately 4 m. OH and HO$_2$ radicals were detected sequentially in the first cell (the HO$_x$ cell), whilst HO$_2$* and total RO$_2$ radical observations were made using the second FAGE cell (the RO$_x$ cell), which was coupled with a flow reactor to facilitate RO$_2$ detection (Whalley et al., 2018). A Nd:YAG pumped Ti:Sapphire laser was used to generate 5 kHz pulsed tunable UV light at 308 nm and used to excite OH via the Q1(1) transition of the $\mathbf{A^2\Sigma^+, v' = 0 \leftarrow X^2\Pi_i, v'' = 0}$ band. On-resonance fluorescence was detected using a gated micro-channel plate photomultiplier and photon counting. A background signal from laser and solar scatter and detector noise was determined by scanning the laser wavelength away from the OH transition (OHWAVE-BKD). For the entire campaign the HO$_x$ cell was equipped with an inlet pre injector (IPI) which chemically scavenged ambient OH by periodically injecting propane into the air stream just above the FAGE inlet. The removal of ambient OH by chemical reaction provided an alternative means to determine the background signal (OH$_{CHEM-BKD}$) without the need to tune the laser wavelength. By comparison with OH$_{WAVE-BKD}$, OH$_{CHEM-BKD}$ was used to identify if any OH was generated internally within the FAGE cell, acting as an interference signal. In general, good agreement between OH$_{CHEM-BKD}$ and OH$_{WAVE-BKD}$ was observed, with a ratio of 1.07 for the whole campaign (Woodward-Massey, 2018). In this paper, the OH$_{CHEM}$ observations are used. The instrument was calibrated every few days by over-flowing the detection cell inlet with a turbulent flow of high purity humid air containing a known concentration of OH (and HO$_2$) radicals generated by photolysing a known concentration of H$_2$O vapour at 185 nm. The product of the photon flux at 185 nm and the time spent in the photolysis region was measured before and after the campaign using N$_2$O actinometry (Commane et al., 2010).

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OH reactivity measurements

880   OH reactivity measurements were made using a laser flash photolysis pump-probe technique (Stone et al., 2016). Ambient air, sampled from the roof of the FAGE container, was drawn into a reaction cell at a flow rate of 15 SLM. A 1 SLM flow of high purity, humidified air which had passed by a Hg lamp, generating ~50 ppbv of ozone, was mixed with the ambient air at the entrance to the reaction cell. The ozone present was photolysed by 266 nm laser light at a pulse repetition frequency of 1 Hz along the

885   central axis of the reaction cell, leading to the generation of a uniform profile of OH radicals following the reaction of $O(^1D)$ with H_2O vapour. The decay in the OH radical concentration by reaction with species present in the ambient air was monitored by sampling a portion of the air into a FAGE cell positioned at the end of the reaction cell. A fraction of the 5 kHz, 308 nm radiation generated by the Ti:Sapphire laser passed through the OH reactivity FAGE cell perpendicular to the air stream,

890   electronically exciting the OH radicals, and the subsequent laser-induced fluorescence signal was detected with a gated channel photomultiplier tube. The 1 Hz OH decay profiles were integrated for 5 minutes and fitted to a first-order rate equation to determine the observed loss rate of OH (k_{obs}). The total OH reactivity, k(OH), was calculated by subtracting the rate coefficient associated with physical losses of OH (k_{phys}) from k_{obs}. k_{phys} was determined by monitoring the decay of OH when the ambient air was replaced with a

895   flow of 15 SLM high purity air. A small correction to account for dilution of the ambient air by the 1 SLM flow of ozone-containing synthetic air was also applied.

Box Modelling

The box modelling that feeds into Figure 3 was performed using the Dynamically Simple Model of

900   Atmospheric Chemical Complexity (DSMACC), zero-dimensional box model (Emmerson and Evans, 2009), together with the isoprene scheme, together with the relevant inorganic chemistry, from the near explicit chemical mechanism the Master Chemical Mechanism (MCM) v3.3.1 (Jenkin et al., 1997; Jenkin et al., 2015). The complete isoprene degradation mechanism in MCM v3.3.1 consists of 1926 reactions of 602 closed shell and free radical species, which treat the chemistry initiated by reaction with OH

905   radicals, NO_3 radicals and ozone. It contains much of the isoprene HO_X recycling chemistry identified as

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important in recent years under "low NO" conditions, including the peroxy radical 1,4 and 1,6 H-shift chemistry described in the LIM1 mechanism (Peeters et al., 2009; 2014), as summarized in Wennberg et al. (2018). Model photolysis rates were calculated using the Tropospheric Ultraviolet and Visible Radiation Model (TUV v5.2) (Madronich, 1993).

The box model was initialised with a range of different concentrations of isoprene (1.7 ppb, 3.4 ppb, 5.0 ppb, 6.7 ppb), and OH (0.25, 0.5, 1.0, 3.0, 10, 20 × 10^6 cm^{-3}). [CH$_4$] was fixed at 1.85 ppmv and [CO] at 110 ppbv, T = 298 K, and [H$_2$O] = 2.55 × 10^{17} cm^{-3}. Entrainment loss rates for all model species were set to 1 × 10^{-5} cm^{-3} s^{-1}. For the box model, a column average value for deposition velocity, V_d, was calculated according to the functionalities of each species (Table S2). These terms prevent the build-up of secondary products. The values are based on reported deposition rates in Nguyen et al. (2015). A boundary layer height (*BLH*) of 1.5 km was assumed. Loss rates (L_d) for each species to dry deposition are then $L_d = V_d/BLH$. Photolysis rates were fixed to mean rates for the day time period 09:00-17:00 calculated for July 1. The model was then run to steady state for a range of fixed NO mixing ratios from 0 – 16,000 pptv.

GEOS-Chem Modeling

GEOS-Chem version 11-01 (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_v11-01) with the inclusion of the aromatic component of RACM2 (regional atmospheric chemistry mechanism 2) was run nested at 0.25 x 0.3125 degree resolution, with 4 x 5 degree boundary conditions using GEOS-FP meteorology. The NO emissions were added via the default MIX emission inventory, which required a 0.9x multiplier on the total daily emissions to match observations from the APHH summer campaign. The diurnal scale factor was considerably steeper than the default GEOS-Chem NO diurnal, with a day-time scale factor on the order of 1.7x and a 0.25x night-time multiplier.

Data availability

Data are available at http://catalogue.ceda. ac.uk/uuid/7ed9d8a288814b8b85433b0d3fec0300 (last access: 13 Feb 2020). Specific data are available from the authors on request (jacqui.hamilton@york.ac.uk).

Author Contributions

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Competing Interests

The authors declare that they have no conflict of interest.

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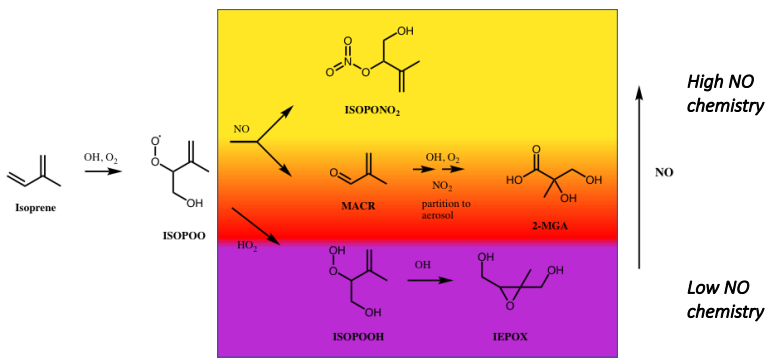
Figure 1: Formation pathways of isoprene oxidation products used as tracers of high / low-NO chemistry in this work. Following reaction of the primary VOC, isoprene, with OH, a peroxy radical intermediate (ISOPOO) is formed. At low NO concentrations, ISOPOO reacts with HO_2 (or other RO_2), to yield hydroperoxide (ISOPOOH) isomers ((4,3)-ISOPOOH isomer is shown), which can be rapidly oxidized to isoprene epoxydiol (IEPOX) isomers. At high NO concentrations, ISOPOO reacts with NO, a minor product of which is an isoprene nitrate (ISOPONO2). One of the major products of ISOPOO reaction with NO is methacrolein (MACR), the subsequent oxidation of which, in the presence of NO_2, can lead to 2-methylglyceric acid (2-MGA) and its corresponding oligomers and organosulfates in the aerosol phase. Measurements of these products in the gas or aerosol phase can be used as tracers for the chemical environment in which they were formed.
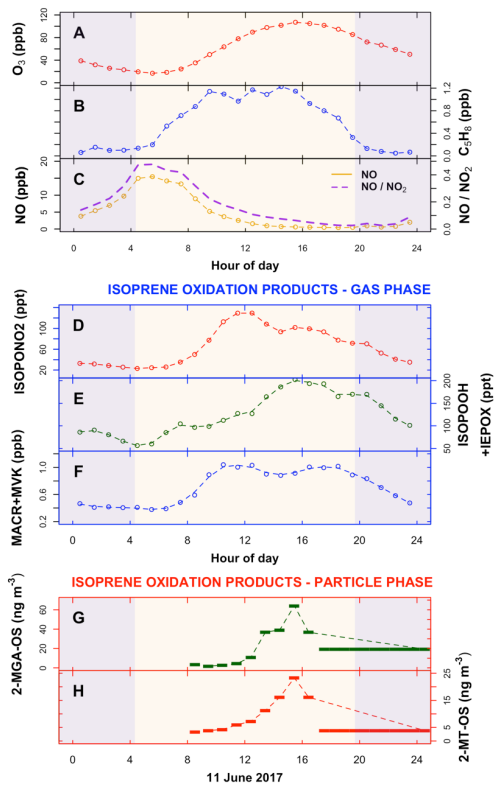
Figure 2: Mean diurnal variation of measured organic and inorganic species in the gas phase and aerosol during the Beijing summer observations (data is filtered to only include 'typical' chemistry days – see text for details). a. Mean diurnal cycle of the inorganic species NO and ozone (O_3) and of the product precursor isoprene (C_5H_8). Shaded areas are at night; area between the dotted lines indicates where > 25% of the isoprene chemistry is driven by low NO pathways (Fig. 3). Mean diurnal cycles of: (b) the gas phase isoprene 'high NO' oxidation product, isoprene nitrate (ISOPONO2); (c) the isoprene 'low NO' oxidation products, ISOPOOH + IEPOX; (d) the gas phase isoprene 'high NO' oxidation products methacrolein (MACR) (precursor to 2-MGA) + methyl vinyl ketone (MVK). (e&f) SOA components: 2-methyltetrol-organosulfate (2-MT-OS) and 2-methylglyceric acid-organosulfate (2-MGA-OS), both measured on the 11/12th June 2017, the last filter sample was taken from 17:30 11 June - 08:30 12 June.

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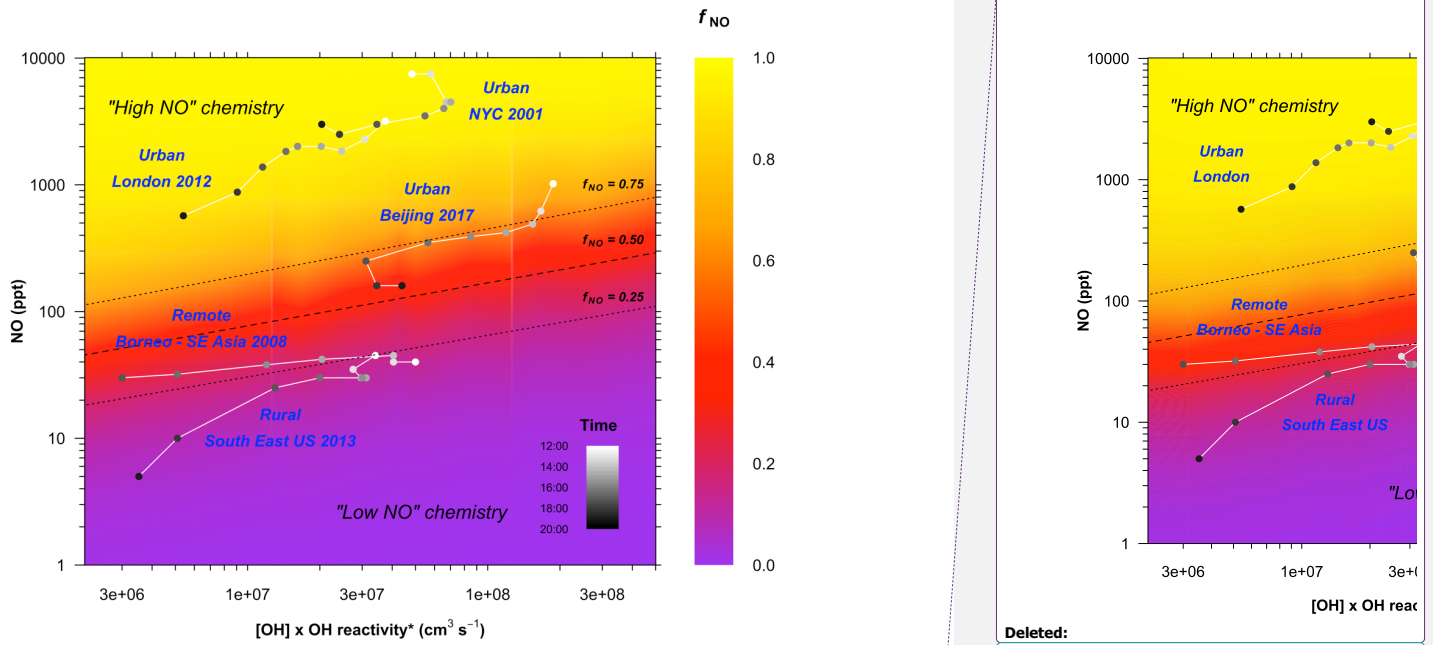
290 **Figure 3:** Variation of the fraction of ISOPOO reacting with NO as a function of NO concentration and the reactivity of the system. The plot is derived from a series of zero-dimensional box model runs performed as a function of fixed concentrations of [NO], [OH], and [isoprene]. Photolysis is fixed to an average of 09:00-17:00 conditions. OH reactivity* is total OH reactivity of the chemical system minus the contribution from OH + NOx (Equation E1), since these reactions do not produce RO2.

OH reactivity* = $\sum k_{OH+VOC}$ [VOC]   (E1)

295 The dashed line shows the fraction of ISOPOO reacting with NO f_{NO} = 0.50, dotted lines show f_{NO} = 0.25 and 0.75. Points are average diurnal hourly measurements of NO, OH, and OH reactivity* for the period 12:00 – 20:00 pm from a range of different environments: The rural sites, Borneo (Whalley et al., 2011) (only shown for 12:00-18:00) and the Southeast US (Sanchez et al., 2018), and the urban sites London (Whalley et al., 2016), New York City (Ren et al., 2003), and Beijing (this work). See the SI for full details.
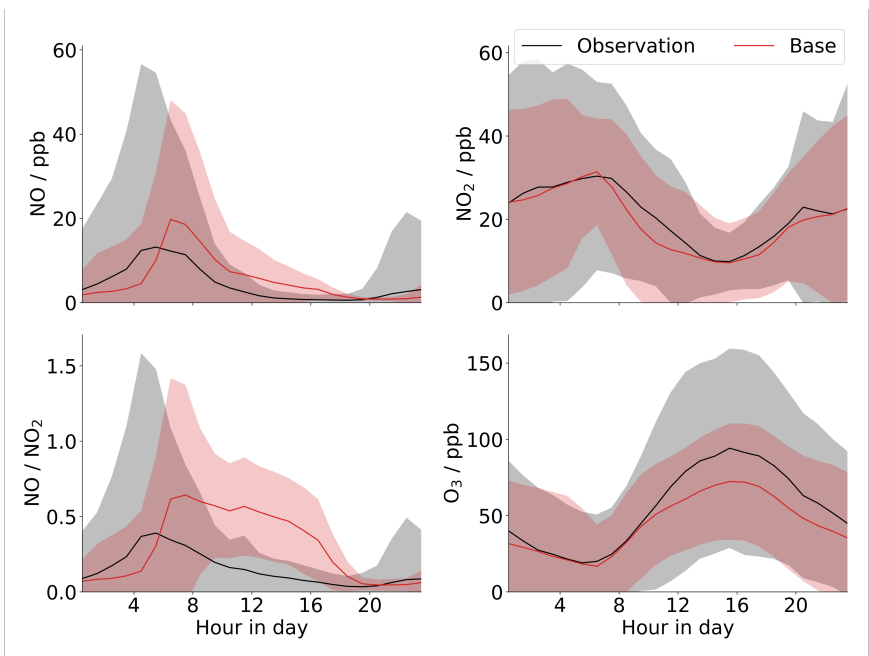
Figure 4 Comparison of GEOS-Chem model output (red) to mean diurnal measurements for the campaign (black) for NO, NO$_2$, O$_3$ and the NO/NO$_2$ ratio for Beijing.

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the modelling tools used to develop urban air quality policy need to adequately represent both high- and low-NO

regimes if they are to have utility.

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On oxidation environments in cities / remote.

Previous studies in Beijing have focused on … and found that …. .

The VOC mix in Beijing is …. Here we use isoprene oxidation products as tracers of the environment in which the products were formed. These measurements are corroborated by ….

The OH reactivity, i.e. $k_{VOC+OH}[VOC]$ has been shown to be dominated by

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However, model runs with the global chemical transport model GEOS-Chem, with a nested grid over China (see Methods – GEOS-Chem modelling), show that the low NO levels cannot be explained solely through suppression by ozone using current understanding of atmospheric chemistry (Supplementary Information). The major driver of the very low afternoon NO mixing ratios is the high levels of ozone.

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