Variations of ground-level O3 and its precursors in Beijing in summertime between 2005 and 2011 (No. acp-2013-977)

Response to Dr. D. Parrish

Zhang et al.

This paper presents a comprehensive overview of measurements related to photochemical ozone production in the Beijing urban area in a clear and concise manner. Beijing is mega-city that currently suffers from some of the world's most severe air quality problems. The combination of the urban emissions plus the transport of regional pollution into the city likely presents new challenges to our understanding of degraded air quality, and hence to our ability to effectively identify the most efficient control efforts. This paper provides a much-needed synthesis of important research that has been conducted into these issues including a review of that discussed in previous papers plus much that is new here. As such, I expect this paper to serve as an important reference, and as a very useful guide for future field measurements and analyses. This comment presents some suggestions intended to increase the clarity of the analysis and further increase the value of the paper.

Response: Thank you for your commendation.

The detailed information regarding Beijing ozone concentrations is particularly important; I suggest an expanded discussion. Particular suggestions include:

Response: We expanded discussion in revised version following your advice.

- Combine Figure 1 and 2 into a two-panel figure spanning a common time period: 2005-2011.

Response: Accepted and modified.

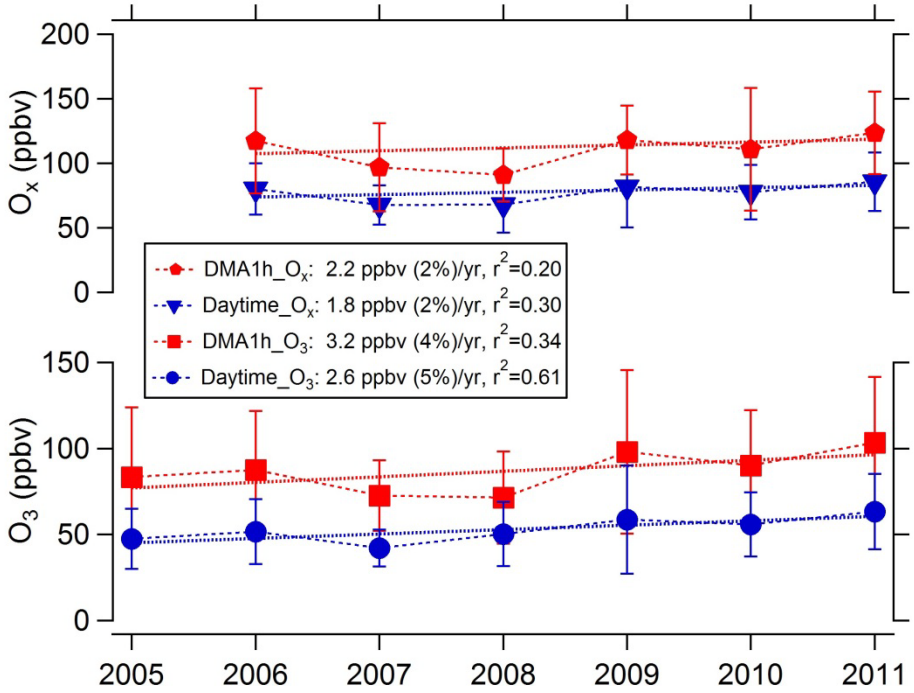

Figure S1 (Upper) Variations in daytime averages (blue triangles) and daily maximum averages (red pentagons) of total oxidants (O_x); (Lower) Variations in daytime averages (blue dots) and daily maximum averages (red squares) of ozone (O_3) in Beijing, August between 2005 and 2011

- Include a second panel in Figure 3 that shows the diurnal cycle of Ox in the same manner as ozone in the current figure. This will more clearly illustrate the photochemical formation of total oxidant, and minimize the influence that ozone titration by fresh NO emissions has on the diurnal cycle.

Response: Accepted and modified.

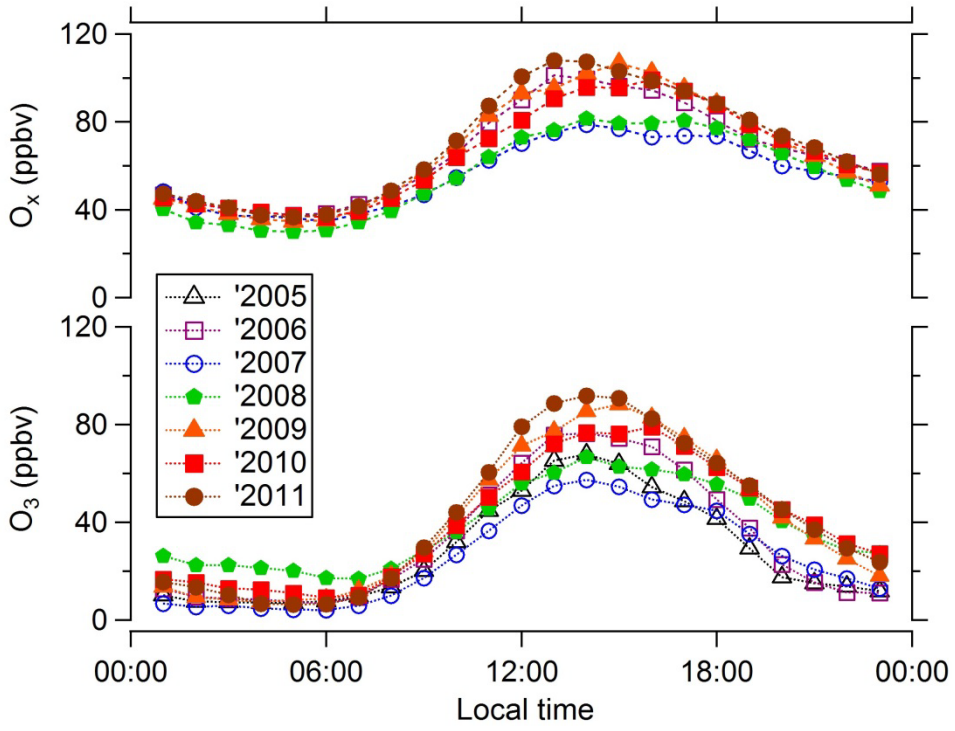

Figure S2 Diurnal variations of O_x (upper) and O_3 (lower) in Beijing, August between 2005 and 2011

- Include a figure that shows the cumulative distribution functions for ozone and for Ox (e.g., see Fig. 2.1 of Dentener et al., 2011). This would preferably be done for the daily maximum 1-hr ozone averages, since that is evidently the basis for the air quality standard in Beijing. Future studies could compare with this figure to gauge progress in improving Beijing's air quality.

Response: Accepted and added. Ambient abundance of ozone and its precursors is subject to log-normal distribution (Dentener et al., 2011). We plotted expected cumulative probability from log-normal distribution at y axis with logarithmic measured ozone and O_x at x axis in Fig. S3. If ozone and O_x mixing ratios in our measurements also obey distribution of log-normal distribution, the plotted curve in Fig. S3 should be closed to a straight line similar to the principle of P-P plot, which is just shown in Fig. S3.

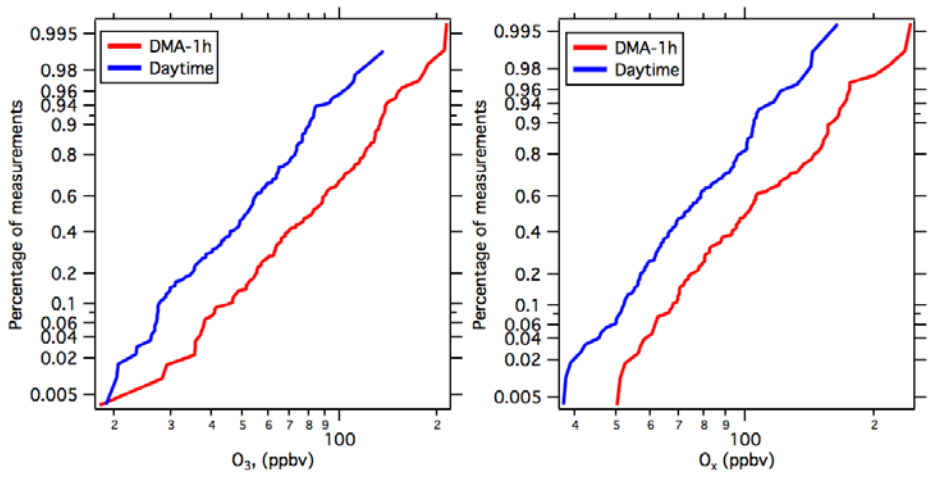

Figure S3 Logarithmic plots of probability vs. measurement values in terms of ambient O_3 (left) and O_x (right) in 1-h daily maximum averages (red) and 12-h daytime averages (blue), respectively, in Beijing, August between 2005 and 2011

This paper discusses measurement intercomparisons, which are important, particularly when measurements are made with instruments designed for environments that may be different from the Beijing region. The comparison of in situ measurements of NO2 with satellite column measurements is particularly welcome, since satellites indicate continuing increases of NO2 over the North China Plain, while ambient NO2 concentrations in Beijing itself are decreasing. Explicitly showing and discussing this apparent inconsistency is important. Figure 6 could perhaps be improved by expanding the scale for the NO2 VCD, (and VCD should be defined). Additionally, the NMHC measurements were made by a variety of instruments and different groups over the years. Including more details of the intercomparisons of these measurements, perhaps in the Supplementary Material, would be useful.

Response: Thank you for your comments. As the basis of data availability, we did make and discuss intercomparison between measurements during these years (Liu et al., 2008;Shao et al., 2009) and we expanded this part in revision especially about NMHC measurements according to the referee's comments. VCD of NO_2 within Beijing from

satellite results by our estimation showed U-shape variations between 2005 and 2010 which is consist with results from ground-level monitoring (though they didn't change in the same percentage). The variations of NO_2 VCD in Beijing disagreed with trends of NO_2 VCD in the NCP. That is the point in Fig. 6. We also found some evidence of emission inventory variations to support that (Wang et al., 2012). Ozone production in vicinity of Beijing is sensitive to VOC whereas large areas in the NCP are sensitive to NO_x (Zhao et al., 2009). In such case, decease of NO_x within Beijing accompanying increase of NO_x in regional area will promote ozone photochemistry in the same direction so as to aggravate ozone pollution in Beijing. We explained meaning of VCD of NO_2 and expanded the scale of Fig. 6 in the revised manuscript.

Our VOC data were done by three laboratories: Peking University (PKU), NOAA Aeronomy lab, and Research Center for Environmental Changes, Academia Sinica of Taiwan (RCEC). During each campaign we conducted calibration of instrument and inter-comparisons when two labs involved. Two ways of inter-comparisons were preformed: first is check of VOC standards used by different labs, second is the measurements of the same blind samples by different labs. The standard deviations for VOC standard check were less than 10% for all species except for isoprene (which was around 15%), ratios of PKU results and RCEC results varied between 0.87 and 1.11 for all measured species, the inter-comparison between PKU lab and NOAA lab agreed between 0.85-1 (Liu et al., 2008;Shao et al., 2009). Fig. S1 and S2 illustrate inter-comparison of measurement results by GC-FID/PID and GC-FID/MSD both in PKU lab in 2010. Different measurements show good consistency in time-series data, regression and bias analysis also demonstrate acceptable ratios between them. We were confidant that the VOC data in this work were obtained under reliable QA/QC procedures.

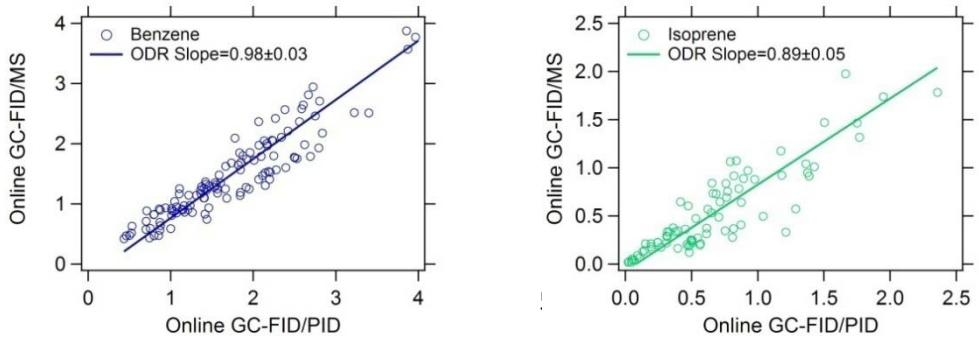

Figure S4 Inter-comparison among GC-FID/PID (GC955 811 or 611 series), GC-MS/FID at PKU site in 2010. Isoprene (right) represents C3-C6 species detected by GC955-811 VOC analyzer and benzene (left) represents C6-C9 species detected by GC955-611 VOC analyzer. Green and blue lines represent orthogonal distance regression (ODR) between two instruments.

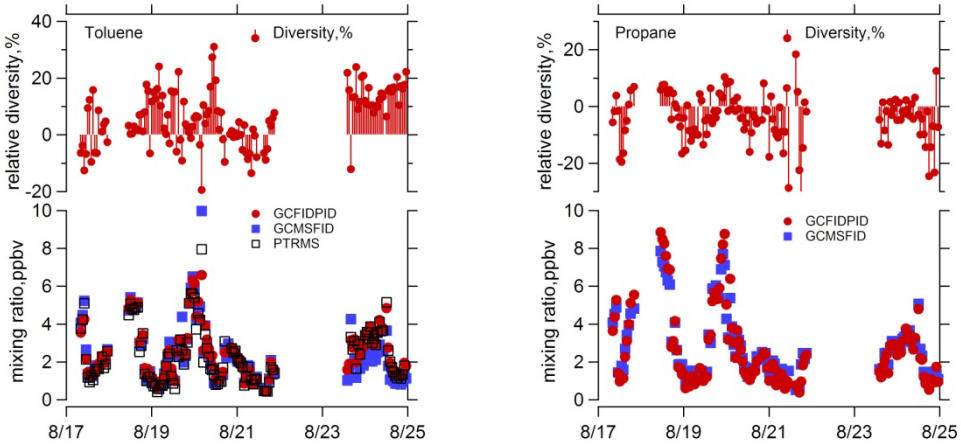

Figure S5 Time-series comparison among GC-FID/PID, GC-MS/FID and PTR-MS (if available) at PKU site in 2010. Toluene (left) and propane (right) are two of most abundant and typical VOC species as examples and red dot and sticks represent relative differences between GC-FID/PID and GC- MS/FID, which appears less than 20% in general.

The discussion at the beginning of Section 2.4 seems to imply that ozone air quality in Beijing can be considered only from a local perspective. While the investigation of the local photochemistry is very important, it should be more clearly emphasized that transport of regional pollution into Beijing is also important. The regional modeling of Zhao et al. [2009] and Nawahda et al. [2013] deserves more emphasis in the discussion of ground-level ozone in Beijing, although the measurements discussed in this paper cannot directly address the impact of regional transport.

Response: Fully agree. We have never intended to draw any judgment like that only local pollutants and relevant photochemistry leads to severe ozone pollution in Beijing. We do think both global and regional background variations are constructive when analyzing ground-level ozone trends. Long-term measurement evidences of elevated ozone background in the Eastern and Southern China were reported by (Xu et al., 2008) and (Wang et al., 2009). Moreover, ozone pollution is typically a piece of regional environmental issue. Modelling of (Zhao et al., 2009) demonstrated high ozone pollution suffered in a large scale in the NCP under adverse meteorological condition. Results from (Nawahda et al., 2012) revealed ozone pollution deteriorated from 2000 to 2005 in the NCP area including the Beijing city. We added some discussion to emphasize this point. We admit that it is hard to separate explicitly results of photochemistry within Beijing and from regional transport via measurements at a single site, but we did a simplified estimation to weight contribution from variations of photochemistry and regional background.

The multi-year perspective that the authors take in this paper is very enlightening. Presenting the results of the special controls instituted in Beijing for the 2008 Olympic Games in the context of the long-term trends is particularly welcome. I suggest that the

trends of ozone precursors and other primary pollutants in Figures 4, 5 and 7-9 be presented in a somewhat different manner. Ambient concentrations of these species tend to decrease exponentially in response to control efforts [see e.g., Pollack et al.,2013], so that if trends are plotted on semi-log scales, approximate straight lines are defined, and the slope of this line is directly related to the rate of decrease in percent per year.

Response: Accepted and modified these figures on semi-log scales in the revised manuscript.

Finally, I suggest that the authors take the opportunity this paper provides to briefly discuss their perspective of future research that is required to arrive at a fuller understanding of Beijing's air quality issues.

Response: Thank you for your valuable comments. Based on the insight from this work, we will persist in working on following aspects to deepen our knowledge on these issues We are continuing the measurement at PKU site to maintain and lengthen this hard-won dataset. We are finding more reliable modelling to test more effective emission control measures and working on more detailed analysis of VOC and OVOC variations in Beijing during the past decade. Our new settled measurement of OH reactivity tends to reveal direct evidence on variations of atmospheric oxidation capacity in Beijing. We also plan to conduct new series of field campaign in the North China Plain to investigate both local and regional contribution to Beijing's air quality. Other important things that can not be addressed by this study include: (1) explicitly determination of regional ozone transportation and local chemistry to Beijing ozone trend; (2) The trend of other secondary products, e.g. PAN, HNO3 and OVOCs; (3) Key parameter measurements including HO_x, OH reactivity. We added a paragraph in the Conclusion Section to discuss the perspective of future research for the air quality of Beijing, especially for atmospheric photochemistry in Beijing and its surrounding areas.

References not included in Discussion Paper

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Zhao, C., Y. Wang, and T. Zeng (2009), East China Plains: A "basin" of ozone pollution, Environ. Sci. Technol, 43, 1911–1915.

Response: Thanks for the suggestion. All of these literatures are included in the revised manuscript.

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Zhao, C., Wang, Y., and Zeng, T.: East China plains: A “basin” of ozone pollution, Environ. Sci. Technol., 43, 1911-1915, 2009.