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

Anonymous Referee #1

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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"

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Discussion paper

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.

While I find the study interesting it does not offer a clear explanation how high afternoon O3 at rather low NO occur. The title is misleading and has to be changed. 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

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.

-Observed low NO values cannot be explained solely by the increased O3 in the afternoon according to GEOS-Chem. -One explanation would need additional NO sinks that recycle OH without producing O3. -Another speculation would need the presence of halogen oxides.

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

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 NOx. Atmos. Chem. Phys. 2015, 15, 11257–11272.

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 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 ISOPOOH and IEPOX in your special inlet design.

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