

Interactive comment on “Rainforest-like Atmospheric Chemistry in a Polluted Megacity” by Mike J. Newland et al.

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

C1

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

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. The results section should reference the methods section as needed. 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.

Additionally, references to the supplement just state “see Supplementary Information”. For information that remains in the supplement after addressing the comment above,

C2

please provide more detail either by adding section numbers in the supplement or referring to specific supplementary figures.

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.

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?

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 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

C3

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.

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.

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.

Figure 3.

It would be beneficial to the reader to add the year for all the campaigns (not just for

C4

NYC) as the fno will greatly depend on when the measurements were taken and how much NO_x was present.

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.

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.

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

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?

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?

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.

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.

Page 9 line 274.

What was the relative humidity used in the box-model?

C5

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C6