

Responses to referee #1:

This paper reports summertime measurements of ozone and its precursors at a central urban site and a less-central site in two different megacities in China. A box model is used to explore the mechanisms responsible for ozone production in the two megacities, which are shown to have different limitations on ozone production. The reasons for this are briefly discussed in terms of precursor emissions, and implications for effective control strategies in each megacity are discussed. This is an interesting study, especially since there have so far been comparatively few studies of air quality in this region published in the international literature, and because of the large population affected. I recommend that the publication after some revisions have been made. The measurement methods are clearly stated. The Figures and Tables are generally clear. Figures 2 and 3 should be combined into one 4-panel figure. The standard of English is fair, and would benefit from careful and extensive editing by a native English speaker, if possible. The text is too long and should be condensed by about a quarter.

We highly appreciate the referee's instructive suggestions. We have combined figures 2 and 3 into one 4-panel figure. We have worked hard on improving the interpretations by carefully reading the manuscript through for several times and corrections have accordingly been made. We have shortened the manuscript where it is necessary and appropriate to do so. In addition, we have addressed each concern as below and corresponding revisions have been made in the manuscript.

Specific comments follow:

1. All measurements were taken during the summer. The word 'summer' should be added to the title of the paper, and this seasonal limitation should be acknowledged in the Abstract.

Thank you. The title of this paper has been revised as "Ozone Production in summer in the Megacities of Tianjin and Shanghai, China: A Comparative Study". We have also pointed out that data used for this comparative study were all acquired from in-situ measurements during summer.

2. The conclusion that ozone pollution in Tianjin is a regional problem is rather strong, given the reliance on only one measurement site outside the urban core. This conclusion should be more strongly substantiated with supporting meteorological data, or it should be re-phrased to acknowledge the limitations of the data.

We thank the referee for the helpful comment and suggestion. We agree with the referee that the conclusion is somewhat strong, if just drawn from the probability distributions on basis of in-situ measurements at five sites over NCP and two sites in the Shanghai region. We have added more discussions involving OMI NO₂ satellite data displayed in figure 1 to help reinforce the conclusion: "Generally, NO₂ (NO_x) pollution is more severe in the NCP region than in the YRD as illustrated by OMI NO₂ tropospheric column amounts in Fig. 1. Besides, average distributions of OMI NO₂ exhibit clear differences in

NO₂ concentrations within the Shanghai region, in contrast to the high-NO₂ belt over the entire Tianjin-Beijing region. This might also imply that ozone issues in Tianjin are probably on a regional scale, while on an urban scale in Shanghai.” We have revised the last paragraph in Section 4 as “Finally, it is found that ozone problem extends over a larger area in the Tianjin region than in the Shanghai region based on both in-situ ozone measurements and OMI NO₂ observations. We thus conclude ... By contrast, ozone pollution in Tianjin is probably a regional problem ...”

3. Since the direction of the prevailing wind is so important for the type of sources influencing each site, it would be helpful to add a figure showing wind roses or sampling sectors for each sampling site/period. This would also be a good place to include captions with the sampling dates for each site.

We thank the referee for this comment. We agree with the referee that wind condition during the sampling period could influence NMHC characteristics and restrict their representativeness, especially in our case (short sampling period, not simultaneously sampled). Thus, we have discussed the variability of NMHC and winds in the third paragraph in Section 3.2, Analysis revealed local emissions dominated in the two urban centers during the sampling period, with negligible meteorological influences on NMHC characteristics. Easterly/Southeasterly winds often prevailed in Jinshan in summer, also the case for the sampling period. Therefore, we reckon a good representativeness of NMHC samples at these three sites. The exception is site Wuqing, where a change in synoptic system was observed during the sampling period (Wind speed and direction shown in figure 4 in Ran et al., 2011). Accordingly, distinct compositional variations of NMHCs were observed and analyzed therein.

4. The term ‘suburban’ suggests a mainly residential landuse. This term is inappropriate for Jinshan, which is described as a well-vegetated and sparsely-populated industrial area. Another term should be used. (industrial/vegetated? extra-urban?)

We thank the referee for pointing this out. We realize that the term we used to describe Jinshan is not precise. As a matter of fact, Jinshan is that kind of suburbs commonly found in China, less populated than the urban area (also fewer automobiles) yet not so less as to be described as sparsely-populated. We have revised the description of Jinshan as “The residential population there is much less than in the urban center and the land cover is generally well vegetated.”

5. This reviewer found it a little confusing that two different names are used for each of the 4 main measurement sites, e.g. ‘urban Tianjin’ is used interchangeably with Tieta. It is very helpful that both names are used side-by-side (i.e. “Tieta, urban Tianjin”) in the legends for Figs 2 and 3, and in the header of Table 2. I suggest that the headers of Tables 1 and 3 be changed to follow this convention.

According to the referee’s suggestion, we have revised the manuscript and used two

names side by side in Tables 1 and 3.

6. In the text, it would be helpful to use the same type of name when several sites are being compared (e.g., “110 ppbv is found in Wuqing, followed by about 95 ppbv in both Xujiahui and Jinshan”). It is not appropriate in the Discussion to refer to the Wuqing / Jinshan sites only in terms of “suburban Tianjin / Shanghai” because the regions surrounding the urban core of each megacity are large and probably not homogeneous in terms of influences on air quality. The measurements at the two sites, while interesting, should not be implied as representing the entire region.

We thank the referee for this helpful comment. We have revised the manuscript accordingly.

7. Pg 9163, line 26: Please add more recent references?

Thank you. We have added two references here:

- 1. Van der A, R. J. et al., Detection of the trend and seasonal variation in tropospheric NO₂ over China, J. Geophys Res., 111, D12317, doi:10.1029/2005JD006594, 2006.**
- 2. Van der A, R. J. et al., Trends, seasonal variability and dominant NO_x source derived from a ten year record of NO₂ measured from space, J. Geophys Res., 113, D04302, doi:10.1029/2007JD009021, 2008.**

8. Pg 9164 line 8: typo: it's Haagen-Smit (not Haggen-Smit)

Thank you. We have corrected the typo.

9. Pg 9167 line8-9: Do you mean: “Hourly averages were calculated for each hour with at least 75% valid data.”?

Yes, thank you. We have revised it accordingly.

10.Pg 9167 line 15-16: Please explain more clearly about your sampling duration, your sampling interval, and how each of these relates to the 2-hour sampling period.

We have rephrased the description of ambient air sampling at Wuqing site as “An 8L Teflon bag was used to collect instant air samples at a 30-minute interval. Each 8L air sample thus represents the average condition for the 2-hour sampling period.”

11.Pg 9169 line 7: Please give the name of the model. (It sounds as though it's the NCAR Master Mechanism, yes?). Please state version number and / or date of download, as appropriate.

We thank the referee for pointing this out. We have supplemented corresponding information in Section 2.3 “A photochemical box model NCAR_MM (NCAR Master

Mechanism, Version 2.3) with a detailed description of ...”

12.Pg 9170 line 19: “...monitoring sites should be needed...” Perhaps you mean “should be used” or “would be needed”?

Thank you. We have revised it as “would be needed”.

13.Pg 9170 line 26: please insert a reference to the relevant Figure.

Thank you. We have revised it accordingly.

14.Pg 9171 lines 7-9: Isn't the ozone mixing ratio ALWAYS the result of a dynamic balance between production and destruction processes? What are you trying to say about this specific situation?

We appreciate the referee's comment on this unspecified and confusing statement. We have removed this sentence.

15.Pg 9173: It would help the discussion if Fig 4 also showed the two different categories of Wuqing data (with error bars), as well as the average.

Thank you. In figure 4 (now figure 3), we have shown the standard deviations (displayed as error bars) of both Propy-Equiv concentrations and the ratios of Propy-Equiv concentration to carbon-atom based concentration at all four sites.

16.Pg 9174 & Table 2: For what time of day is the VOC (OH) reactivity assessed? If it's a daily average, can you add an 'average' column to Figure 7, and refer to that here?

Thank you. The assessment of VOC reactivity is based upon the daily averages. We have added an average column in figure 7 (now figure 6) and referred to that in this part of discussion.

17.Pg 9174 line 10: please add references.

Thank you. We have referred to:

Lu, S. H., Bai, Y. H., Zhang, G. S., and Ma, J.: Study on the characteristics of VOCs source profiles of vehicle exhaust and gasoline emission, Acta Sci. Natur. Uni. Pek., 39, 507-511, 2003.

Song, Y., Shao, M., Liu, Y., Lu, S. H., Kuster, W., Goldan P., and Xie, S. D.: Source apportionment of ambient volatile organic compounds in Beijing, Environ. Sci. Technol., 41, 4348-4353, 2007.

Cai, C. J., Geng, F. H., Tie, X. X., Yu, Q., and An, J. L.: Characteristics and source apportionment of VOCs measured in Shanghai, China, Atmos. Environ., 44, 5005-5014, 2010.

18.Pg 9174 lines 18 & 20: “could be” is ambiguous. Do you mean “might be” (tentative association) or “were able to be” (stronger association)?

Thank you. We have revised it as “This was ascribed to strong isoprene emission in the well vegetated suburb and a much higher OH reactivity of isoprene compared to most anthropogenic species. Trans-2-butene and cis-2-butene might be associated with production of petroleum and manufacture of synthetic rubber.”

19.Pg 9175 lines 10 & 11: “except for VOC data that would be insufficient for analysis if only selected ones were considered.” It is not clear what you mean. Please be more precise.

Thank you. We have rephrased this as “As mentioned in Section 2.2, selected ozone and NO_x data are used to discuss their average diurnal variations under photochemistry-dominant conditions. Average diurnal cycle of NMHCs during the sampling period is also examined for each site.”

20.Pg 9175 lines 17-18: “enough depletion of ozone”. Enough for what?

Thank you. We have rephrased it as “efficient depletion of ozone”.

21.Pg 9175 line 21: Instead of “inconsiderable”, try “low” or “negligible” (as appropriate).

Thank you. We have changed “inconsiderable” to “low”.

22.Pg 9175 line 24: “that brings in above ozone-rich air in the residual layer”. Perhaps you mean “that brings in ozone-rich air from above the residual layer”.

Yes, thank you. We revised it accordingly.

23.Pg 9176 line 1: Instead of “speed fueling” try “initiate”, “accelerate” (as appropriate)

Thank you. We have changed it to “accelerate”.

24.Pg 9176 line 8: In figure 5, ozone is >80 ppbv in Tianjin for 5 hours, not 6.

Averagely, ozone concentrations above 80 ppbv last for more than 6 hours at Wuqing and slightly less than 6 hours at Tieta (Fig. 5(a), now Fig. 4(a)). Here we generally indicated that the duration of hourly ozone concentrations >80 ppbv is averagely around 6 hours in the Tianjin region.

25.Pg 9176 lines 9-12: Please reconcile the statements that Shanghai has no daytime ozone exceedances, but it does have some that last for 4 hours.

We mean to indicate that the occurrence of ozone exceedances lasting for more than 6

hours did not exist during the observational periods. To be more clear, we have rephrased this sentence as **“On about 25% of the observational days, the occurrence of daytime ozone exceedances (>80 ppbv) lasting for more than 6 hours was observed in Tianjin region, while none was encountered in Shanghai.”**

26.Pg 9176 line 17: instead of “elevates”, try “increases”

Thank you. We have corrected it accordingly.

27.Pg 9177 line 12: instead of “apparently”, try “clearly”, or omit.

Thank you. We have omitted this word.

28.Pg 9178 lines 17-20. This sentence is not clear. Please re-phrase.

Thank you. We have rephrased it as “Since ozone production rates depend on NO_x and VOCs, which are both largely from automobile emissions in cities, a second thought should be given before implementing control strategies on automobile emissions that may lead to the migration of chemical regime.

29.Pg 9179 line 9: use “attributable” instead of “attributed”

Thank you. We have corrected it accordingly.

30.Pg 9179 line 26: do you mean daytime NO_x concentrations are often below 25 ppbv?

Here we mean all NO_x concentrations, not specifically limited to data during the daytime.

31.References: please add DOIs to all references.

Thank you. We have added available DOIs to corresponding references.

32.Figure 5: Please state in the caption which days were selected, or what criteria were used for the selection. Please show the standard deviations about the means. (This might require adding more panels to the Figure).

We have pointed out the selection criteria used in section 2.2 in the caption of figure 5 (now figure 4). We provide 3 figures below to show the standard deviations of each item. Seeing that the results and related discussions will not be affected when the standard deviations taken account in and to avoid redundancy, the standard deviations about the means are not shown in figure 5 (now figure 4).

