Strong ozone production in urban plumes from Beijing, China

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Received 27 July 2006; revised 15 September 2006; accepted 4 October 2006; published 7 November 2006.

[1] We report recent measurements of ozone (O_3) and related trace gases obtained in June–July 2005 in a mountainous area north of Beijing. Of the 39 days of observation, there were 13 days whose 1-hr O_3 mixing ratio exceeded 120 ppbv, with a maximum level of 286 ppbv, which is the highest reported value in open literature for China. Analysis of plume characteristics and air-mass back trajectories show the highest concentrations of O_3 (and other trace gases) were mainly due to emissions from the Beijing urban area. O_3 was strongly correlated with NO_y with O_3-NO_y regression slopes of 3–6 ppbv/ppbv in the six episodes examined. In contrast to some observations from North America, the positive O_3-NO_y correlation in the Beijing plumes extended to NO_y mixing ratios up to 55 ppbv, suggesting an important role of NO_x in the formation of O_3 in Beijing. The very high concentrations of O_3 revealed in our study imply significant negative effects on vegetation and regional air quality. **Citation:** Wang, T., A. Ding, J. Gao, and W. S. Wu (2006), Strong ozone production in urban plumes from Beijing, China, *Geophys. Res. Lett.*, *33*, L21806, doi:10.1029/2006GL027689.

1. Introduction

[2] With a population of over 15 million, Beijing is one of the world's largest metropolises. Like other megacities (defined as having a population of 10 million or more), Beijing faces serious air pollution problems which have been characterized by high concentrations of particulate matter and sulfur dioxide, due to the burning of coal, fugitive dusts, and more recently a rapid increase in vehicular emissions [e.g., *Hao and Wang*, 2005; *Molina and Molina*, 2004]. Previous research and air-management efforts have focused on particulate matter and sulfur compounds; only limited and scattered studies were published regarding photochemical ozone pollution. Nevertheless available data indicate rather serious ozone pollution in Beijing [*Tang*, 2004; *Hao and Wang*, 2005; *Molina and Molina*, 2004]. For example, data from the Beijing Environmental Protection Bureau show that in 1998 O_3 concentrations exceeded 200 $\mu g/m^3$ (approximately 100 ppbv) - China's standard for urban residential areas (Grade II) - for 101 days with a maximum hourly value of 384 $\mu g/m^3$ [*Hao and Wang*, 2005]. However there were few studies that attempted to examine the chemical and meteorological processes that control the formation and transport of ozone (and other secondary pollutants) in urban plumes, and there were limited ozone measurements outside urban center. Such studies/data are needed to improve our understanding of the chemical transformation as urban plumes advect to downwind areas, and of the impact of the ozone pollution on vegetation and regional air quality.

[3] In summer 2005, a six-week measurement campaign took place at a site downwind of the Beijing urban area, during which numerous gases and aerosols were measured. In this article we report the results on ozone and some gaseous pollutants including carbon monoxide (CO), total reactive nitrogen (NO_y) and sulfur dioxide (SO_2). These trace gases provide useful information on the impact of general urban (vehicular) emissions (CO and NO_y) and of coal-fired power plants (SO_2 and NO_y). The data reveal serious (very high and frequent) ozone pollution in the mountainous areas north of Beijing with hourly ozone levels reaching 286 ppbv, which is the highest value reported in the literature for China. We examine wind and back trajectories, and other trace gas data to show source region and characteristics of the measured plumes. We then examine O_3-NO_y correlations in O_3-laden plumes and discuss ozone production potential and photochemical regime in the Beijing plumes.

2. Description of Experiment

2.1. Measurement Site and General Weather Conditions

[4] The study was conducted in a mountainous area (40°21′N, 116°18′, 280 m above sea level) approximately 50 km north of the center of Beijing (see Figure 1). Satellite-derived NO_2 column data is also shown in the figure indicating that Beijing was located on the northern edge of the North China Plains which is one of most populated and polluted regions in China. Another large city, the Tianjin Municipality (population: ~10 million) is 150 km southeast. Chang Ping, a satellite town of Beijing with a population of 110,000, is 15 km southwest. Within 10 km of the site, there are only small villages with a low population density and thus very sparse anthropogenic emission sources. The study site is a fruit farm growing peaches and apricots, and the surrounding mountainous areas are densely covered by trees and other vegetations in the summer season.

[5] The field measurement took place from 20 June to 31 July 2005. Examinations of the mean surface pressure fields (not given here) show that a Subtropical/Pacific High dominated eastern China during this period. Beijing was located just at the northwest edge of the High, and was frequently affected by southwesterly or southeasterly winds. The weather during this period was characterized by very hot and humid conditions on some days, and convective clouds sometimes developed into storms in late afternoon; occasionally dry continental air masses from Siberia impacted Beijing giving rise to northwesterly winds. A prom-

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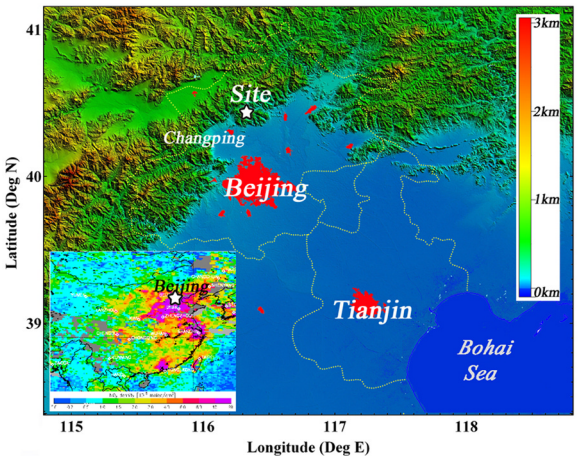

Figure 1. Map showing the location of the study site, topography, and land use in Beijing and surrounding regions. Urban areas are shown in red color. The figure in the bottom-left corner gives the mean tropospheric NO_2 column concentration during the measurement period of this study, which is derived from SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) onboard ENVISAT satellite (http://www.temis.nl/airpollution/no2.html).

inent mesoscale feature was the mountain-valley breezes that led to a strong diurnal variation in surface winds as shown in Section 3.1.

2.2. Instruments

[6] The setup of the instruments, their precisions and accuracies, and calibration methods has been described in detail elsewhere [e.g., *Wang et al.*, 2001, 2003]. Briefly O_3 was measured with a UV photometric analyzer; CO was measured with a non-dispersive infrared analyzer; SO_2 was measured by using a pulsed UV fluorescence analyzer. Nitric Oxide (NO) and NO_y was measured with a commercial chemiluminescence analyzer equipped with an externally placed molybdenum oxide (MoO) catalytic converter. The instruments were housed in a temperature-controlled room with ambient air being drawn through a PFA Teflon tube (inside diameter = 9.6 mm; length = 7.3 m) connected to a PFA manifold with a by-pass pump. The residence time of air in the sampling system was approximately 2 seconds [*Wang et al.*, 2001]. The analyzers were calibrated daily by injecting a span gas mixture in scrubbed ambient air (see *Wang et al.* [2001, 2003] for details). The CO analyzer was zeroed every two hours using an internal catalytic converter. Meteorological parameters were also measured at the site, including wind, temperature, relative humidity, and total solar radiation.

3. Results and Discussions

3.1. Ozone Statistics and Diurnal Variations

[7] During 39 days with complete measurement data, there were 18 days when maximum hourly ozone concentration exceeded 100 ppbv, which is China's standard for urban residential areas (Grade II). With reference to the US National Ambient Air Quality Standard (NAAQS), 13 days were found to have exceeded the 1-hour standard of 120 ppbv, and 20 days exceeded the 8-hour 80-ppbv standard. Moreover, there were 8 days when hourly O_3 was above 180 ppbv, with the maximum value of 286 ppbv being the highest reported concentration in China. These statistics reveal that the areas downwind of Beijing suffer from very serious photochemical pollution during summertime. The ozone concentrations found in our study are comparable to those observed in downwind U.S. urban areas during the 1970s [e.g., *Wolff et al.*, 1977; *Spicer et al.*, 1979], but the maximum concentration of O_3 and the frequency of episodes in Beijing have exceeded recent records [*Kleinman et al.*, 2002; *Berkowitz et al.*, 2004] in Houston, which is one of the most polluted U.S. metropolitan areas in terms of O_3.

[8] Figure 2 shows the average diurnal values for O_3, other trace gases, and surface winds measured at the site over the entire study period. The mean winds showed a clear diurnal variation with NW winds at night and SE flows during daytime, indicating the site was often influenced by the mountain-valley breezes resulting from the topography of the region. The mean O_3 concentration had a minimum of ~30 ppbv at 0700 LT (local time) and a maximum of ~90 ppbv at 1600 LT. NO_y and SO_2 also showed highest or elevated mean values at time of the O_3 peak, while the diurnal difference in the average CO concentration was less significant (with a mean value in the range of 600–700 ppbv). The generally higher trace gases concentration in daytime together with SE winds indicates transport of pollution from Beijing and other regional sources in the flatland to the mountainous areas in the afternoon. The relatively large standard errors shown in Figure 2 and the somewhat different diurnal profiles of the three primary pollutants reflect variability in source impact, chemical transformation/deposition, and dispersion characteristics for individual episodes as shown in Section 3.2. Examina-

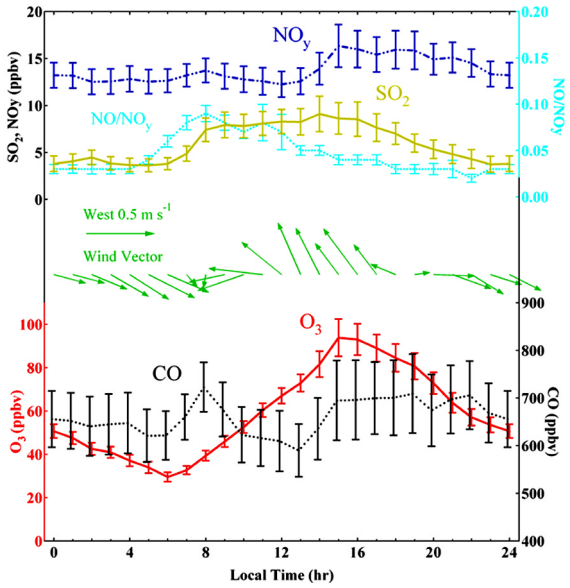

Figure 2. Average diurnal patterns of O_3, CO, SO_2, NO/NO_y, NO_y and vector wind at the site. Vertical bars are standard errors.

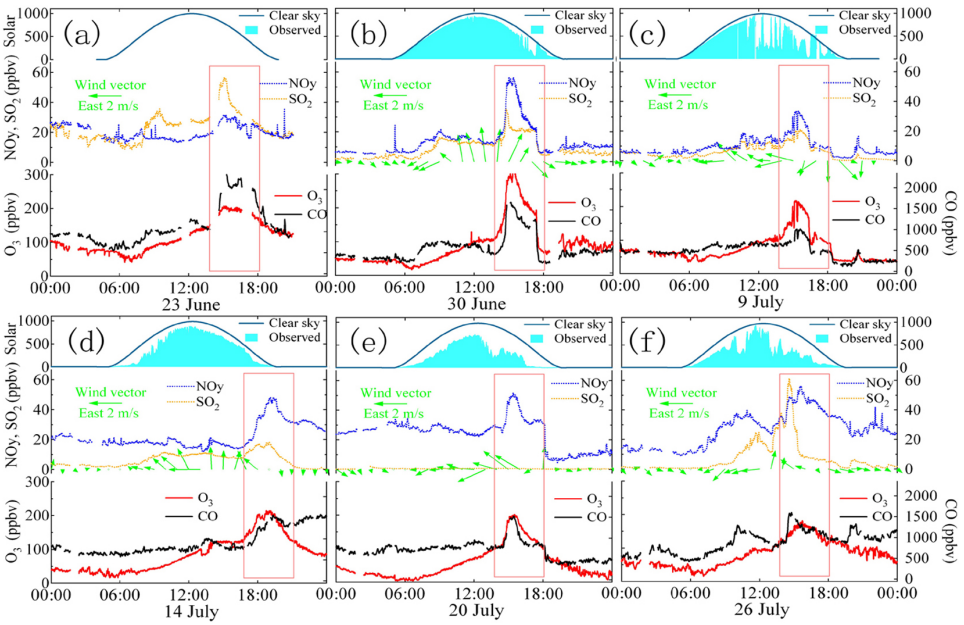

Figure 3. Times series of trace gases and meteorological parameters for (a) 23 June, (b) 30 June, (c) 9 July, (d) 14 July, (e) 20 July, and (f) 26 July, 2005. The "well-defined" urban plumes are shown in the panes.

tion of real-time aerosol data (not shown) also indicated elevated concentration of particulate in the afternoon.

3.2. Origin and Characteristics of Pollution Plumes

[9] To elucidate the source and atmospheric processes that caused the elevated concentrations of ozone (and other pollutants), we analyzed in detail six of the eight episodes during which hourly ozone exceeded 180 ppbv. Figure 3 gives minute-resolved data for O_3, CO, NO_y, SO_2, wind, measured solar radiation and calculated clear-sky solar radiation (wind was not measured on 23 June). These six cases were chosen as the data clearly indicated an impact of a well distinguished urban plume at the site. The clear-sky solar radiation was calculated using an empirical fit described by *Long and Ackerman* [2000] and was compared with the observed radiation to show the influence of clouds and/or pollutants on solar radiation.

[10] In all the episodes shown in Figure 3, O_3-laden plumes impacted the site in late afternoon, i.e. about 1400 $\sim$ 1800 LT, except on 14 July when the center of the plume arrived at the site at 1900 LT. The primary gases also showed sharp increases in concentrations along with ozone. The well-defined shape and the narrow width of the plumes suggest that these plumes had not experienced significant degree of dispersion and mixing since emission, implying that the plumes observed in the afternoon came from a large source not very far away from the study site. As Beijing is the closest metropolitan area in the upwind direction with strong emissions, plumes from the city could reach the site in a few hours of time, giving rise to the elevated concentrations of O_3 and other gases observed in the afternoon (see back trajectory analysis shown below).

[11] While the afternoon O_3 peaks can be attributed to same-day emission from Beijing, there were indications in our data of contributions from regional sources. Figure 3 shows that the concentrations of primary pollutants in some cases (23 and 30 June, 9 and 26 July) showed moderate enhancements between morning and early afternoon; this feature can be interpreted as the contribution of regional pollutants (including that from Beijing) emitted during the previous day and at night. Thus the afternoon peak was an additive effect from Beijing's emission. On July 14 and 20, the primary pollutant stayed high throughout the preceding night and morning, indicative of the 'trapping' of pollution in the mountain area due to very light winds.

[12] To gain further insights into the source region(s) of the observed high O_3, we calculated 3-day back trajectories with HYSPLIT4 model (HYbrid Single-Particle Lagrangian Integrated Trajectory model version 4.7, http://www.arl.noaa.gov/ready/hysplit4.html) for each hour of the observation. The wind fields were obtained from nesting mesoscale meteorological simulations (down to a 9-km resolution) using PSU/NCAR MM5 model. The model settings and physical parameterizations were identical to those described by *Ding et al.* [2004]. Based on the hourly trajectories, residence time of sampled air masses [*Ashbaugh*, 1983] are plotted to show the potential source region for the highest 25% (>75 ppbv) of O_3 (Figure 4). Consistent with the discussions above, the residence time analysis shows that during the period of highest O_3 pollution a majority of air-mass trajectories passed over the Beijing urban area from the south, suggesting significant contribution of emissions from the city during these events. By comparison, the back trajectories for the second highest 25% of O_3 were of more diverse origins (figure not shown), indicative of contribution from regional sources.

[13] Inspection of Figure 3 also shows that most of the episodes occurred under a cloudy condition, especially on 20 and 26 July during which only 50$\sim$60% integrated solar energy reached the ground level. MODIS imagery indicated coverage of clouds over Beijing and the surrounding areas on these two days, and yet hourly ozone concentrations could still reach over 180 ppbv indicating a very strong production potential of O_3 in these plumes. The 'super'

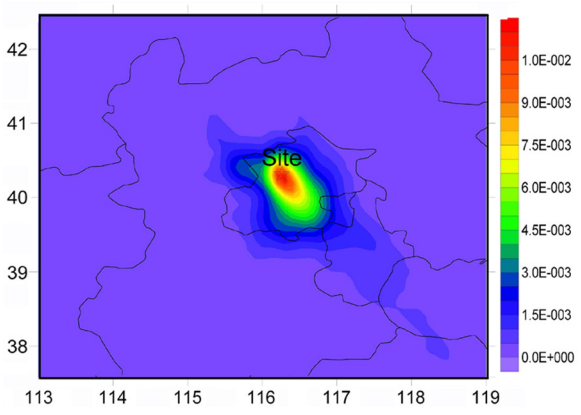

Figure 4. Potential source regions for the highest 25% of O_3 mixing ratios measured at the site.

episode observed on June 30 (1-h O_3 = 286 ppbv) was a result of intensive solar radiation and presence of abundant precursors in the plume ($NO_y \sim 60$ ppbv). We further examined the CO-NO_y regression slopes (figure not shown) and found no significant difference between the 'super' episode and the rest of the cases examined (28 versus 20–30 ppbv/ppbv), except for the June 23 episode which had a very high CO/NO_y of 78. The very large CO/NO_y ratio together with the highest SO_2/NO_y ratio on that day (see Figure 3a) may suggest an impact of emissions from the steel factories in the Shijingshan district, west of Beijing. The moderate CO-NO_y ratios (20–30) in most of the episodes were similar to the urban Beijing values determined from an analysis of the samples collected in a Tedlar bag during the study, suggesting dominant contribution of urban traffic sources for the majority of the episodes examined. The CO/NO_y ratios in Beijing are much larger than those in US vehicular emissions (~10) [*Parrish et al.*, 2002], reflecting difference in emission characteristics in Beijing and the US cities.

3.3. Ozone Production Efficiency in Beijing Plumes

[14] The amount of O_3 produced in a plume depends on the chemical mix of the plume (abundance of NO_x and VOC and their ratio) as well as meteorological conditions that affect the dispersion and removal of constituents in the plume. The ozone production efficiency is the number of O_3 molecules produced by oxidation of each NO_x molecule within a parcel of air, and empirically this value can be inferred from the regression slope of observed scatter plot of O_3 versus NO_z ($NO_z = NO_y$-NO_x) [*Trainer et al.*, 1993]. NO_2 was not measured in our study, but based on various indicators of photochemical age in our data, it is expected that NO_y in the afternoon during the episode days was dominantly in the form of NO_z. Thus we use here NO_y as a surrogate of NO_z.

[15] Figure 5 shows the O_3-NO_y scatter plot for 1-minute data obtained during afternoon hours (shown in pane in Figure 3) for all the six urban plumes. A strong positive correlation ($r^2 > 0.9$) was found in each of these plumes. The regression slope was in the range of 3.0–5.6 (ppbv/ppbv), with smaller values (3.0–3.3) obtained on cloudy days indicating a decreased production efficiency of O_3 as a result of reduced sunlight. We further calculate the photostationary state (PSS) concentrations of NO_2 based on the measured O_3 and NO for the 6 episodes. The photolysis rate constant for NO_2 (jNO2) was calculated using the NCAR Tropospheric Ultraviolet-Visible (TUV) model [*Madronich*, 1987] with cloud optical thickness diagnosed from the measured and modeled total solar radiation. We then obtain the inferred NO_x ($NO_{meas.} + NO_{2cal.}$) and NO_z. The O_3-NO_z regression slopes ranged from 3.3 to 7.6 for the six episodes examined, with an averaged afternoon NO_x to NO_y ratio of 0.2–0.3. Here we should note that the assumption of NO_2 in PSS has led to an underestimate of NO_2 concentrations (thus an overestimate of NO_z), because the conversion of NO to NO_2 by HO_2 and RO_2 has not been taken into account. The inferred O_3-NO_z slopes for Beijing are similar to the observed value in Nashville (4.7) [*Zaveri et al.*, 2003], but smaller than the values (6–11) observed in Houston [*Berkowitz et al.*, 2004; *Daum et al.*, 2004] and larger than the observation of 2.7 in Phoenix with a very dry climate [*Kleinman et al.*, 2002].

[16] An interesting observation in the Beijing study is that the positive O_3-NO_y relationship in the Beijing plumes extends to very high NO_y values (55 ppbv; see Figure 5). This feature is different from some of the observations in the US showing a leveling off of the O_3-NO_y slope at NO_y levels >15 ppbv or of the O_3-NO_z slope at NO_z > 10 ppbv [e.g., *Trainer et al.*, 1993, 1995; *Olszyna et al.*, 1998]. The latter can be explained by a reduced efficiency of O_3 production in concentrated urban plumes in which ozone chemistry is often in a VOC-limited regime. The linear correlation over the entire observed NO_y concentration range in our study imply that the ozone formation in Beijing is limited by NO_x or by both NO_x and VOC, that is, the O_3-rich plumes contained a moderate to large VOC to NO_x ratio. This in turn suggests that control of NO_x may be needed to reduce the photochemical ozone pollution in rural plume-impact areas of Beijing.

4. Conclusions

[17] Our six-week observation revealed frequent occurrences of O_3 pollution episodes in mountainous areas north of Beijing, with the highest 1-h O_3 value of 286 ppbv

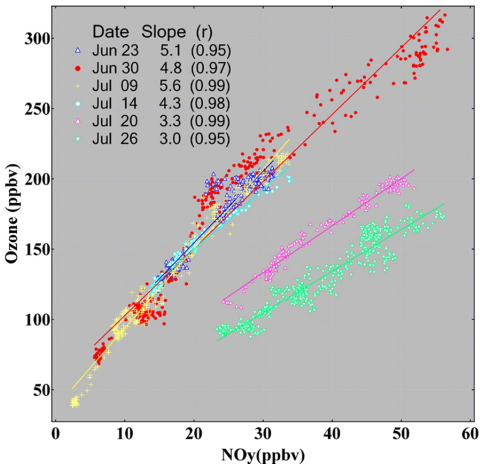

Figure 5. Scatter plot of O_3 versus NO_y for the six urban plumes given in Figure 3.

recorded. Concurrently measured O_3 and other gases (and aerosols) provided valuable insights into the source and character of the observed plumes. The highest O_3 concentrations were due to transport of the Beijing plumes superimposed on pollution contributed by regional sources. O_3 and NO_y were strongly correlated in individual plumes even for NO_y levels as high as 55 ppbv, indicating the important role of oxides of nitrogen in the formation of O_3 in Beijing. The very high levels of O_3 suggest strong emissions of NO_x and VOC from Beijing and imply significant negative effects on vegetation and regional air quality around Beijing. Results suggest that current air-quality management efforts in Beijing should give more emphasis on the control of photochemical ozone pollution.

[18] **Acknowledgments.** The authors are grateful to Tang Jie and Liu Xiang for their help in selecting the measurement site, Steven Poon, Joe Cheung, Anson Wong, and Zhou Xuehua for their contributions to the field study, and Joey Kwok for his help in data reduction. We also thank Wang Wenxing for his support of this study, NOAA Air Resources Laboratory for provision of HYSPLIT model, and the two anonymous reviewers for their helpful comments and suggestions. This research was funded by the Research Grants Council of Hong Kong Special Administrative Region (project PolyU5144/04E).

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