

Dear Editor,

We have carefully considered and addressed all the comments of the reviewers, and revised our manuscript accordingly. The revised manuscript is attached at the end of this response, with the changes highlighted in red for your easy reference. Thank you for your efforts in processing our manuscript.

Best regards,

Tao Wang

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 N₂O₅ uptake to produce ClNO₂, HO₂ uptake to aerosol, and conversion of NO₂ 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 NO₂ instrument and then interpreted as NO_y? Similarly, the OBM would have required an input for NO_x, not just NO. Was the NO₂ 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 °C. 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 NO₂ in these early studies, so that had to simulate NO₂ with inputs of NO, O₃ and photolysis rates, etc. The modeled daytime-average (08:00-18:00) NO₂ 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 NO₂ at the same site to the 2005 study. The average daytime NO₂ 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 NO₂ 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 be 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 “ClNO₂ production” rather than “N₂O₅ hydrolysis”, since the conclusions come from comparison of runs that both include N₂O₅ uptake, but differ in the amount of ClNO₂ produced.*

Response: the title of this section has been modified to “ClNO₂ production from N₂O₅ hydrolysis”.

11. *The model approach should be clarified. The ClNO₂ is the integral of the locally produced ClNO₂ 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 ClNO₂ is only the integral of the locally produced ClNO₂. We cannot take into account the transported ClNO₂ by our model. Indeed, transport such as intrusion of the air aloft in the early morning may have important contribution to the ClNO₂, given its relatively long lifetime during nighttime. Therefore, the model-simulated ClNO₂ 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 ClNO₂, and that our estimation of the ClNO₂ 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 ClNO₂ 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 ClNO₂. Presumably there could be more ClNO₂ 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 ClNO₂ 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 ClNO₂ 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 ClNO₂ photolysis on O₃ formation in the early morning period.

Indeed, there could be more ClNO₂ above the surface sites in the nocturnal boundary layer, due to less ozone titration. Vertical gradient of ClNO₂/N₂O₅ 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 ClNO₂, and hence our estimation of the impact of ClNO₂ 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 ClNO₂ that has relatively long lifetime at night. ClNO₂ may present a positive altitude profile in the nocturnal boundary layer due to less O₃ titration above the ground. Intrusion of the air aloft in the early morning might contribute considerably to the ClNO₂ at surface sites. Therefore, our estimation of the impact of ClNO₂ 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 N₂O₅ uptake in equation (3)? If this is simply a consequence of the range of uptake coefficients involved (large for HO₂), 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 HO₂ 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 μm²/cm³) 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 O₃ production by releasing OH via HONO photolysis.”

16. Page 15, line 26: *Justify choice of daytime NO₂ uptake coefficient to aerosol? Seems arbitrary relative to the choice made for ground uptake?*

Response: the uptake coefficient of NO₂ 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 $\gamma_a = 1 \times 10^{-6}$ 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.

Response to Anonymous Referee #2

General comments:

This work focuses on the ozone pollution in four large cities of China. Observation based methods are used in the analyses to understand the impacts of photochemistry, regional transport and deposition. In addition, some heterogeneous processes are considered and preliminary results show that they might be important to local ozone levels and should be incorporated into photochemical mechanisms.

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:

1. *Site selection: The four sites are rural or suburban, not far from large cities (the biggest distance is about 50 km from the cities). However, the Beijing site is different in nature from other three sites, i.e. it's a pure rural mountain site and is the most distant from cities of the four sites. These features determine that the Beijing site is dominated by distant/regional transport, and the photochemical evolution processes (including the heterogeneous processes) might not be reflected by precursor concentrations observed. On the other hand, at this rural site the authors observed/recorded the highest ozone concentration (286 ppbv) in the area, which may not occur at a suburban site. It would be clearer if the authors explain the differences of the results between Beijing site and other three sites caused by the site locations.*

Response: yes, the difference in the type of station between Beijing site and the other three sites determines to a large extent the differences of the results. For clarity, the following statements have been added in the revised manuscript (Section 2.1).

“The rural nature of the site determines to a large extent the ‘unique’ results obtained in Beijing (i.e., highest O₃, lowest O₃ precursors, and dominant role of regional transport) compared to the other three cities (suburban sites), which should be kept in mind when comparing the results among the four sites.”

2. *Model validation: The observed based box model used to quantify the in-situ ozone production is built on the MCM v3.2 mechanism. However, no model validation results are provided in the manuscript.*

Response: the OBM is usually used to calculate the chemical reaction rates and simulate the highly reactive species, based on the known chemical kinetic data and high-quality measurements. The model has been successfully utilized for this purpose in many previous studies such as Xue et al. (2013), Xue et al. (2014a) and Xue et al. (2014b). The following statement has been added in the revised manuscript.

“The model has been successfully applied in the previous studies (Xue et al., 2013, 2014a and 2014b).”

Xue, L. K., Wang, T., Guo, H., Blake, D. R., Tang, J., Zhang, X. C., Saunders, S. M., and Wang, W. X.: Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory, *Atmos. Chem. Phys.*, 13, 8551-8567, 2013.

Xue, L. K., Wang, T., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., and Xu, Z.: Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities, *Environ. Sci. Tech.*, 48 (18), 10769-10775, 2014a.

Xue, L. K., Wang, T., Wang, X. F., Blake, D. R., Gao, J., Nie, W., Gao, R., Gao, X. M., Xu, Z., Ding, A. J., Huang, Y., Lee, S. C., Chen, Y. Z., Wang, S. L., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, *Environ. Pollution*, 195, 39-47, 2014b.

3. *The Guangzhou site: Some parameters were not observed at this site and took observations of same season at Tung Chung, Hong Kong. The authors did not mention which parameters were not measured at Guangzhou site. For some parameters, e.g. aerosol properties, there might be differences between Guangzhou and Hong Kong. It would be convincing if comparisons are provided when data sources are available (like PM_{2.5} measurements by the Hong Kong EPD and Guangzhou EPB) for the two sites or cities.*

Response: the aerosol surface area was not measured at the Guangzhou site (Wanqingsha), and we used the measurements collected at Tung Chung. To our knowledge, measurements of aerosol size distribution are still not available at the Wanqingsha site, while PM₁₀ mass concentrations have been routinely monitored since 2006 by the Pearl River Delta Air Quality Monitoring Network that includes both Wanqingsha and Tung Chung. According to the monitoring results, the PM₁₀ level at Wanqingsha was about 30% higher than that at Tung Chung (<http://www.gdep.gov.cn/hjjce/>). For example, the annual mean PM₁₀ concentration at Wanqingsha was 89 µg/m³ in 2006, compared to that of 61 µg/m³ at Tung Chung.

To evaluate the uncertainty of our base model results, we conducted a sensitivity study by magnifying the aerosol surface area by 50% (the adjusted levels are still much lower than those of Beijing and Shanghai, but comparable to those of Lanzhou). The results indicate that its impact on the modeling results is insignificant (i.e., ~1% in net O₃ production rates). The following statements have been added in the revised manuscript.

“The aerosol surface and radius were calculated from the aerosol number and size distribution measurements. For Guangzhou where such measurements were not available, we used the average diurnal data obtained from a similar suburban site in Hong Kong (Tung Chung, close to the WQS site; see Fig. S1) in the same season (May 2012). Sensitivity studies using 50% higher aerosol surface indicated little impact on the modeling results (i.e., ~1% in net O₃ production rate).”

Technical corrections: The writing of the manuscript is acceptable.

Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes

L. K. Xue^{1,2*}, T. Wang^{1,2,3*}, J. Gao³, A. J. Ding⁴, X. H. Zhou², D. R. Blake⁵, X. F. Wang², S. M. Saunders⁶, S. J. Fan⁷, H. C. Zuo⁸, Q. Z. Zhang², and W. X. Wang^{2,3}

5 ¹Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China

²Environment Research Institute, Shandong University, Ji'nan, Shandong, China

³Chinese Research Academy of Environmental Sciences, Beijing, China

⁴Institute for Climate and Global Change Research and School of Atmospheric Sciences, Nanjing
10 University, Nanjing, Jiangsu, China

⁵Department of Chemistry, University of California at Irvine, Irvine, CA, USA

⁶School of Chemistry and Biochemistry, University of Western Australia, WA, Australia

⁷College of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou, Guangdong, China

15 ⁸College of Atmospheric Sciences, Lanzhou University, Lanzhou, Gansu, China

**To whom correspondence should be addressed*

E-mail: cetwang@polyu.edu.hk and xuelikun@gmail.com, Tel: +852-2766 6059, Fax: +852-2330 9071

Abstract.

We analyzed the measurements of ozone (O_3) and its precursors made at rural/suburban sites downwind of four large Chinese cities – Beijing, Shanghai, Guangzhou and Lanzhou, to elucidate their pollution characteristics, regional transport, *in-situ* production, and impacts of heterogeneous processes. The same measurement techniques and observation-based model were used to minimize uncertainties in comparison of the results due to difference in methodologies. All four cities suffered from serious O_3 pollution but showed different precursor distributions. The model-calculated *in-situ* O_3 production rates were compared with the observed change rates to infer the relative contributions of on-site photochemistry and transport. At the rural site downwind of Beijing, export of the well-processed urban plumes contributed to the extremely high O_3 levels (up to an hourly value of 286 ppbv), while the O_3 pollution observed at suburban sites of Shanghai, Guangzhou and Lanzhou was dominated by intense *in-situ* production. The O_3 production was in a VOCs-limited regime in both Shanghai and Guangzhou, and a NO_x -limited regime in Lanzhou. The key VOC precursors are aromatics and alkenes in Shanghai, and aromatics in Guangzhou. The potential impacts on O_3 production of several heterogeneous processes, namely, hydrolysis of dinitrogen pentoxide (N_2O_5), uptake of hydro peroxy radical (HO_2) on particles and surface reactions of NO_2 forming nitrous acid (HONO), were assessed. The analyses indicate the varying and considerable impacts of these processes in different areas of China depending on the atmospheric abundances of aerosol and NO_x , and suggest the urgent need to better understand these processes and represent them in photochemical models.

1 Introduction

Air quality in the metropolitan areas has drawn increasing attention in recent years (Molina and Molina, 2004; Parrish and Zhu, 2009). A typical and difficult issue is photochemical smog characterized by unhealthily high concentrations of ground-level ozone (O_3), which is a product of atmospheric photochemistry involving nitrogen oxides ($NO_x=NO+NO_2$) and volatile organic compounds (VOCs). The ozone problem is a complex coupling of primary emissions, chemical transformation, and dynamic transport at different scales (Jacob, 1999). Challenges in regulating O_3 pollution primarily lie in understanding its non-linear chemistry with respect to precursors (i.e., NO_x , CO and VOCs) and contributions from both local and regional sources.

China has become home to several megacities and many large cities owing to its fast-paced

urban-industrialization processes. It is not surprising that these cities have been experiencing air quality deterioration in light of their fast expansion in economics, energy use and motor vehicles in the past decades. High O₃ concentrations exceeding the national ambient air quality standards have been observed frequently in and downwind of large cities (e.g., Wang et al., 2006, 2010b; Zhang J. et al., 2007; Zhang Y. et al., 2008; Ran et al., 2009; Chou et al., 2011). Recent studies also indicated increasing O₃ trends in several highly urbanized regions, i.e., the North China Plain (NCP; 1995–2005, Ding et al., 2008; 2005–2011, Zhang et al., 2014), Yangtze River delta (YRD; 1991–2006, Xu et al., 2008) and Pearl River delta (PRD; 1994–2007, Wang et al., 2009b). Furthermore, a worsening prospect of the problem is even foreseen in view of the projected continuing increase in emissions of NO_x and VOCs in the near future (Ohara et al., 2007). Consequently, effective control strategies based on scientifically sound knowledge must be in place in order to return to the clearer and cleaner skies.

Atmospheric models are the common tools used to understand the O₃ formation processes. The chemical mechanisms underlying the models are usually simplified representations of the complex atmospheric chemistry, with the organic species of similar reactivities and structures grouped into one model species (Stockwell et al., 2012). This chemical lumping gives reduced computational runtimes, but may produce extra uncertainties when applied to different atmospheric conditions (e.g., with different VOC emissions; the lumped mechanisms are usually optimized with emission estimates in some developed regions). The Master Chemical Mechanism (MCM) is a nearly-explicit mechanism that has the minimum amount of chemical lumping (Jenkin et al., 2003; Saunders et al., 2003), and hence is the best choice to investigate atmospheric photochemistry for a variety of environments. Another source of uncertainty is heterogeneous chemical processes which have recently been found to be more complex than previously thought. Several cases in point are the hydrolysis of dinitrogen pentoxide (N₂O₅), uptake of hydro peroxy radical (HO₂) on particles, and surface reactions of NO₂ forming nitrous acid (HONO) (Brown et al., 2006; Thornton et al., 2008; Su et al., 2011). These processes are believed to be more relevant in China given its very high aerosol loadings. However, they are usually **neglected** by most of the current mechanisms (such as MCM), and to date only very limited studies have attempted to evaluate their potential impacts and suggested the important role of HO₂ uptake in O₃ formation (e.g., Kanaya et al., 2009; Liu et al., 2012).

Another challenge in understanding ground-level O₃ problem is to dissect the local and regional contributions. Two types of methods have been widely used for this. One is the chemical transport model that is ideal to quantify local and regional contributions but may be subject to uncertainties from the emission inventory estimates (Wang et al., 2010c; Tie et al., 2013). The other approach is observation-based and usually comprises concurrent measurements from at least a pair of stations (Wang et al., 2010b; Berlin et al., 2013). It assumes that the O₃ concentrations at the upwind site can be regarded as the regional background for the receptor site. To our knowledge, there are very limited studies that estimated the contributions of local production and regional transport based on the observations at a single locale (e.g., Frost et al., 1998).

To evaluate the atmospheric impacts of emerging Chinese megacities, intensive observations of O₃ and O₃ precursors were conducted from 2004 to 2006 in suburban/rural areas near four Chinese major cities, namely Beijing, Shanghai, Guangzhou, and Lanzhou. These cities are located in different regions of China (see Fig. 1) and have different geographies, climates, industries and emission patterns. The same measurement techniques were utilized in all campaigns to minimize uncertainties arising from experiments in comparison of the results. These studies generated much high-quality data in the mid-2000s in major urban areas of China, which will be invaluable for assessing the atmospheric impact of on-going rapid urbanization in China. For data analysis, an observation-based MCM model (OBM) was deployed to quantify the contributions of *in-situ* photochemistry and regional transport and to assess the potential impacts of several heterogeneous processes. Overall, this study reveals the similarly serious O₃ pollution, different distributions in O₃ precursors, and varying impacts of heterogeneous chemistry in major cities of China.

2 Methodology

2.1 Study areas and sites

The field experiments were conducted in rural/suburban areas near three megacities in Northern (Beijing), Eastern (Shanghai) and Southern (Guangzhou) China, and a large city in Western China (Lanzhou; see Fig. 1). The sampling sites were selected carefully downwind of city centers during the study periods to allow investigation of regional-scale pollution and processes. These sites have been described separately by Wang et al. (2006); Gao et al. (2009); Zhang et al. (2009a) and Pathak et al. (2009), and here we only give a brief outline.

Beijing is the capital city of China and among the largest cities in the world. It is located on the northwestern periphery of the densely-populated North China Plain, and accommodates more than 19 million inhabitants, 5 million automobiles, and dozens of factories and power plants. The observations were carried out from 21 June to 31 July 2005 in a rural mountainous area in Chang Ping district (CP; 40°21' N, 116°18' E, 280 m a.s.l.), about 50 km north (generally downwind in summer) of the downtown. The site was in a fruit farm with sparse population and anthropogenic emissions about 10 km away (Wang et al., 2006). **The rural nature of the site determines to a large extent the 'unique' results obtained in Beijing (i.e., highest O₃, lowest O₃ precursors, and dominant role of regional transport) compared to the other three cities (suburban sites), which should be kept in mind when comparing the results among the four sites.**

Shanghai is the largest city of China and located in the Yangtze River Delta. It has over 23 million population, 2 million vehicles, China's largest petrochemical complex, steel manufacturer, seaport and other industries. The study site was in the Taicang Meteorological Station (31°27' N, 121°06' E, 20 m a.g.l.), which is approximately 45 km northwest of Shanghai. Although Taicang belongs to Jiangsu Province, it is often affected by urban plumes of Shanghai under the prevailing southeasterly winds in the summer-monsoon season. The observations taken from 4 May to 1 June 2005 were analyzed in the present study.

Guangzhou is a megacity of over 12 million people in southern China. It is in the center of the Pearl River Delta, which has been a 'world factory' for a wide range of consumer products. The measurements were made at Wan Qing Sha (WQS; 22°42' N, 113°33' E, 17 m a.g.l.), a suburban area about 50 km southeast of downtown Guangzhou. The data collected between 20 April and 26 May 2004 were analyzed in this paper. Thus the present study targets the O₃ pollution in late spring, and can be compared with and supplement previous investigations that focused on autumn (Zhang J. et al., 2007; Zhang Y. et al., 2008).

Lanzhou is a large city of over 3 million people and an industrial center in the interior western China. It is situated in a narrow valley basin in **a mountainous region** with a mean altitude of 1520 m a.s.l. This unique topography, together with its petrochemical industry as well as vehicle emissions (0.2 million cars in 2006), makes it a typical 'basin' of O₃ pollution in summer (Zhang et al., 2000). The sampling site was located in Renshoushan Park (RSP; 36°8' N, 103°41' E), a suburban mountainous area with some peach trees and other vegetation (Zhang et al., 2009a). The

industrial zone (Xigu petrochemical district) is located about 5 km to the southwest, and the urban center is about 15 km to the southeast. The intensive campaign was conducted from 19 June to 16 July 2006.

2.2 Measurement techniques

5 The same set of techniques were deployed to measure O₃, CO, SO₂, NO, NO_y, VOCs, particle number and size distribution, and meteorological parameters at the four cities. O₃ was monitored by a UV photometric instrument (*Thermo Environmental Instruments (TEI), Model 49i*). CO was measured by a non-dispersive infrared analyzer (*Advanced Pollution Instrumentation, Model 300EU*) with internal zeroing automatically done every 2 hours. SO₂ was observed with a pulsed
10 UV fluorescence analyzer (*TEI Model 43c*). NO and NO_y were detected by a chemiluminescence analyzer (*TEI Model 42cy*) coupled with an external molybdenum oxide catalytic converter to reduce NO_y to NO (Xue et al., 2011). 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*) in Beijing, Shanghai and Lanzhou. Temperature, pressure, relative
15 humidity (RH), wind direction and speed, and solar radiation were continuously measured by a weather station. All the above measurement techniques and quality assurance/control procedures have been described elsewhere (Gao et al., 2009; Xue et al., 2011).

Methane and C₂-C₁₀ non-methane hydrocarbons (NMHCs) were measured by collecting whole air samples in evacuated stainless-steel canisters with subsequent analysis by gas chromatography
20 with flame ionization detection, electron capture detection, and mass spectrometry (the analysis was undertaken in the University of California at Irvine) (Xue et al., 2013). Generally, one sample was collected at noon each day during the field campaigns (note that the sampling was not made consecutively at Lanzhou). In addition, multiple samples were taken on selected ozone episode days, normally one sample every two hours from 7:00 to 19:00 LT. Such a sampling strategy aimed at
25 facilitating both a thorough evaluation of VOC pollution for the campaigns and a comprehensive modeling analysis for the high O₃ events. In total, 130, 68, 76, and 24 VOC samples were collected in Beijing, Shanghai, Guangzhou, and Lanzhou, respectively.

2.3 Observation-based model

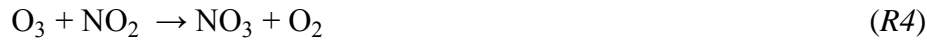
An observation-based chemical box model was utilized to quantify the *in-situ* O₃ production.

The model has been successfully applied in the previous studies (Xue et al., 2013, 2014a and 2014b). Briefly, it is built on the Master Chemical Mechanism (v3.2), a nearly-explicit mechanism describing oxidation of 143 primary VOCs together with the latest IUPAC inorganic nomenclature (Jenkin et al., 2003; Saunders et al., 2003). In addition, heterogeneous processes including uptake of N₂O₅, NO₃ and HO₂ on aerosols and reactions of NO₂ on ground/particle surfaces producing HONO are also incorporated (see details in Section 3.4). Dry depositions of inorganic gases, peroxides, PANs, carbonyls and organic acids are adopted in the model from the recent compilation (Zhang et al., 2003). The mixing-layer height affecting dry deposition rates was assumed to vary from 300 m at night to 1500 m in the afternoon. Sensitivity model runs with other maximum mixing heights (i.e., 1000 and 2000 m) showed that its impact on the modeling results was negligible (i.e., <3% in net O₃ production rates).

The observed data of O₃, CO, SO₂, NO, CH₄, C₂-C₁₀ NMHCs, H₂O, temperature, pressure, and aerosol surface and radius were averaged or interpolated with a time resolution of 1-hour and used as the model inputs. The aerosol surface and radius were calculated from the aerosol number and size distribution measurements. For Guangzhou where such measurements were not available, we used the average diurnal data obtained from a similar suburban site in Hong Kong (Tung Chung, close to the WQS site; see Fig. S1) in the same season (May 2012). Sensitivity studies using 50% higher aerosol surface indicated little impact on the modeling results (i.e., ~1% in net O₃ production rate). For hydrocarbons for which the observations were not in real-time, the time-dependent concentrations at hourly resolution were estimated as follows. During the daytime (i.e., 7:00-19:00) when multiple samples were taken, the data gaps were filled by time interpolation. The nighttime concentrations were estimated based on the regressions with CO (for most hydrocarbons except for isoprene) and temperature (for isoprene), for which continuous measurements were available. Photolysis frequencies were computed as a function of solar zenith angle (Saunders et al., 2003), and were further scaled by the measured solar radiation. The model calculations were made for the identified O₃ episode days with 00:00 LT as the initial time. Before each simulation, the model pre-ran for nine days with constraints of the campaign-average data so that the model approached a steady state for the unmeasured species (e.g., NO₂ and radicals).

The model read the inputs every hour to calculate the *in-situ* O₃ production and destruction rates. The ozone production rates calculated by the OBM usually correspond to the production of total

oxidant ($O_x=O_3+NO_2$) other than O_3 alone (by considering the oxidation of NO to NO_2 by peroxy radicals; Kanaya et al., 2009; Xue et al., 2013). Here we determined directly the reaction rates of O_3 instead of O_x with our model. In the troposphere, O_3 production is eventually achieved by the combination of O atom with O_2 (R1), and O_3 destruction is mainly facilitated by O_3 photolysis (R2) and reactions with NO (R3), NO_2 (R4), OH (R5), HO_2 (R6), atoms of O (R7) and Cl (R8), and unsaturated VOCs (R9) (In general, the O_3 destruction was dominated by reactions of R2-R4, while the other reactions may also make considerable contributions at specific conditions (e.g., at high VOCs)).



Thus the O_3 production and destruction rates can be calculated as:

$$20 \quad P(O_3) = k_1 [O_2] [O] [M] \quad (E1) \quad (M \text{ denotes } N_2 \text{ or } O_2)$$

$$L(O_3) = J_{O_3} [O_3] + k_3 [NO][O_3] + k_4 [NO_2][O_3] + k_5 [OH][O_3] + k_6 [HO_2][O_3] + k_7 [O][O_3] \\ + k_8 [Cl][O_3] + \sum(k_{9i} [VOC_i])[O_3] \quad (E2)$$

Then the net O_3 production rate can be determined from the difference between $P(O_3)$ and $L(O_3)$. We also compared our-derived O_3 net rates with those of O_x from the traditional method, and found both methods showed overall good agreement (see Fig. S2).

25 **3 Results and discussion**

3.1 Overview of O_3 and O_3 precursors

Table 1 summarizes the overall O_3 pollution conditions observed in the four cities. At the rural

site of Beijing, eighteen O₃ episode days (here defined as days when the peak hourly O₃ exceeded 100 ppbv; 44% of the total) were observed during the 6-week measurement period. The maximum hourly O₃ mixing ratio was 286 ppbv, which is by far the highest value reported in China in open literatures (Wang et al., 2006). Such frequency of episodes and extreme O₃ levels highlight the serious problem in the Beijing area. At the suburban site near Shanghai, six episode days (21%) occurred during the 4-week campaign with the maximum hourly O₃ of 127 ppbv observed. The pollution in Shanghai (YRD) seemed relatively lighter than those in other three cities, which may be due to the titration effect of its high NO_x levels (Ding et al., 2013). At the downwind site of Guangzhou, seven episodes (19%) were encountered throughout the 37 measurement days. The maximum hourly O₃ concentration was recorded at 178 ppbv. This indicates that the O₃ pollution in the PRD is serious not only in autumn but also in late spring. In Lanzhou, eight episodes (29%) took place during the 4-week campaign with a maximum hourly O₃ of 143 ppbv. Our observations highlight the serious ozone pollution in the large cities of China.

We then examined the distributions of major O₃ precursors observed in the four cities. The mean diurnal profiles of NO_y and CO are shown in Figure 2. At the rural site of Beijing with little local emissions, both precursors showed high levels in the late afternoon till the evening, corresponding to regional transport of urban plumes. At the suburban sites downwind of Shanghai, Guangzhou and Lanzhou, in comparison, they exhibited a morning maximum and/or another evening peak, which were mainly caused by the shallow boundary layer and enhanced emissions in the rush hours. The NO_y levels measured in Shanghai (24–39 ppbv) and Guangzhou (24–52 ppbv) were significantly higher than those in Beijing (rural site; 11–16 ppbv) and Lanzhou (7–27 ppbv), while the CO levels were comparable in the four cities despite the relatively lower afternoon concentrations in Lanzhou.

Figure 3 documents the average reactivities towards OH of major hydrocarbons in the four cities (see Supplement for the OH reactivity calculation). To facilitate interpretation of the hydrocarbon speciation, the 50+ species were categorized into anthropogenic hydrocarbons (AHC; encompassing most species except for isoprene and α/β -pinenes) and biogenic hydrocarbons (BHC; comprising isoprene and α/β -pinenes), with AHC further grouped into reactive aromatics (R-AROM; including all aromatics except for benzene), alkenes, alkanes with ≥ 4 carbons (C4HC), and low-reactivity hydrocarbons (LRHC; including methane, ethane, propane, acetylene and benzene; see in Table S1). The highest hydrocarbon reactivity was determined in Lanzhou (9.33 s⁻¹ in total), followed by those

in Shanghai (5.85 s^{-1}) and Guangzhou (5.23 s^{-1}). This is opposite to the patterns for NO_y and CO as shown in Fig. 2. The lowest reactivity (2.77 s^{-1}) was measured at the Beijing site, which should be ascribed to the fact that our site is located in a rural mountainous area with few local anthropogenic emissions. It also implies that the urban plumes had undergone extensive photochemical processing during transport and were less reactive when reaching the Beijing site.

Furthermore, different hydrocarbon distributions among the four cities were also illustrated. In Beijing and Shanghai, the AHC reactivities were dominated by both alkenes (35% and 43%) and R-AROM (34% and 39%). In Guangzhou, R-AROM was the dominant AHC class with an average contribution of 46%. And in Lanzhou, alkenes played a predominant role and composed on average 70% of the AHC reactivity. In particular, the propene and ethene levels were extremely high, both of which contributed 53% of the AHC reactivity. These results suggest distinct emission patterns of O_3 precursors and imply different O_3 formation regimes in the four cities (see next section).

3.2 Process analysis: regional transport vs. *in-situ* formation

To understand the processes contributing to high O_3 pollution in the four cities, we analyzed in detail twelve O_3 episodes (3 per city; Beijing: 9, 26, 30 July 2005; Shanghai: 7, 8, 22 May 2005; Guangzhou: 18, 23, 24 May 2004; Lanzhou: 5, 11, 12 July 2006). These cases were chosen because elevated O_3 levels were observed and the most comprehensive measurements (i.e., multiple daily VOC samples) were made. (The time series of O_3 and related parameters during these episodes are shown in Figures S3-S6.) At a given location, the change of O_3 mixing ratios is a combined result of *in-situ* photochemistry, regional transport (both horizontal and vertical) and deposition. The contributions of chemistry and transport can be either positive (i.e., production and import) or negative (i.e., destruction and export). In the present study, we examined the contributions of *in-situ* photochemistry and regional transport to the observed O_3 pollution by using observations coupled with OBM analysis. We first determined the rate of change in O_3 concentrations from the observed O_3 time series (R_{meas}). The *in-situ* net O_3 production (R_{chem}) and deposition rates (R_{deps}) were computed every hour by the OBM as described in Section 2.3. Then the difference ($R_{\text{trans}} = R_{\text{meas}} - R_{\text{chem}} - R_{\text{deps}}$) can be considered as the contribution from regional transport (note that the effect of atmospheric mixing was also included in this term).

Figure 4 displays the time series of O_3 and contributions of *in-situ* production, deposition and regional transport for typical O_3 episodes at the four cities (the results were similar for other cases

for each city and are not shown). Two interesting phenomena are illustrated. One is the intrusion of residual boundary-layer air contributing to O₃ increase during the early morning period. At all four cities, in particular Lanzhou, R_{trans} presented an important contributor to the O₃ increase in the early morning. This should be attributed to mixing with the O₃-rich air aloft when the nocturnal boundary layer is broken down. The other is the sudden changes of the transport effect corresponding to the variation in surface winds. During the Beijing case (Fig. 4a), for example, the southeasterly winds brought urban plume to the study site, resulting in an O₃ peak at 14:00–15:00; but after that the wind direction shifted to northerly, leading to a sharp O₃ decrease. Similar wind effects were also noticed for the Guangzhou and Lanzhou cases. These results suggest that our method can capture the variations in physical processes and hence is capable of quantifying the contributions of regional transport.

We are particularly interested in the relative roles of *in-situ* photochemistry and transport in the extremely high O₃ levels observed at the rural site downwind of Beijing. As shown in Figure 4a, both *in-situ* production and regional transport contributed to the O₃ accumulation from morning (~40 ppbv at 8:00 LT) to noon (~100 ppbv at 12:00 LT). In the afternoon, however, the O₃ mixing ratios increased sharply from ~100 ppbv to ~220 ppbv within less than two hours (14:00-15:00 LT), during which the *in-situ* O₃ production had been weakened due to the relatively low levels of VOCs and NO_x. Thus such a sharp O₃ rise was attributed to the transport of urban plumes from Beijing that had undergone extensive photochemical processing and contained high amounts of produced O₃. This is a very typical case at CP in summer, and highlights the efficient export of Beijing urban pollution in the afternoon, which can adversely affect the vegetation and crops in downwind areas.

In comparison, the *in-situ* production dominated the O₃ accumulation throughout the daytime at suburban sites downwind of Shanghai, Guangzhou and Lanzhou (see Figures 4b-d). Very strong O₃ formation was determined during these episodes (e.g., up to 50, 90 and 40 ppbv/h at Shanghai, Guangzhou and Lanzhou). Regional transport generally made a negative contribution (i.e., export) to the observed O₃ pollution. This indicates that the air masses at these sites were reactive enough to sustain the observed O₃ increase and even had potential to export the produced O₃ to downwind regions.

We then examined the ozone formation regimes in Shanghai, Guangzhou and Lanzhou, where *in-situ* photochemistry dominated the O₃ pollution, by calculating the relative incremental reactivity

(RIR) with the OBM. RIR is defined as the ratio of decrease in O₃ production rate to decrease in precursor concentrations, and can be used as a metric for the effect of a given emission reduction on O₃ concentrations (Cardelino and Chameides, 1995). The daytime-average RIRs for major groups of O₃ precursors during the episodes are shown in Fig. 5. Overall, the O₃ formation regimes were consistent among cases for each city but different among cities. In Shanghai and Guangzhou, the *in-situ* O₃ production was highly VOC-sensitive, specifically AHC-controlled (see Fig. 5a). The RIRs for NO_x were negative. Within the AHC dominated were reactive aromatics and alkenes in Shanghai and aromatics in Guangzhou (see Fig. 5b). This suggests that reducing emissions of aromatics (and also alkenes for Shanghai) would weaken the O₃ formation in both cities, yet cutting NO_x emissions may aggravate the local O₃ problems.

In Lanzhou, the O₃ formation was most sensitive to NO_x and to a lesser extent to AHC. Within the AHC, alkenes were the most important compounds responsible for the O₃ production. In particular, light olefins such as propene and ethene were the most abundant reactive species, both of which presented approximately half of the AHC reactivity (figure not shown). Such high levels of olefins are attributable to the industrial structure of Lanzhou, which is a well-known petrochemical city in West China with the China National Petroleum Corporation – Lanzhou Petrochemical Company and many small petrochemical plants located in its Xigu district. Light olefins are major components of the petrochemical plant emissions (Ryerson et al., 2003). The results suggest that the most efficient way to alleviate the O₃ pollution in Lanzhou is to cut the NO_x emissions (from petrochemical and power plants as well as vehicles), while reducing emissions of olefins (from the petrochemical plants) could also result in considerable decrease in O₃ formation.

3.3 Impact of heterogeneous processes

In this section, we assess the potential impacts of several poorly-understood heterogeneous processes on the ozone production in the four target cities, by incorporating them in the OBM and conducting sensitivity analyses.

3.3.1 ClNO₂ production from N₂O₅ hydrolysis

The hydrolysis of N₂O₅ may produce nitryl chloride (ClNO₂), which is usually accumulated at night and can enhance the next-day's O₃ formation by releasing both NO₂ and chlorine atom (it can oxidize hydrocarbons like OH) via photolysis. The hydrolysis rate is considered to be first order of

the N₂O₅ concentrations (Chang et al., 2011). This process has not been considered by most of the current mechanisms (e.g., MCM), and is here parameterized in our MCM-based model as follows.



Where, ϕ is the production yield of ClNO₂, and k_{10} is the first order rate constant and estimated by

$$k_{10} = \frac{1}{4} \times v_{\text{N}_2\text{O}_5} \times \gamma_{\text{N}_2\text{O}_5} \times S_{\text{aero}} \quad (E3)$$

Where $v_{\text{N}_2\text{O}_5}$ is the mean molecular speed of N₂O₅ and can be calculated from the gas kinetic theory (Aldener et al., 2006); $\gamma_{\text{N}_2\text{O}_5}$ is the reactive uptake coefficient of N₂O₅ on aerosol surfaces; S_{aero} is the aerosol surface area concentration and is calculated based on the measured particle number size distributions. The current uncertainty of this process primarily lies in the uptake coefficient of N₂O₅ and production yield of ClNO₂, which are highly variable and dependent on the aerosol composition, humidity and temperature (Chang et al., 2011). The $\gamma_{\text{N}_2\text{O}_5}$ derived on real atmospheric particles from limited available field observations were in the range of 0-0.04 (Chang et al., 2011, and references therein). In the present study, we adopted a moderate value of $\gamma_{\text{N}_2\text{O}_5} = 0.03$ with no production of ClNO₂ ($\phi = 0$) in the base model, and conducted sensitivity analyses by including ClNO₂ production with a moderate yield of 60%.

Figure 6 illustrates the impacts of ClNO₂ formation from N₂O₅ hydrolysis on the O₃ production during the selected episodes in the four cities. Overall, the ClNO₂ produced/accumulated at night may enhance considerably the next-day's O₃ formation, and this impact is highly dependent on the abundances of both aerosol surface density (more interface) and nitrogen oxides (more reactants). For instance, including the ClNO₂ formation would result in an average nighttime ClNO₂ peak of 1.3 ppbv at the Shanghai site with high concentrations of both NO_x and particle surface, which in turn would enhance the daytime-average O₃ production rates by ~3 ppb/h on average (or 14% in percentage; the enhancement was the most significant in the early morning with the maximum percentage of ~26%, and then decreased over the course of the day). In comparison, this process seems to be less significant (<10% for the daytime-average) at the other three sites due to their relatively lower levels of NO_x and/or aerosol surface. It is noteworthy that the OBM cannot take into account the transport of ClNO₂ that has relatively long lifetime at night. ClNO₂ may present a positive altitude profile in the nocturnal boundary layer due to less O₃ titration above the ground. Intrusion of the air aloft in the early morning might contribute considerably to the ClNO₂ at surface

sites. Therefore, our estimation of the impact of ClNO₂ in the present study should be a lower limit.

Nonetheless, our results indicate that the nighttime heterogeneous process of N₂O₅ is a considerable uncertainty in the current understanding of O₃ photochemistry in the high-NO_x and high-aerosol environments such as Shanghai. Clearly, *in-situ* measurements of N₂O₅ and ClNO₂ are urgently required to better understand this process and to provide more realistic parameterizations of $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} which can be adopted in air quality models.

3.3.2 Uptake of HO₂ by aerosols

The heterogeneous loss of HO₂ on aerosol surface can act as an efficient radical sink at high aerosol loadings and thus attenuate O₃ production (Kanaya et al., 2009). This process is also usually ignored by the current mechanisms, and here was included in our model by adding the following reaction.



The reaction rates were assumed to be first order in the HO₂ concentrations. k_{11} is the reaction constant that can be calculated by

$$k_{11} = - \left(\frac{r}{D_g} + \frac{4}{\gamma_{HO_2} \times v_{HO_2}} \right)^{-1} S_{aero} \quad (E4)$$

Where r is the surface-weighted particle radius; D_g is the gas phase diffusion coefficient and is assumed to be 0.247 cm² s⁻¹ (Mozurkewich et al., 1987) (the gas diffusion limitation is accounted for here given the potential larger uptake of HO₂ to aerosol; see below); γ_{HO_2} is the uptake coefficient of HO₂ on particles; v_{HO_2} is the mean molecular speed of HO₂; and S_{aero} is the aerosol surface density. Similar to N₂O₅ hydrolysis, the uptake coefficient (γ_{HO_2}) is a parameter with large uncertainty and is related to the aerosol composition, temperature and RH (Thornton et al., 2008). The laboratory studies determined the γ_{HO_2} in the range of 0.01-0.2 for different types of non-metal aerosols at room temperatures, with much higher values (>0.2) measured on the Cu-doped aqueous surfaces (Mao et al., 2010, and references therein). Taketani et al. (2012) recently reported relatively large γ_{HO_2} values for ambient aerosols at Mt. Tai (0.13-0.34) and Mt. Mang (0.09-0.40) in China. Here we adopted a value of $\gamma_{HO_2} = 0.02$ in the base model, and changed it to an upper limit (0.4) for sensitivity model runs.

Figure 7 elucidates the effects of heterogeneous HO₂ loss on the modeled HO₂ concentrations

and O₃ production rates during episodes in the four cities. Varying impacts of this process in different cities are clearly illustrated. These impacts mainly depend on the abundances of aerosol surface, and are also related to the levels of nitrogen oxides (*i.e.*, at high-NO_x conditions, the HO₂ loss is dominated by its reactions with NO_x and its heterogeneous loss is less important) as well as the O₃ formation regimes (*i.e.*, the same HO₂ reduction would lead to less reduction in O₃ formation at NO_x-limited regime than at the VOCs-limited regime). At the Shanghai, Guangzhou and Lanzhou sites with relatively higher levels of NO_x or lower loadings of aerosols, adopting a higher uptake coefficient ($\gamma_{HO_2} = 0.4$) would only lead to little to moderate reductions in the HO₂ concentrations (<21%) and O₃ production rates (<10%). At the Beijing site, however, a faster uptake would reduce significantly the HO₂ levels by about 50% due to its very high loadings of aerosol surface (~1600 $\mu\text{m}^2/\text{cm}^3$). Such HO₂ reduction would in turn result in an average decrease of ~15% in the daytime-average O₃ production rates (note that a relatively smaller reduction in O₃ production should be attributed to the more NO_x-sensitive O₃ production regime at our rural site). This indicates that the uptake of HO₂ presents another large source of uncertainty in current studies of O₃ photochemistry in the high-aerosol environments like Beijing, and more observational studies are required to quantify the γ_{HO_2} on the real particles.

3.3.3 Surface reactions of NO₂ forming HONO

HONO is a key reservoir of the hydroxyl radical (OH) and hence plays a crucial role in atmospheric chemistry. Recent studies have indicated possible existence of ‘missing’ source(s) for daytime HONO, which cannot be reproduced by current models only considering the homogeneous source from the OH+NO reaction (*e.g.*, Su et al., 2008 and 2011). It has been suggested that the photo-enhanced heterogeneous reactions of NO₂ on various surfaces should be an important source of HONO (Su et al., 2008; Li et al., 2010). In the present study, HONO was not measured but simulated within the model. In addition to the homogeneous source, heterogeneous sources from reactions of NO₂ on the ground and aerosol surfaces were also taken into account in the base model by adopting the parameterizations used by Li et al. (2010). The reaction rates were assumed to be first order of the NO₂ concentrations (Aumont et al., 2003), and the processes were simplified as follows.



k_g and k_a are the first order rate constants for the ground and aerosol surface reactions, and can be estimated as

$$k_g = \frac{1}{8} \times v_{NO_2} \times \gamma_g \times \left(\frac{S}{V}\right) \quad (E5)$$

$$k_a = \frac{1}{4} \times v_{NO_2} \times \gamma_a \times S_{aero} \quad (E6)$$

5 Where v_{NO_2} is the mean molecular speed of NO_2 ; γ_g and γ_a are the uptake coefficients of NO_2 on the ground and aerosol surfaces; S/V is the effective surface density of the ground, and S_{aero} is the aerosol surface area concentration. Considering the photo-enhanced production of HONO from the surface reactions (George, 2005; Monge et al., 2010), higher values of γ_g and γ_a were used during the daytime than at night. For γ_g , we used a value of $\gamma_g = 1 \times 10^{-6}$ at nighttime, and increased it to
 10 2×10^{-5} during the daytime with solar radiation smaller than 400 W/m^2 . With more intense solar radiation, a higher γ_g value of $2 \times 10^{-5} \times (\text{solar radiation}/400)$ was used (Li et al., 2010). **As to γ_a , we used a value of $\gamma_a = 1 \times 10^{-6}$ at nighttime and increased it to 5×10^{-6} during the day, according to Li et al. (2010).** An effective surface area of 1.7 m^2 per geometric ground surface was used to calculate the S/V (Vogel et al., 2003).

15 **The heterogeneous HONO formation may enhance O_3 production by releasing OH via HONO photolysis.** We conducted sensitivity model runs by turning off the heterogeneous HONO sources, which is the case of most current atmospheric models. The results are shown in Fig. 8. We can see that including these processes would enhance the daytime-average O_3 production rates by ~ 6.8 ppb/h and ~ 3.2 ppb/h on average ($\sim 25\%$ and $\sim 16\%$) in Shanghai and Guangzhou respectively, but
 20 lead to little change for the Beijing and Lanzhou sites ($< 1\%$). This corresponds well to the distributions of nitrogen oxides observed at the four sites (see Fig. 2). And aerosol surface loading seems not a key factor here, which is in line with the fact that the heterogeneous HONO formation on the ground generally dominates than those on the aerosol at the ground level (Su et al., 2008). These results suggest that the heterogeneous processes of NO_2 may play an important role in
 25 atmospheric photochemistry in the high- NO_x environments such as Shanghai and Guangzhou, and need to be included in the air quality models.

In-situ measurements of HONO, which were not available in China until recent years, have shown surprisingly elevated concentrations of HONO (up to the ppb level) throughout the daytime in the PRD region (e.g., Su et al., 2008). Such high levels of daytime HONO cannot be explained

by only including the above heterogeneous reactions of NO₂, and some additional sources have been proposed (e.g., Su et al., 2011). It is not known if this phenomenon was also the case at our study sites, however identification of additional HONO source(s) is beyond scope of the present study. The analyses presented here clearly indicate that the surface reactions of NO₂ at least present an important HONO source and can enhance O₃ production. Undoubtedly, *in-situ* measurements of HONO are critical for better understanding the atmospheric photochemistry including O₃ formation, and further efforts are needed to determine the ‘missing’ source(s).

4 Summary

Measurements of O₃ and O₃ precursors were made at a rural site downwind of Beijing and suburban sites of Shanghai, Guangzhou and Lanzhou. The data were analyzed to elucidate the O₃ precursor distributions, roles of transport and *in-situ* production, and impacts of heterogeneous processes. The major findings are summarized as follows.

- (1) The four cities suffered from severe O₃ pollution and showed different precursor distributions. The NO_y levels in Shanghai and Guangzhou were higher than that in Lanzhou, while an opposite pattern was found for the VOC reactivity. The dominant anthropogenic hydrocarbons were alkenes in Lanzhou, aromatics in Guangzhou, and both alkenes and aromatics in Beijing and Shanghai.
- (2) Transport of ‘aged’ urban plumes resulted in the extremely high O₃ levels (up to 286 ppbv) at the rural site downwind of Beijing, while intense *in-situ* photochemical production dominated at the suburban sites of Shanghai, Guangzhou and Lanzhou. The O₃ production was VOCs-limited in Shanghai and Guangzhou and NO_x-limited in Lanzhou. The key VOC species were aromatics and alkenes in Shanghai and aromatics in Guangzhou.
- (3) The potential impacts of several poorly-understood heterogeneous processes on O₃ production were assessed. The N₂O₅ hydrolysis was more significant at the Shanghai site due to its high levels of both aerosol and NO_x. The HO₂ loss on aerosols was more relevant for Beijing because of its very high aerosol loadings. The HONO formation from surface reactions of NO₂ was more important for the Guangzhou and Shanghai sites mainly owing to their high NO_x levels. And the O₃ production at the Lanzhou site seemed to be less sensitive to all of these processes due to its relatively low concentrations of aerosol and NO_x. These findings indicate the varying impacts of

heterogeneous processes on the O₃ photochemistry in different regions of China, and suggest further necessity to better understand these processes.

- (4) In summary, the results of this study have provided insights into O₃ pollution, local chemistry versus outside impact, and potential impacts of heterogeneous chemistry in major urban areas of China. The high-quality data taken in the mid-2000s will be particularly valuable for assessing the atmospheric impact of rapid urbanization/industrialization process in China.

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Table 1. Overview of ozone pollution conditions in four Chinese cities.

Site	Location	Observation Period	Number of O₃ episode days^a	Maximum hourly O₃ (ppbv)
Beijing <i>CP</i>	116.30 °E, 40.35 °N	June 21 – July 31 2005	18	286
Shanghai <i>Taicang</i>	121.10 °E, 31.45 °N	May 4 – June 1 2005	6	127
Guangzhou <i>WQS</i>	113.55 °E, 22.70 °N	April 20 – May 26 2004	7	178
Lanzhou <i>RSP</i>	103.69 °E, 36.13 °N	June 19 – July 16 2006	8	143

^aThe ozone episode day is defined here as the one with the maximum hourly ozone exceeding 100 ppbv.

Figure Captions:

Fig. 1. Map showing the study areas and anthropogenic NO_x emissions over China. The emission data was obtained from Zhang et al. (2009b).

Fig. 2. Observed average diurnal profiles of (a) NO_y and (b) CO in the four cities. The data time interval is 10 minutes, and the error bar is standard error.

Fig. 3. Average OH reactivities of major hydrocarbons at the four cities. The error bar is standard error.

Fig. 4. O_3 accumulation and contributions from *in-situ* chemistry, regional transport, and deposition during episodes in (a) Beijing (9 July 2005), (b) Shanghai (7 May 2005), (c) Guangzhou (24 May 2004), and (d) Lanzhou (11 July 2006). Note that the blue bars are added to the red ones.

Fig. 5. The OBM-calculated RIRs for (a) major O_3 precursor groups and (b) the AHC sub-groups during high O_3 events in Shanghai, Guangzhou and Lanzhou.

Fig. 6. Average increase in the daytime-average O_3 production rates by including ClNO_2 formation ($\phi_{\text{ClNO}_2}=0.6$) during episodes at four cities. Also shown are the model-simulated nighttime ClNO_2 concentrations and the product of NO_2 with aerosol surface. The error bars are standard deviations. The number in parentheses gives the increase in percentage.

Fig. 7. Average reductions in the daytime-average HO_2 concentrations and O_3 production rates by adjusting γ_{HO_2} from 0.02 to 0.4 during episodes at four cities. Also shown are the observed aerosol surface area concentrations (note that the data in Guangzhou was inferred from the measurements at a nearby station in Hong Kong). The error bars are standard deviations.

Fig. 8. Average increase in the daytime-average O_3 production rate by including HONO formation from heterogeneous NO_2 reactions during episodes at four cities. Also shown are the modeled daytime-average HONO concentrations. The error bars are standard deviations. The number in parentheses gives the increase in percentage.

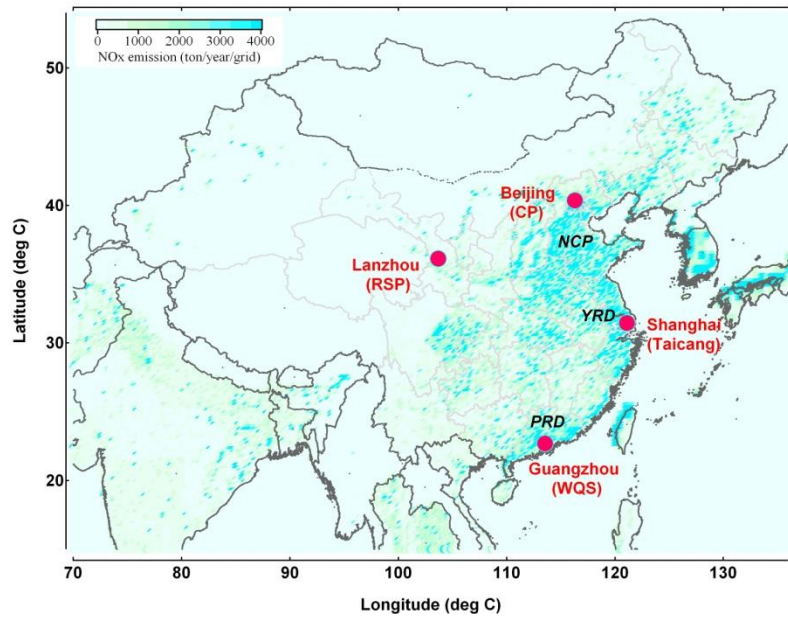


Fig. 1

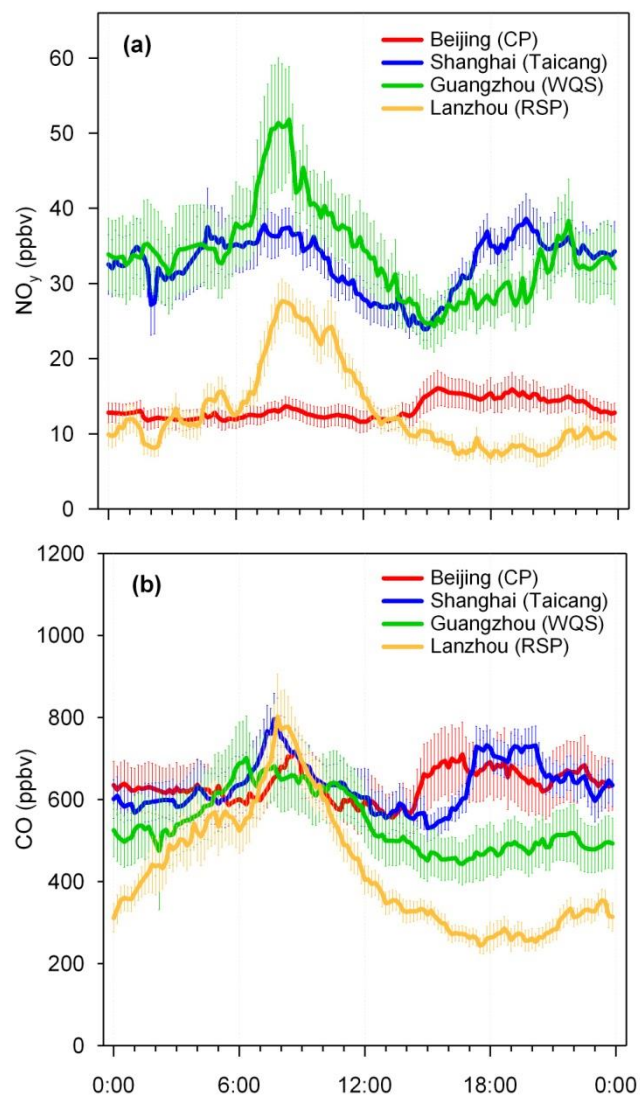


Fig. 2

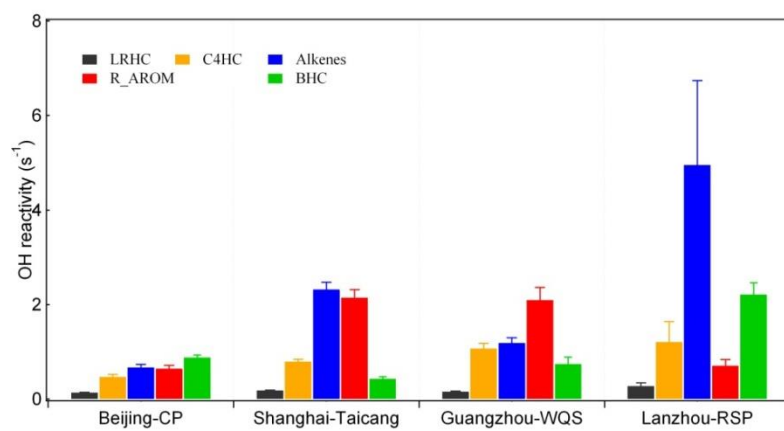


Fig. 3

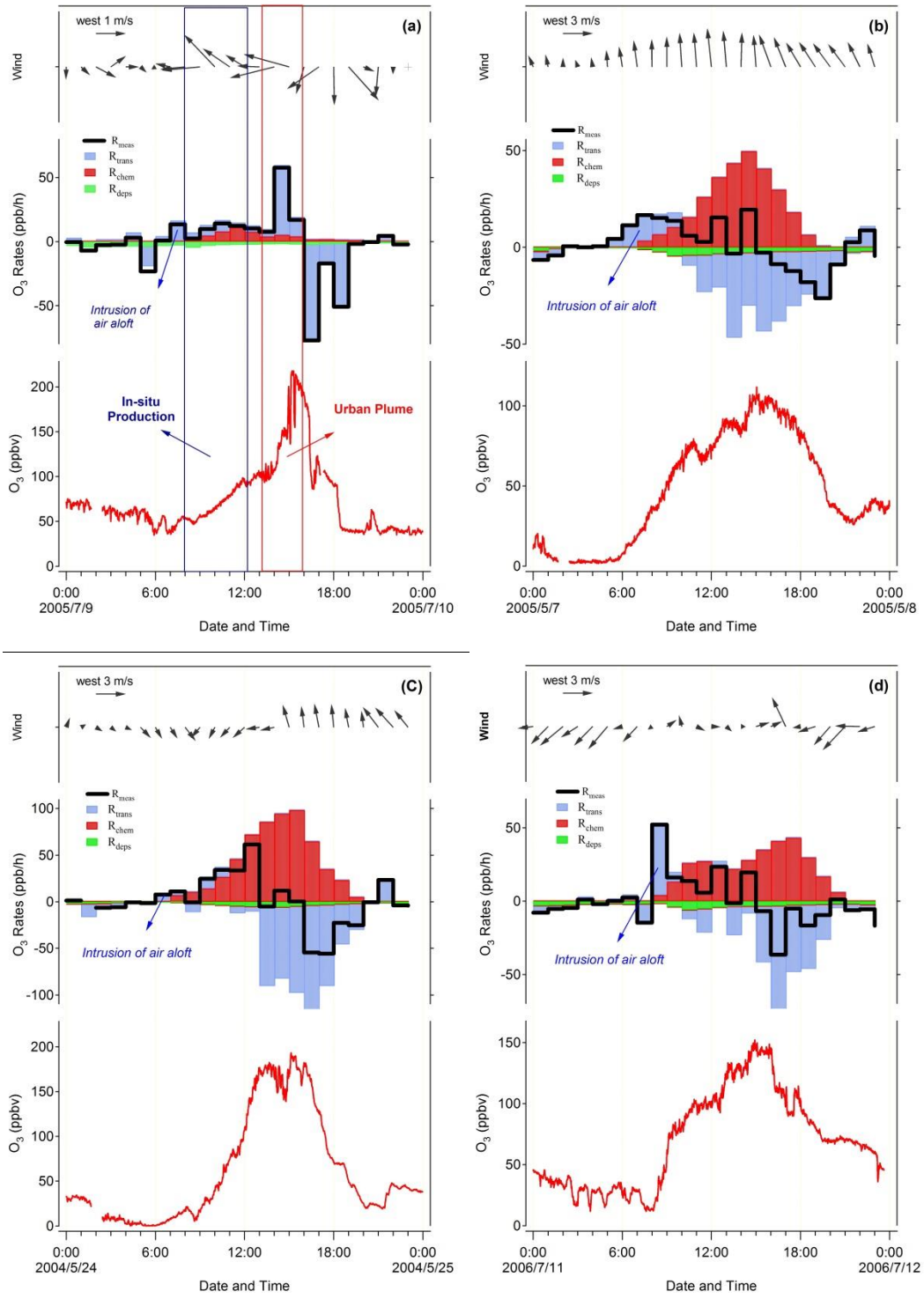


Fig. 4

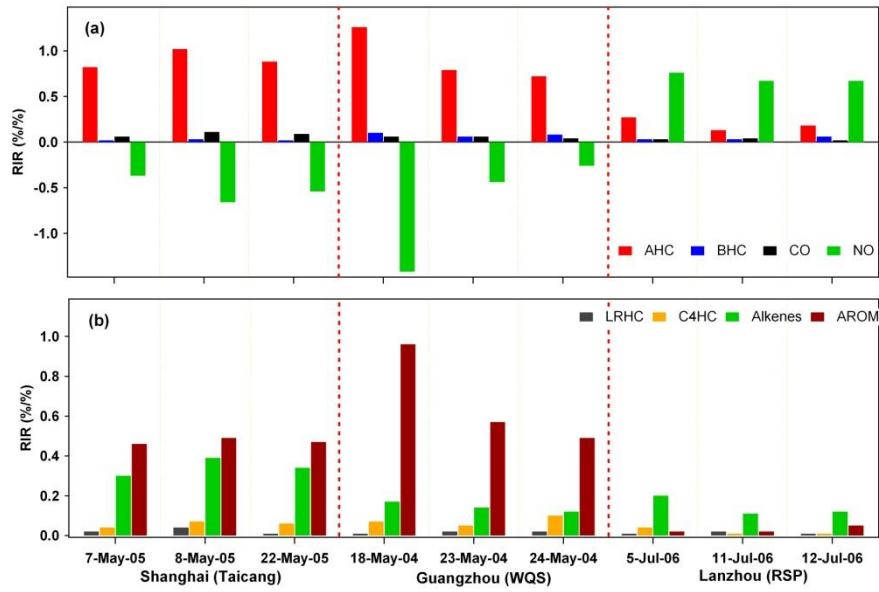


Fig. 5

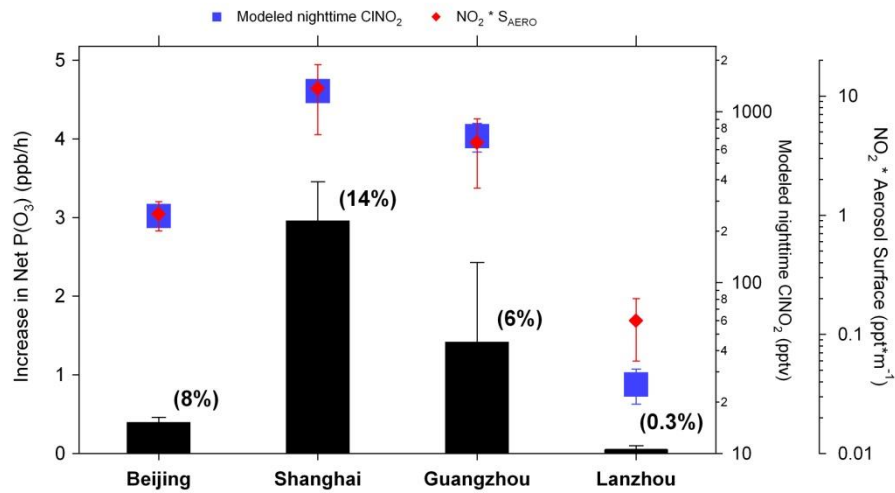


Fig. 6

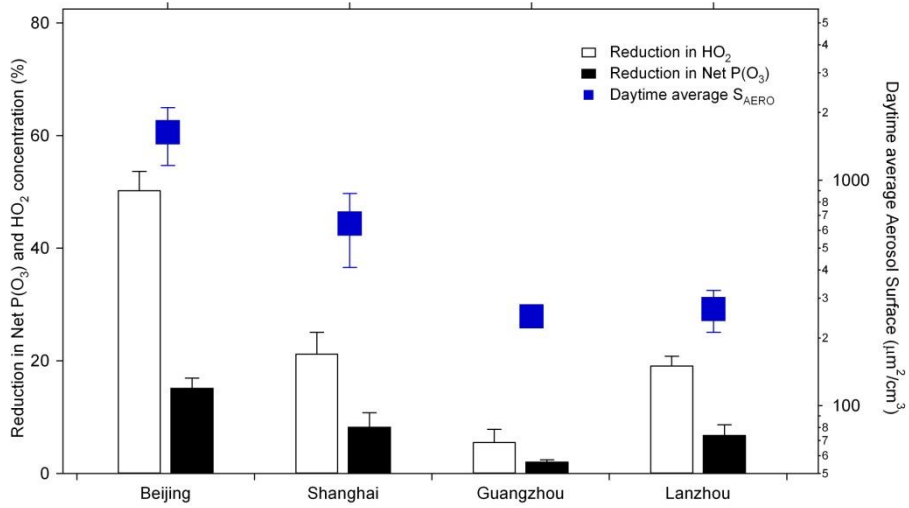


Fig.7

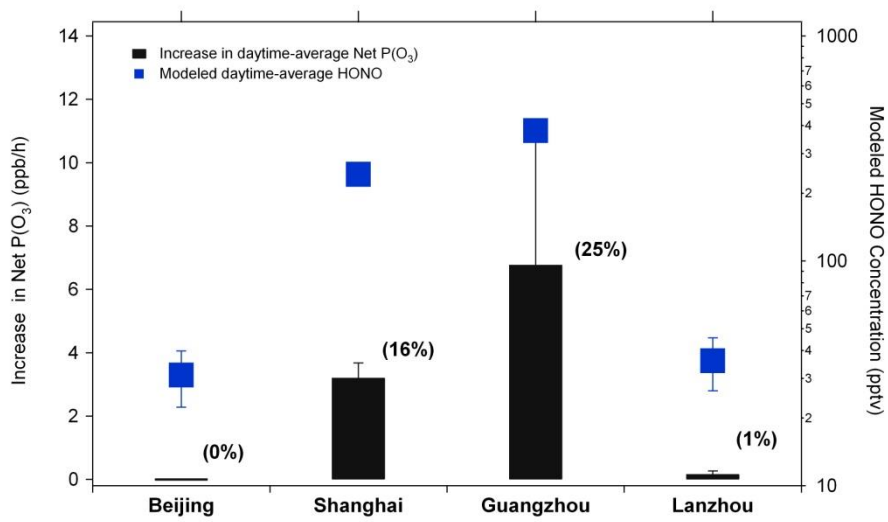


Fig. 8