Response to Review of "Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes" by L. K. Xue et al for Atmospheric Chemistry and Physics

The four cities mentioned in the title are, from an atmospheric point of view, quite interesting. With one possible exception they fall into the megacity category. A master mechanism box model constrained with observations of CO, NO, O_3, and VOCs is used to determine O_3 production rates and the sensitivity of O_3 to NO_x and VOCs. Scenarios are considered that include poorly understood heterogeneous processes, namely loss of N_2O_5 and peroxy radicals and production of HONO. Although I can't point to ground breaking findings, it is an interesting and nicely crafted study.

One concern is that the data used for the current study is from field campaigns conducted in 2004 to 2006. I know in general terms that there has been increased industrialization in China. Quite likely NO_x and VOC emissions have increased. I would expect that ozone sensitivities have changed since anything resembling a proportional increase in NO_x and VOCs will make O_3 more VOC limited. Another concern is that there have been many publications using these data sets. I see some (inevitable) similarities between this and previous publications but no obvious duplication.

I recommend publication after minor revisions addressing points below.

Response: we thank the reviewer for the helpful and positive comments. We first address the two major concerns below and then make itemized responses to the specific comments.

The concern of the previous nature of measurement data is relevant. Indeed, China's industrialization process has been ongoing, which would have resulted in an increase of NO_x and VOCs emissions from the measurement period (2004-2006) to now. But in China the observational data is still lacking (although many efforts have been made recently in Beijing and Pearl River Delta), especially the data collected from several places using the same set of measurement techniques and QA/QC procedures. Such data should be valuable for making such a comparison study. Furthermore, from our own estimate, the ozone formation regimes estimated from the present study (e.g., VOC-control in Shanghai and Guangzhou) should not be changed qualitatively, in view of (1) the almost proportional increase of VOCs and NO_x in China according to the emission inventory data and (2) current state of air pollution control in China (i.e., little VOC control). But anyway, this need be carefully examined by conducting more such observational studies. We will add some sentences to state this limitation of our study and call for future efforts.

Indeed, some of our measurement data have been published previously from different perspectives (we have cited these previous works when describing the field studies). But actually there is only one addressing ozone and directly related with the present study (the

others mostly focused on aerosol with one addressing PAN in Lanzhou). This paper (*Wang et al., GRL.*, 2006) used the Beijing data, and was a quick report of the highest O_3 values ever-recorded in China (286 ppbv). As stated by the reviewer, the present paper is totally different from the previous ones but with inevitable little overlap, i.e., we re-mentioned the extremely high O_3 values in Beijing in this manuscript.

1. *p 27246, line 2 "A typical and intractable issue is photochemical smog …" Intractable may be the wrong word. Can the problem not be understood? Is there nothing that can be done about it?*

Response: we will change "intractable" to "difficult".

2. *p 27246, line 24 "ozone levels show an increasing trend over the last decade" Please provide an explicit time frame. The papers cited are dated 2006 to 2008. Xu et al (2008) refers to studies done up to 2006. From this I would infer that the last decade is 1996 to 2006. Are there other studies that describe ozone trends in a period ending closer to the present.*

Response: we will add the explicit periods of the O_3 trend studies we cited, namely, 1995-2005 in Beijing (*Ding et al.*, 2008), 1991-2006 at Lin'an (*Xu et al.*, 2008), and 1994-2007 in Hong Kong (*Wang et al.*, 2009).

Recently we analyzed the data collected in Hong Kong in southern China from 2002-2012, and confirmed the increasing trends of ozone (the manuscript is now under review). Another recent study also indicated the sharp increase of O_3 in Beijing from 2005 to 2011 (*Zhang et al.*, 2014). We will include this recent work in the revised manuscript.

Zhang Q., Yuan B., Shao M. et al.: Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011, Atmos. Chem. Phys. Discuss., 14, 1019-1050, 2014

3. *p27249, line 3 free from uncertainties due to differences in methodology. This thought is said better later on. Uncertainties are minimized. Two identical instruments are not necessarily going to give identical results.*

Response: Yes, the latter statement ("uncertainties are minimized") is more correct. We will revise the phrases as suggested.

4. *p 27253, line 8 – 16. nine day pre-run used to generate concentrations of unmeasured species. Are there any comparisons that can be made for some intermediate lifetime species such as NO_2, HCHO, and H_2O_2?*

Response: we didn't measure these species during our field studies, so that we don't have the data for direct comparison. We have set up the model to output the concentrations of NO_2 and

HCHO. The model-simulated daytime-average (08:00-18:00) concentrations were ~3.1 ppbv, ~27 ppbv, ~26 ppbv and ~5.2 ppbv for NO_2, and ~7 ppbv, ~15 ppbv, ~8 ppbv and ~18 ppbv for HCHO at the Beijing, Shanghai, Guangzhou and Lanzhou sites, respectively. These levels should be within the reasonable ranges considering the different distributions of NO_y and VOCs (e.g., high NO_y levels at Shanghai and Guangzhou and high VOC reactivity at Lanzhou and Shanghai; see *Figures 2-3* in the manuscript).

An indirect comparison can be made for Beijing. In summer 2008, we measured NO_2 at the same site (Changping) to the 2005 study. The average daytime NO_2 concentration was 2.2 (± 1.7) ppbv, which was comparable in magnitude to the modeled level in 2005 (~3.1 ppbv). In summer 2008, we also measured HCHO at another suburban site in Beijing, but more close to the urban center (see *Wang et al.* 2010 for the description of study sites in the 2008 study). The measured average HCHO concentration was 11.0 (± 3.3) ppbv (unpublished data), compared to the modeled levels (~7 ppbv) at a further downwind rural site.

T. Wang, et al.: Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, Atmos. Chem. Phys. 10, 7603-7615, 2010.

5. *p27253 line 6. photolysis frequencies were further scaled with measured solar radiation. How was this done? Were there clear sky days that you could use to normalize an actinic flux on a day that was not clear? A straight ratio would still not capture the different contributions of direct and diffuse radiation to photolysis.*

Response: we did this as follows. We have measured the J_{NO2} by a filter radiometer (*Metcon Corp.*) at several sites in Hong Kong, along with the measurements of solar radiation. The filter radiometer consists of two actinometers in parallel but facing opposite directions, allowing the determination of upward and downward J_{NO2} values. We combined these data and got a very good correlation (r^2 =0.9) between J_{NO2} and solar radiation. We then applied this equation to the solar radiation measurements at the four cities in the present study to calculate the J_{NO2} values. Such derived J_{NO2} values were further used to constrain the model and adjust the model-calculated J values. We will add a description of this method in the supplementary information.

6. *p27253, Eq. 2 There are arguments that can be made for and against including loss of NO_2 in Eq. 2. An alternate view is that O_3 is lost when emitted NO is converted to NO_2.*

Response: we have modified the model-calculation of O_3 production and destruction rates after considering the review comments. Actually the currently calculated rates are the production/destruction rates of O_x instead of O_3. In the revised manuscript, we will directly calculate the O_3 production rate from the reaction of $O + O_2 + M = O_3 + M$, and the O_3 destruction rate without the loss terms of NO_2. We have completed the model re-calculations and the main conclusions remain with the newly-estimated O_3 production rates.

7. *p27255 line 5-9. discussion of traffic and industrial contributions to diurnal pattern. The CO and NO_y traces from TMS and especially CP do not look like local traffic, which is characterized by a morning peak with the highest concentrations of the day, caused by a shallow boundary layer.*

Response: Yes, here the shallow boundary layer should be a key factor contributing to the morning peaks of CO and NO_y. We will add a discussion on this in the revised manuscript.

8. *p27257 line 4. 286 ppb ozone Please clarify that this is not in Fig. 5a. Was the observation of 286 ppb O_3 during the campaign that is analyzed here? I recall reading about it several years ago.*

Response: it is a pity that the episode with 286 ppbv of O_3 was not analyzed here because multiple VOC samples were not taken during that episode. The episode in Fig. 5a is another severe pollution event with the peak O_3 level exceeding 200 ppbv.

9. *p 27261 Eq 3. k10 includes a term for interfacial mass transfer but not a diffusion term such as in Eq 4. Was the mass transfer term regarded as rate limiting in all circumstances?*

Response: yes. The real heterogeneous processes are very complex, and here we only adopted a widely-used simple representation of this process in our model.

10. *p27261 line 20-25. important heterogeneous loss pathway at night Pathway is a large fraction of total loss of O_3 at night. However absolute amount of O_3 lost at night is small.*

Response: we agree with this comment and will remove the discussion of the nighttime O_x loss through N_2O_5 hydrolysis. We will focus on its impact on the daytime O_3 formation.

11. *Section 3.4 Heterogeneous chemistry. The reader must be given some sense of aerosol concentrations in order to put results in perspective. Loss rates depend on surface area, which must be in model. It would be a service to the reader if you can convert to the more familiar units of volume and size (assuming a single size would be OK).*

Response: in the present study, we measured in real-time the particle number and size distributions in Beijing, Shanghai and Lanzhou, which were used to calculate the aerosol surface area concentrations. The aerosol surface used in Guangzhou was inferred from the measurements taken at a nearby station in Hong Kong. These data were read in the model to calculate the heterogeneous reaction rates.

The average daytime (08:00-18:00 LT) aerosol surface concentrations during the episodes were 1633 (±469), 642 (±232), 249 and 268 (±57) $\mu m^2/cm^3$ in Beijing, Shanghai, Guangzhou and Lanzhou, respectively. We will add a discussion on the distributions of aerosol surface at four sites when interpreting the heterogeneous processes.

12. *p27265 line 7 13% enhancement in O_3 production. I can't tell from figure where there is a 13% enhancement. Integrated over a day the enhancement appears to be very small.*

Response: the daytime-average net O_3 production rate with and without heterogeneous HONO formation were 56 ppb/h and 49.2 ppb/h respectively (note that we have revised the calculation method as stated in the Response to Comment 6). So the increase by including the heterogeneous sources was 6.8 ppb/h, which is 13.8% in percentage. It may be the display problem of such type of figures. We will modify the figure in the revised manuscript.

13. *p27265 line 11. observed daytime HONO concentration up to the ppb level. The figure shows calculated HONO at ppb level until 09:00, so it is not that different during the time of day when HONO is thought to be an important radical source.*

Response: here the more correct statement should be "elevated HONO of up to ppb level until **noontime**". Recent studies have found surprisingly high HONO throughout the daytime in the PRD region, and we also observed HONO of ppb level around noontime in Hong Kong. In comparison, the modeled HONO was at ppb level only in the early morning (*i.e.*, until 09:00) and then would sharply decrease due to the fast photolysis. We will elaborate this in the revised manuscript.

14. *Fig. 5. The red bars sometimes hide the blue bars. This is not a problem except for a sliver of blue below zero in the panel a during the in-situ production time period. A note in the Fig 5 caption would be useful.*

Response: actually the blue bars are separately added to the red bars in the figure. We will add a note for clarity in the figure caption.

15. *The quantification of transported O_3 vs. in situ production was of particular interest. Section 3.3.3 ends with an appropriate disclaimer about the lack of universality of model predictions.*

Response: we do agree. Thanks.