Response to Anonymous Referee #1

General Comments:

This paper presents data on ozone, NO_x, VOCs and aerosol distributions from four cities in China that are subject to severe ozone pollution episodes. All data are from the mid 2000's, and thus likely representative of a point in time during the recent industrial and urban growth that has occurred in China.

After summarizing the characteristics of the sites and the data collected at each, the authors present two separate analyses, both based on an MCM box model. They first analyze chemical ozone production rates, the influence of transport, and the contribution of NO_x and speciated VOCs to local ozone production at each site. In a separate set of model runs, they examine the sensitivity of local ozone production to heterogeneous processes, including N_2O_5 uptake to produce $ClNO_2$, HO_2 uptake to aerosol, and conversion of NO_2 to HONO. They demonstrate that for reasonable values of heterogeneous reaction rates, these processes have a non-negligible influence on chemical ozone production rates.

The paper is well written and presents new results relevant to ozone in China and to heterogeneous process chemistry. I recommend publication following attention to the specific comments below.

Response: we thank the reviewer for the helpful comments and suggestions. We have revised the manuscript accordingly and address the specific comments below.

Specific comments and technical corrections:

1. *Abstract, line 10: "Rural site of Beijing" should be replaced by "Rural site downwind of Beijing"*

Response: changed.

2. *Abstract, lines 14-15: "VOC-limited" and "NO_x-Controlled" regimes. Do the authors mean the same thing by "limited" and "controlled" in this context? If so, recommend using a consistent terminology (either NO_x-limited and VOC-limited, or NO_x-controlled and VOC-controlled).*

Response: we will use "NO_x-limited" and "VOC-limited" in the revised manuscript.

3. *Page 20771, line 9: Recommend using the term "neglected" rather than "ignored" since the former does not imply any ill intent.*

Response: changed.

4. *Page 20773, line 16: "a mountainous region" rather than "mountains regions"*

Response: changed.

5. *Page 20774, line 3: What is the estimated efficiency of the NO_y converter? Was this optimized for NO_y, or run as an NO_2 instrument and then interpreted as NO_y? Similarly, the OBM would have required an input for NOx, not just NO. Was the NO_2 calculated from photolysis rates for this purpose? If so, the authors should specify.*

Response: the instrument was optimized to measure NO_y, with a MoO converter placed outside at the sampling inlet. The NO_y species were converted to NO at the surface of MoO at 350 ℃. During the measurements, the conversion efficiency was checked every 1-3 days by an n-propyl nitrate standard, which indicated near complete (~100%) conversion throughout the campaigns. In the revised manuscript, we have added a reference of *Xue et al.* (2011) that describes in detail the operation and quality assurance of our NO_y measurements.

We didn't measure NO_2 in these early studies, so that had to simulate NO_2 with inputs of NO, O_3 and photolysis rates, etc. The modeled daytime-average (08:00-18:00) NO_2 concentrations were ~3.1 ppbv, ~27 ppbv, ~26 ppbv and ~5.2 ppbv at the Beijing, Shanghai, Guangzhou and Lanzhou sites, respectively. These levels should be within reasonable ranges considering the measured NO_y levels (see *Figure 2* in the manuscript). An indirect comparison was made for Beijing. In summer 2008, we measured NO_2 at the same site 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). We have clarified in the revised manuscript that NO_2 was not measured but simulated by the OBM.

Xue, L. K., Wang, T., Zhang, J. M., Zhang, X. C., Deliger, Poon, C. N., Ding, A. J., Zhou, X. H., Wu, W. S., Tang, J., Zhang, Q. Z., and Wang, W. X.: Source of surface ozone and reactive nitrogen speciation at Mount Waliguan in western China: New insights from the 2006 summer study, *J. Geophys, Res.-Atmos.*, 116, 2011

6. *Page 20774, last line: Replace "besides" with "In addition"*

Response: changed.

7. *Page 20775, line 11-12: Here, and in the instrument section above. Were the aerosol size distributions measured under dry or ambient humidity conditions? Were the surface area calculations done for dry aerosol or corrected for relative humidity? Such a correction could substantially alter conclusions regarding rates of heterogeneous processes, and requires some further experimental details.*

Response: the aerosol size distributions were measured under ambient humidity conditions, hence should representative of the real atmospheric conditions. The surface area was calculated based on the measurement data without further correction for relative humidity. In the revised manuscript (instrument section), we have clarified that the aerosol size distributions were measured under ambient humidity conditions by the following statement.

"Aerosol number and size distribution (10 nm – 10 μm) were measured in real-time under ambient humidity conditions by a Wide-range Particle Spectrometer (*MSP, WPS model 1000XP*)…"

8. *Page 20776 and equations (1) and (2). The authors should state which terms in (E2) are dominant. Likely there are several that are relatively small compared to others.*

Response: the destruction of ozone was generally dominated by the reactions of O_3+NO_x as well as O_3 photolysis. Note that we determined directly the reaction rates of O_3 (other than for O_x), thus the reactions of O_3+NO_x were regarded as O_3 sinks here. Under some conditions (e.g., high VOCs and low NO_x), reactions of O_3 with HO_x and/or VOCs may also make considerable contributions to the

ozone destruction. We have added the following statement in the revised manuscript.

"In general, the O_3 destruction was dominated by reactions of R2-R4, while other reactions may also make considerable contributions at specific conditions (e.g., at high VOCs)."

9. *Figure 4. The calculation of the transport contribution is not straightforward from the figure itself. It would be helpful if the quantity R_{meas} were plotted on the figure as a line so that that subtraction to determine R_{trans} could be determined.*

Response: Figure 4 has been improved in the revised manuscript with "R_{meas}" being plotted as a line.

10. *Section 3.3.1: The section should perhaps be titled "$ClNO_2$ production" rather than "N_2O_5 hydrolysis", since the conclusions come from comparison of runs that both include N_2O_5 uptake, but differ in the amount of $ClNO_2$ produced.*

Response: the title of this section has been modified to "$ClNO_2$ production from N_2O_5 hydrolysis".

11. *The model approach should be clarified. The $ClNO_2$ is the integral of the locally produced $ClNO_2$ at each site, with no transport term, correct? Thus, the transport effects discussed in the preceding section need to be neglected?*

Response: yes, the model-simulated $ClNO_2$ is only the integral of the locally produced $ClNO_2$. We cannot take into account the transported $ClNO_2$ by our model. Indeed, transport such as intrusion of the air aloft in the early morning may have important contribution to the $ClNO_2$, given its relatively long lifetime during nighttime. Therefore, the model-simulated $ClNO_2$ and its impact on ozone production in the present study should be a lower limit. In the revised manuscript, we have clearly stated the limitation of our model in treating transport of $ClNO_2$, and that our estimation of the $ClNO_2$ impact may only present a lower limit.

12. *The conclusions are given in the relatively simple form of a percent increase in ozone production rates – these are presumably an average, and not uniform over the course of a day, since the $ClNO_2$ photolysis will occur mainly in the morning? Finally, the authors may wish to comment on the surface titration of nighttime ozone seen in Figure 4 and its influence on $ClNO_2$. Presumably there could be more $ClNO_2$ formed immediately above each of the measurement sites, where ozone does not fall to zero?*

Response: yes, the results are presented as daytime averages, and the impacts of $ClNO_2$ on ozone production are the most significant in the early morning and decrease with time. For the Shanghai case, for example, the increase in ozone production rates with vs. without $ClNO_2$ formation was as high as 20%~26% at 08:00–09:00 local time. Considering that the ozone production is the most intense at noon and in the afternoon, we chose to present the results as daytime averages. In the revised manuscript, we have indicated the largest impact of $ClNO_2$ photolysis on O_3 formation in the early morning period.

Indeed, there could be more $ClNO_2$ above the surface sites in the nocturnal boundary layer, due to less ozone titration. Vertical gradient of $ClNO_2/N_2O_5$ is now a hot topic in the nighttime chemistry

studies. As stated above, our box model cannot take into account the downward transport of the air aloft containing more $ClNO_2$, and hence our estimation of the impact of $ClNO_2$ should be only a lower limit. We have added the following discussion in the revised manuscript.

"It is noteworthy that the OBM cannot take into account the transport of $ClNO_2$ that has relatively long lifetime at night. $ClNO_2$ may present a positive altitude profile in the nocturnal boundary layer due to less O_3 titration above the ground. Intrusion of the air aloft in the early morning might contribute considerably to the $ClNO_2$ at surface sites. Therefore, our estimation of the impact of $ClNO_2$ in the present study should be a lower limit."

13. *Page 20783, equation (4): Why is diffusion limitation accounted for here, but not with respect to N_2O_5 uptake in equation (3)? If this is simply a consequence of the range of uptake coefficients involved (large for HO_2), this should be explicitly stated.*

Response: yes, the following statement has been added in the revised manuscript.

"The gas diffusion limitation is accounted for here given the potential larger uptake of HO_2 to aerosol"

14. *Page 20785, equations 4 and 5. Which term dominates? Ground or aerosol surface? If ground, would the influence on local ozone production depend on vertical gradients in HONO?*

Response: ground dominates in general, except for the Beijing case where aerosol surface density was very high (~1000 $\mu m^2/cm^3$) and thus the role of aerosol is comparable. Our OBM is one layer and hence cannot take into account the vertical gradient of HONO. Although the heterogeneous formation of HONO may mainly occur near the ground, the deposition of HONO also primarily takes place there. In our model set-up, the height of the box is assumed to increase from 300 m at dawn to 1500 m at noon and then decrease to 300 m till the evening. If we forced the height of the box to the lowest surface layer (e.g., dozens of meters), the HONO production rate from ground process and the loss rate via deposition would be enhanced simultaneously and almost comparable (both terms depend on the mixing layer height). So it is difficult to evaluate the influence of vertical gradient in HONO with our 0-D box model. Furthermore, the HONO vertical gradients are still now under active investigation, which is beyond the scope of the present study.

15. *Page 20786, line 7-8: Does the heterogeneous production of HONO consume NO_x? The photolysis should release NO, leading to no net effect on NO_x and thus no effect on ozone other than from the OH production.*

Response: yes, the reactions (i.e., with OH or photolysis) of HONO recycle the NO_x. The original statements have been revised as follows.

"The heterogeneous HONO formation may enhance O_3 production by releasing OH via HONO photolysis."

16. *Page 15, line 26: Justify choice of daytime NO_2 uptake coefficient to aerosol? Seems arbitrary relative to the choice made for ground uptake?*

Response: the uptake coefficient of NO_2 to aerosol is still of some uncertainty, and here we chose

the widely-adopted parameterization. We have revised the original statement as follows.

"As to γ_a, we used a value of $\gamma_a = 1\times10^{-6}$ at nighttime and increased it to 5×10^{-6} during the day, according to Li et al. (2010)."

Li, G., Lei, W., Zavala, M., Volkamer, R., Dusanter, S., Stevens, P., and Molina, L. T.: Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign, *Atmos. Chem. Phys.*, 10, 6551-6567, 2010.