

Photochemical production of ozone in Beijing during the 2008 Olympic Games

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Abstract. As a part of the CAREBeijing-2008 campaign, observations of O₃, oxides of nitrogen (NO_x and NO_y), CO, and hydrocarbons (NMHCs) were carried out at the air quality observatory of the Peking University in Beijing, China during August 2008, including the period of the 29th Summer Olympic Games. The measurements were compared with those of the CAREBeijing-2006 campaign to evaluate the effectiveness of the air pollution control measures, which were conducted for improving the air quality in Beijing during the Olympics. The results indicate that significant reduction in the emissions of primary air pollutants had been achieved; the monthly averaged mixing ratios of NO_x, NO_y, CO, and NMHCs decreased by 42.2, 56.5, 27.8, and 49.7 %, respectively. In contrast to the primary pollutants, the averaged mixing ratio of O₃ increased by 42.2 %. Nevertheless, it was revealed that the ambient levels of total oxidant (O_x = O₃ + NO₂ + 1.5NO_z) and NO_z were reduced by 21.3 and 77.4 %, respectively. The contradictions between O₃ and O_x were further examined in two case studies. Ozone production rates of 30–70 ppbv h⁻¹ and OPE_x of ~8 mole mole⁻¹ were observed on a clear-sky day in spite of the reduced levels of precursors. In that case, it was found that the mixing ratio of O₃ increased with the increasing NO₂/NO ratio, whereas the NO_z mixing ratio leveled off when NO₂/NO > 8. Consequently, the ratio of O₃ to NO_z increased to above 10, indicating the shift from VOC-sensitive regime to NO_x-sensitive regime. However, in the other case, it was found that the O₃ production was inhibited significantly due to substantial reduction in the NMHCs. According to the observations, it was suggested that the O₃ and/or O_x production rates in Beijing

should have been reduced as a result of the reduction in the emissions of precursors during the Olympic period. However, the nighttime O₃ levels increased due to a decline in the NO-O₃ titration, and the midday O₃ peak levels were elevated because of the shift in the photochemical regime and the inhibition of NO_z formation.

1 Introduction

Urbanization is undergoing worldwide, particularly in the developing countries. The intensive human activities unavoidably result in substantial emissions of air pollutants in urban areas. The anthropogenic compounds can react in the atmosphere and, consequently, lead to the formation and accumulation of secondary pollutants and cause further deterioration of air quality. Exposure to the air pollutants has been identified as one of the major health risks of the residents in megacities (Molina et al., 2004).

With a total population over 10 million, Beijing is one of the megacities in the world. The economic development has brought up the number of vehicles, factories, as well as power plants in the Beijing metropolitan area during the last two decades. As a result, Beijing has suffered from serious air pollution (Wang et al., 2006; An et al., 2007). Being the host city of the 29th Summer Olympic Games, the Beijing government setup rather aggressive action plans to reduce the emissions of air pollutants in Beijing and its surrounding areas during the Olympic period. In particular, the traffics were restricted temporarily to reduce the vehicular exhausts within the Beijing City (Wang et al., 2009a). Emission inventory studies indicated that the traffic emissions of volatile organic compounds (VOCs), carbon monoxide (CO),



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nitrogen oxides (NO_x), and particulate matters (PM_{10}) were reduced by $\sim 50\%$ from their respective normal levels in Beijing (Zhou et al., 2010; Wang et al., 2010c). The estimates of NO_x reduction are consistent with previous reports based on satellite observations, which indicated a reduction of $\sim 40\text{--}60\%$ in the column density of NO_2 over Beijing during the Olympic Games (Mijling et al., 2009; Witte et al., 2009). Besides, the reductions in the vehicular emissions of the other air pollutants have also been validated by a series of ground-based observations (Liu et al., 2009; Wang et al., 2009a, b, 2010a, b). Evidently, the air pollution control measures had successfully reduced the ambient levels of the primary air pollutants in Beijing during the Olympic Games.

In contrast to the substantial reduction of the primary air pollutants, the mitigation of ozone (O_3) in Beijing during the Olympic period was not as expected. Observations at a rural site showed that the monthly averaged daytime mixing ratio of O_3 for August 2008 was reduced by $\sim 20\%$, as being compared with the same month of 2006–2007 (Wang et al., 2009b). However, comparing the observations in Beijing downtown for periods before and after the traffic control indicated an increase of 16% in the mixing ratio of O_3 (Wang et al., 2010b). The increases in the O_3 mixing ratio were not consistent with the decreases in the emissions of precursors, i.e. NO_x and VOCs. In particular, the ozone formation potentials (OFPs) of the non-methane hydrocarbons (NMHCs) had been reduced by 48% (Wang et al., 2010a). Wang and Xie (2009) attributed the inconsistency to the reduced $\text{NO}\text{--}\text{O}_3$ titration, which was a result of the reduction in NO_x emissions. Wang et al. (2009b) suggested that the high O_3 episodes in Beijing during August 2008 were mostly meteorology-driven. Wang et al. (2010b) argued that the transport of photochemical plumes from the surrounding areas to Beijing was the major contributor of the “peaks” of O_3 in Beijing downtown. To date, the high O_3 levels in Beijing during the Olympics are still an open issue.

The “Campaign for Air Quality Research in Beijing and Surrounding Region – 2008” (CAREBeijing-2008) is an intensive experiment for investigating the air quality in Beijing during the Olympic period and evaluating the effectiveness of the air pollution control measures. Furthermore, while the O_3 –precursors relationship was established mostly on theories and/or chamber studies, the air quality control program for the Beijing Olympics provided a unique opportunity to examine the response of ambient O_3 level to a drastic reduction in the emissions of precursors. In this study, the measurements of O_3 and its precursors carried out at the observatory on the campus of the Peking University are presented. The measurements are compared with those conducted in the summer of 2006, i.e. CAREBeijing-2006, to show the air quality effects due to the control measures. Moreover, the data are analyzed in terms of photochemistry to explain the disagreement between O_3 and the primary air pollutants in Beijing during the 2008 Summer Olympics.

2 Experimental methods

To investigate the air quality and atmospheric chemistry in Beijing, an intensive observatory was setup on the campus of the Peking University (PKU) during the CAREBeijing-2008. The detailed geographic characteristics of this site have been presented in other papers of this special issue (e.g., Wang et al., 2010a) and, therefore, are not described here. A comprehensive set of instrument was installed at the PKU station to measure the concentrations of major air pollutants, with emphases upon ozone and aerosols. However, only the instruments relevant directly to this study will be outlined in the followings.

The measurements of nitric oxide (NO), nitrogen dioxide (NO_2), and total reactive nitrogen (NO_y) were carried out concurrently with a time resolution of 1 min. NO was measured using a chemiluminescence detector (Model 42C-TL, Thermo Scientific). NO_2 was measured with a system consisting of a chemiluminescence detector (Model CLD 88p, ECO Physics) and a photolytic converter (Model PLC 860, ECO Physics). The efficiency of the converter kept at $\sim 66\%$ throughout the campaign, which was determined with gas titration method. A NO_y converter (ECO Physics) was employed to reduce the NO_y species to NO with CO on the surface of a gold tube at 300°C . Then, the second CLD 88p detector was used for quantification of NO_y . The efficiency of this converter was $\sim 100\%$, which was checked by HNO_3 measurement in laboratory before the field experiment and is consistent with the literatures (e.g., Fehsenfeld et al., 1987). Daily calibration of the chemiluminescence detectors was accomplished using 0.5–200 ppbv NO, which was generated by dilution of 10 ppmv standard NO (Scott Specialty Gases, USA) with NO-free air from an in-situ zero-gas generator (Model PAG003, ECO Physics). The detection limits of the instruments were estimated by 3 times the standard deviation of the signals of zero-air measurements, which were 0.3, 0.1, and 0.3 ppbv for NO, NO_2 , and NO_y , respectively.

For in-situ measurement of hydrocarbons (65 species, as listed in Table 1), ambient air was analyzed by an automated GC/MS/FID (Varian CP-3800 and Saturn 2200 MS) system using dual-columns and dual-detectors to simultaneously analyze both low- and high-boiling point non-methane hydrocarbons (NMHCs). This system is an upgrade of the one as described by Chang et al. (2003). A built-in cryo-trap packed with fine glass beads was cooled with liquid nitrogen to -170°C . Air sample was drawn from the sample inlet through the cryo-trap at a rate of 12 mL min^{-1} for 20 min, which gave an aliquot of 240 mL air sample. Desorption was made by flash heating the trap to 85°C , and a stream of ultra-high purity helium (99.9999%) was used to flush the trapped hydrocarbons to the columns. A glass Y-splitter was used to divide the flow into two streams for the following two columns, i.e. a PLOT column (Chrompack; $30\text{ m}\times 0.32\text{ mm}$; $\text{df} = 5.0\text{ }\mu\text{m}$) connected to FID for separation and detection of C2–C4 compounds, and a DB-1 column (J&W;

Table 1. The NMHCs measured in this study.

1,2,3-trimethylbenzene*	benzene*	n-butane*
1,2,4-trimethylbenzene*	beta-pinene	n-decane*
1,3,5-trimethylbenzene*	cis-2-butene*	n-heptane*
1-butene*	cis-2-hexene	n-hexane*
1-pentene*	cis-2-pentene*	n-nonane*
2,2,4-trimethylpentane*	cyclohexane*	n-octane*
2,2-dimethylbutane*	cyclopentane*	n-pentane*
2,3,4-trimethylpentane	cyclopentene	n-propylbenzene*
2,3-dimethylbutane	ethane	n-undecane*
2,3-dimethylpentane*	ethene	o-diethylbenzene
2,4-dimethylpentane*	ethylbenzene*	o-ethyltoluene*
2-methyl-1-pentene	ethyne	o-xylene*
2-methyl-2-butene	isobutane*	p-diethylbenzene*
2-methylheptane*	isobutene	p-ethyltoluene*
2-methylhexane*	isopentane*	propane*
2-methylpentane*	isoprene*	propene*
3-methyl-1-butene	isopropylbenzene*	styrene*
3-methylheptane*	m,p-xylene*	toluene*
3-methylhexane*	m-diethylbenzene*	trans-2-butene*
3-methylpentane*	methylcyclohexane*	trans-2-hexene
4-methyl-1-pentene	methylcyclopentane*	trans-2-pentene*
alpha-pinene	m-ethyltoluene*	

* Species measured in the CAREBeijing-2006.

60 m×0.32 mm; $df = 1.0 \mu\text{m}$) connected to MS for the separation and detection of C5-C11 compounds. The GC oven starts at -15°C for 1.5 min, ramps to 0°C at $10^\circ\text{C min}^{-1}$, to 140°C at 5°C min^{-1} , to 180°C at $20^\circ\text{C min}^{-1}$, and ends at 180°C for 9.5 min.

In addition to the $\text{NO}/\text{NO}_2/\text{NO}_y$ and NMHCs instruments for this intensive experiment, the PKU observatory was equipped with a general air quality station. All the instruments were calibrated regularly at the mid-night of each day during the campaign. The data of CO and O_3 from the station will be included in the following analysis and discussion. Besides, the total short-wave irradiance, SWI, ($0.3\text{--}3.0 \mu\text{m}$) was measured using an Eppley precision spectral pyranometers (PSP). The PSP sampled data per second and were subsequently averaged to 1-min resolution.

3 Results and discussion

3.1 Overview of the time series

Figure 1 illustrates the time series of the hourly averaged mixing ratios of the respective species (NO , NO_2 , NO_y , NO_z , O_3 , O_x , CO, and NMHCs) measured at the PKU station during August 2008. Here NO_z is defined as the differences between NO_y and NO_x ($\text{NO}_y - \text{NO}_x$), which are the oxidation products of NO_x . Note that the “total oxidant” (O_x) is defined following Levy et al. (1985),

$$\text{O}_x = \text{O}_3 + \text{O}({}^3\text{P}) + \text{O}({}^1\text{D}) + 0.5 \cdot \text{OH} + 0.5 \cdot \text{HO}_2 + \text{H}_2\text{O}_2 \quad (1) \\ + \text{NO}_2 + 2 \cdot \text{NO}_3 + 3 \cdot \text{N}_2\text{O}_5 + 1.5 \cdot \text{HNO}_3.$$

Given that the mixing ratios of radicals, oxygen atoms, H_2O_2 and N_2O_5 are rather low in the atmosphere, the right hand side of Eq. (1) is dominated by O_3 , NO_2 , and HNO_3 . Further, because HNO_3 is usually the predominant component of NO_z in an urban area, the mixing ratio of O_x was estimated by $[\text{O}_3 + \text{NO}_2 + 1.5 \cdot \text{NO}_z]$ in this study.

In the first week of August 2008, just before the Olympic Games, Beijing experienced an episode of high O_3/O_x . The hourly $[\text{O}_3]$ and $[\text{O}_x]$ reached their respective maxima, 135 and 169 ppbv, at 12:00 (local time = GMT + 08:00) on 3 August. The maximal levels of NO_x , NO_y , and NMHCs were observed at 11:00, i.e. 1 h prior to the peaks of O_3 and O_x . Note that there was another O_3/O_x peak occurred at 17:00 on 3 August, implying the coupling influences of transport and in-situ photochemical production of ozone. This case will be analyzed and discussed in more details later on. The mixing ratio of O_3 declined gradually since 6 August and remained below 100 ppbv, in spite of the daily NO_x/NO_y spikes, during the Olympic Games. Apparently, the emission of NO_x did not contribute efficiently to the formation of O_3 in Beijing during the Olympics. The reduced photochemical activity was also indicated by the absence of NO_z peaks, as shown in the NO_z time series. The mitigation of O_3/O_x during the Beijing Olympic Games has been attributed to the weather conditions and/or the reduction in the emissions of precursors (Wang, et al., 2009b, 2010b). However, it was revealed from the time series that the production of O_3 was not enhanced significantly on some days (e.g., 15–16 August) with strong solar flux. Thus the mechanisms for the observed reduction in O_x need to be studied furthermore.

3.2 Effectiveness of the emission control measures

To examine the effectiveness of the emission control measures upon the air quality in Beijing, the ambient levels of nitrogen oxides, O_3 , O_x , NMHCs, and CO measured in this study were compared with the measurements made during the CAREBeijing-2006 campaign, i.e. 12 August – 9 September, 2006 (Chou et al., 2009). Table 2 tabulates the averages of the measurements for August 2008 and CAREBeijing-2006, respectively, and the differences are interpreted as the effectiveness of the emission control measures. In general, according to the observations, the reduction in the levels of primary pollutants was very significant; NO_x , NO_y , NMHCs, and CO mixing ratios were reduced by 42.2, 56.5, 49.7, and 27.8 %, respectively. This is consistent with the results of previous modeling as well as observation studies (e.g., Wang et al., 2009a, 2010a, b, c). Averaged meteorological parameters (wind speed, T, RH) for 2006 and 2008 campaigns are also listed in Table 2. The ambient temperature and humidity in August 2008 are slightly higher

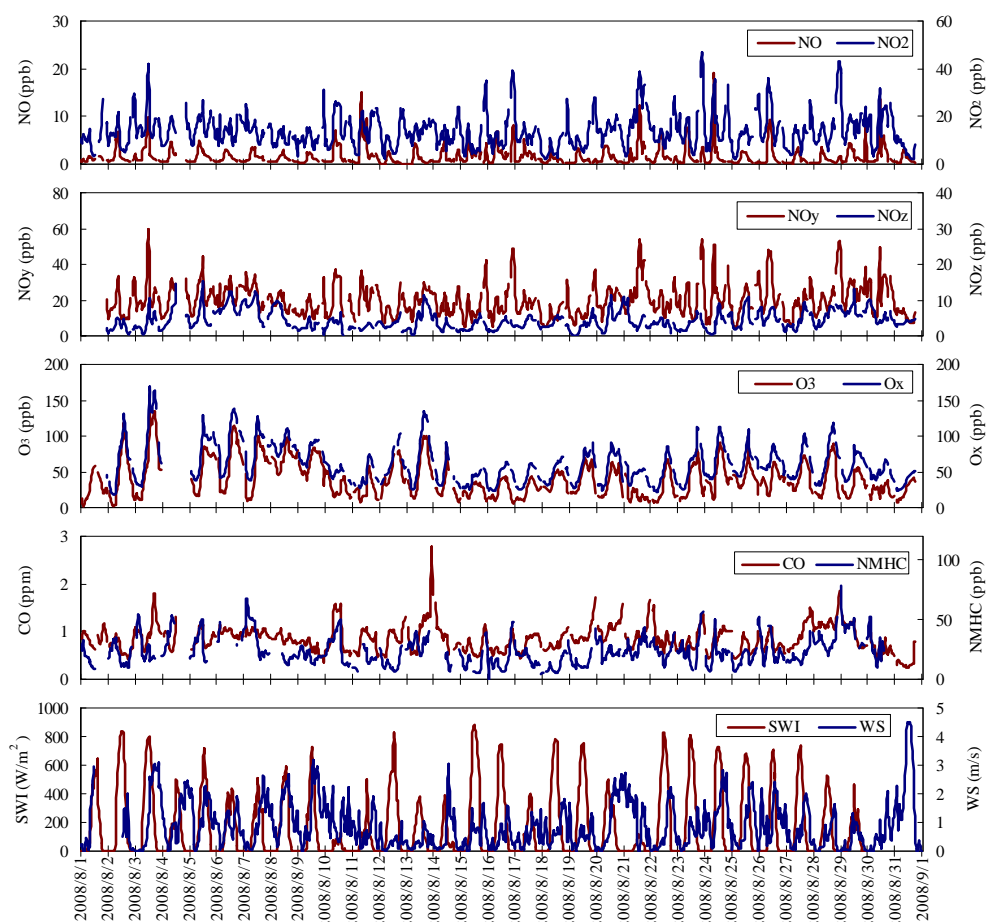


Fig. 1. Time series of the hourly averaged concentrations of the trace gases, wind speed, and short wave irradiance measured at the PKU station during August 2008.

than during the CAREBeijing-2006 campaign, whereas the averaged wind speed decreased by $\sim 30\%$. Obviously, the reduction in the mixing ratios of air pollutants can not be explained by the changes in the meteorological conditions. This is in agreement with the results of Wang et al. (2009b).

In contrast to the primary pollutants, the averaged level of O_3 increased from 28.2 ± 27.2 ppbv to 40.1 ± 25.1 ppbv, or by 42%. Meanwhile, the sum of O_3 and NO_2 mixing ratios increased from 48.2 ± 24.5 ppbv to 53.9 ± 25.0 ppbv (11.8%), which means reduced titration effect between O_3 and NO for the reduction in NO_x emission can explain only partly the increases in ambient O_3 . It is underlined that the averaged level of O_x decreased from 76.6 ± 28.7 ppbv to 60.3 ± 26.9 ppbv, which is equivalent to a reduction of 21%. Among the components of O_x , the mixing ratios of NO_z decreased most significantly. The campaign average of NO_z mixing ratio decreased from 19.0 ± 6.3 ppbv to 4.3 ± 2.7 ppbv, i.e. 77.4%. The major cause of the drastic decreases in NO_z is most likely the reduction in NO_x emissions. Nevertheless, it could also be a result of enhanced wet deposition in the August 2008. It is worth noting that the present study is the first re-

port showing the consistency between the levels of O_x and its precursors and indicating the changes in the composition of oxidant in Beijing during the 2008 Olympics.

In addition to the general assessment, the diurnal variations of the mixing ratios of trace gases could provide further insight, in particular the implications for photochemistry. Figure 2a–d depict the averaged diurnal patterns of NO, NO_2 , NO_z and NO_y , respectively, for the CAREBeijing-2006 and CAREBeijing-2008. The most striking features are that the reduction in NO and NO_2 occurred in the morning and evening but not as significantly during the midday, whereas the reduction in NO_z persisted throughout the whole day. Chou et al. (2009) indicated efficient conversion of freshly emitted NO_x to NO_z in the morning during CAREBeijing-2006. The results of this study further suggest that the diminution of the morning rush-hour emissions of NO_x can contribute most effectively to the reduction of NO_z . However, the persisted levels of NO and NO_2 during midday were not agreeing with the emission control measures. Figure 2e–f display the diurnal variations of the other two major primary pollutants, CO and NMHCs. In contrast to NO_x , the

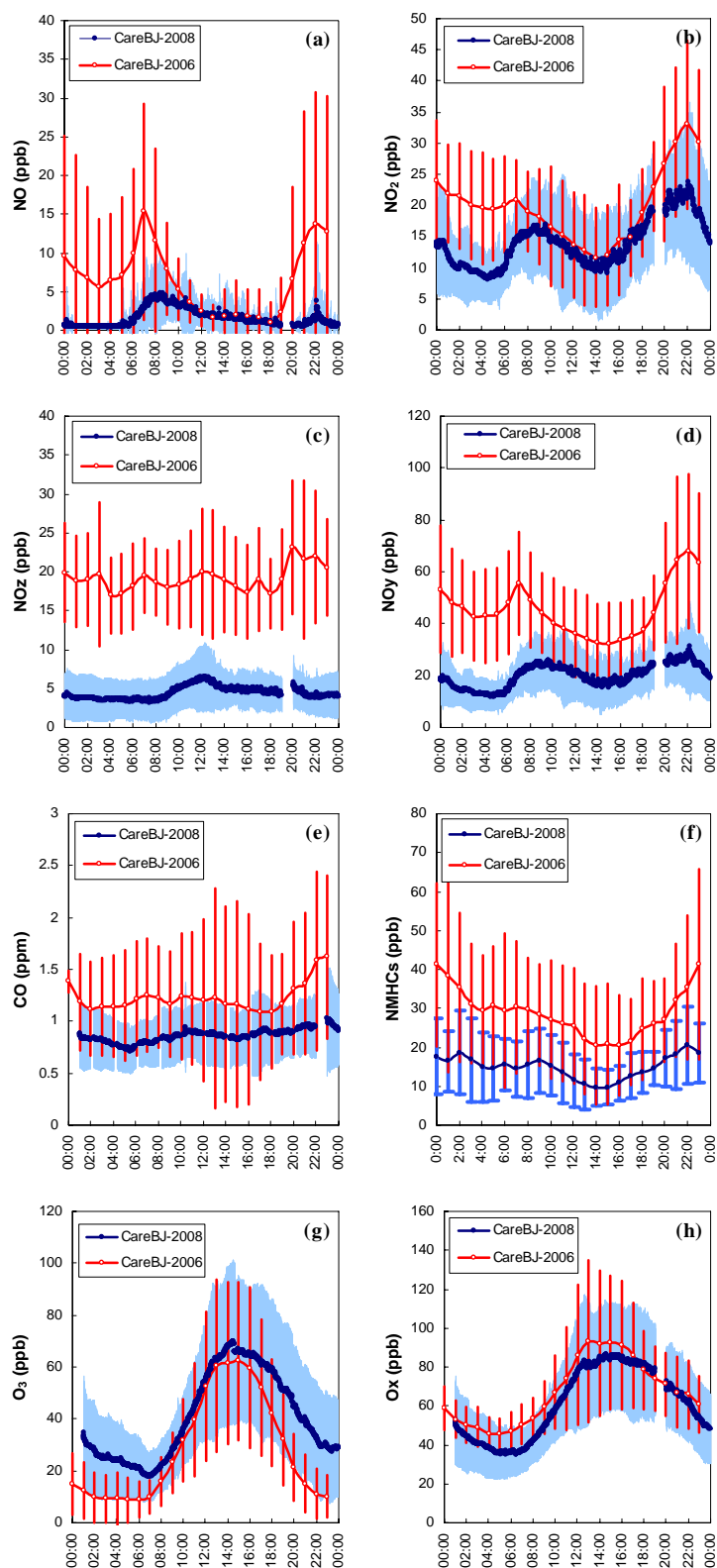


Fig. 2. Averaged diurnal variations in the mixing ratios of trace gases measured at the PKU observatory during the CAREBeijing-2006 and CAREBeijing-2008, respectively. The time resolution of the measurements, except NMHCs, of the 2008 campaign is 1 min, whereas the results of the 2006 campaign are hourly based. The ranges of $\pm 1\sigma$ are indicated by the error bars associated with the hourly means or shaded for the 1-min. data. (a) NO; (b) NO₂; (c) NO_z; (d) NO_y; (e) CO; (f) NMHCs; (g) O₃; (h) O_x.

Table 2. Statistics of the ambient levels of trace gases and meteorological parameters measured in Beijing during CAREBeijing-2006 and CAREBeijing-2008. The standard deviation of each mean value is noted in the parentheses.

	CareBeijing-2006 (12 Aug–9 Sep 2006)	CareBeijing-2008 (1–31 Aug 2008)	Reduction (%)
NO (ppb)	6.9 (11.3)	1.6 (1.9)	76.8
NO ₂ (ppb)	19.5 (10.2)	13.7(7.2)	29.7
NO _x (ppb)	26.3 (17.5)	15.2 (8.2)	42.2
NO _y (ppb)	45.3 (21.5)	19.7 (9.0)	56.5
NO _z (ppb)	19.0 (6.3)	4.3 (2.7)	77.4
NMHC* (ppb)	29.0(17.0)	14.6 (8.0)/23.3 (11.9)	49.7
CO (ppb)	1173 (623)	847 (275)	27.8
O ₃ (ppb)	28.2 (27.2)	40.1 (25.1)	−42.2
O ₃ +NO ₂ (ppb)	48.2 (24.5)	53.9 (25.0)	−11.8
O _x (ppb)	76.6 (28.7)	60.3 (26.9)	21.3
O _{3_max} (ppb)**	69.9 (33.9)	73.3 (25.3)	−4.9
O _{x_max} (ppb)**	120.8 (42.3)	96.5 (29.1)	20.1
Temp (°C)	25.8 (4.8)	27.4 (4.1)	−6.2
RH (%)	64.3 (19.9)	68.8 (17.2)	−7.0
Wind Speed (m s ^{−1})	1.4 (1.3)	0.9 (0.8)	35.7

* The NMHCs measurements of CAREBeijing-2008 include 65 species as listed in Table 1; among which 49 species were measured in CareBeijing-2006. The reduction ratio is based on the measurements of 49 species.

** O_{3_max} and O_{x_max} denote the daily peak levels of O₃ and O_x, respectively.

mitigation of air pollution was quite evident in the figures. Indeed, the reduction in traffics and relevant pollutants' emissions has been validated by on-road measurements (Wang et al., 2009a). Thus the persisted levels of NO and NO₂ during midday is inferred to be a result of photochemical dynamics. This inference will be examined in the following case studies. Figure 2g–h depict the diurnal patterns for O₃ and O_x, respectively. The mixing ratio of O₃ was higher during the 2008 campaign, whereas O_x was higher in 2006. The differences in O₃ were much larger in nighttime than in daytime, indicating the changes in the NO–O₃ titration due to emission reduction. The mixing ratio and the increasing rate of O₃ from morning to noontime are comparable in the two campaigns; meanwhile the O_x of 2008 campaign kept slightly lower than in the 2006 campaign. Note that the mixing ratio of O₃ kept increasing in the early afternoon of 2008 and resulted in significantly higher daily maximum than in 2006, disagreeing with the behavior of O_x. In terms of monthly average, the daily peak level of 1-h O₃ (O_{3_max}) in August 2008 increased by 4.9 % than during the 2006 campaign, whereas the O_{x_max} (daily peak level of 1-h O_x) was reduced by 20.1 % (shown in Table 2). The inconsistency between O₃ and O_x implies that the increasing O₃ in early afternoon was not caused by enhancement in O₃ production, and was more likely a result of changes in the partition among the components of O_x.

3.3 Ozone production efficiency of NO_x: case studies

Despite of the prolonged rainy events in Beijing during August 2008, there were still some days of clear skies in-between the rains (as shown in Fig. 1) that allow in-depth analysis upon the photochemical reactions. Ozone production efficiency of NO_x (OPE_x) is among the key parameters of NO_x–O₃ chemistry, which is defined as the number of ozone molecules produced by one NO_x molecule in the NO_x-catalyzed photochemical reactions (Liu et al., 1987). In the followings, two distinct cases will be presented in the context of OPE_x. The case of 3 August is a high O₃ episode, whereas the O₃ mixing ratio was leveling off at 30–40 ppbv in the daytime of 15 August.

3.3.1 Case 1: 3 August 2008

Figure 3a–e illustrate the mixing ratios of trace gases and the meteorological parameters measured at the PKU observatory on 3 August 2008. As indicated by the solar flux, it was a rather clear day. Advection of air mass was inhibited until the nocturnal boundary layer got broken in the morning and, then, southerly flows were prevailing throughout the day. The common NO_x/NO_y peaks for morning rush hours in an urban area were diminished significantly, as comparing with the measurements of CAREBeijing-2006 (Chou et al., 2009). Nevertheless, the freshly emitted NO was still noticeable. The mixing ratios of O₃, O_x, and NO_z increased drastically from ~09:00 to ~12:00. Note the spikes of NO/NO₂/NO_y peaking at ~11:00, which resulted in the titration dip in O₃.

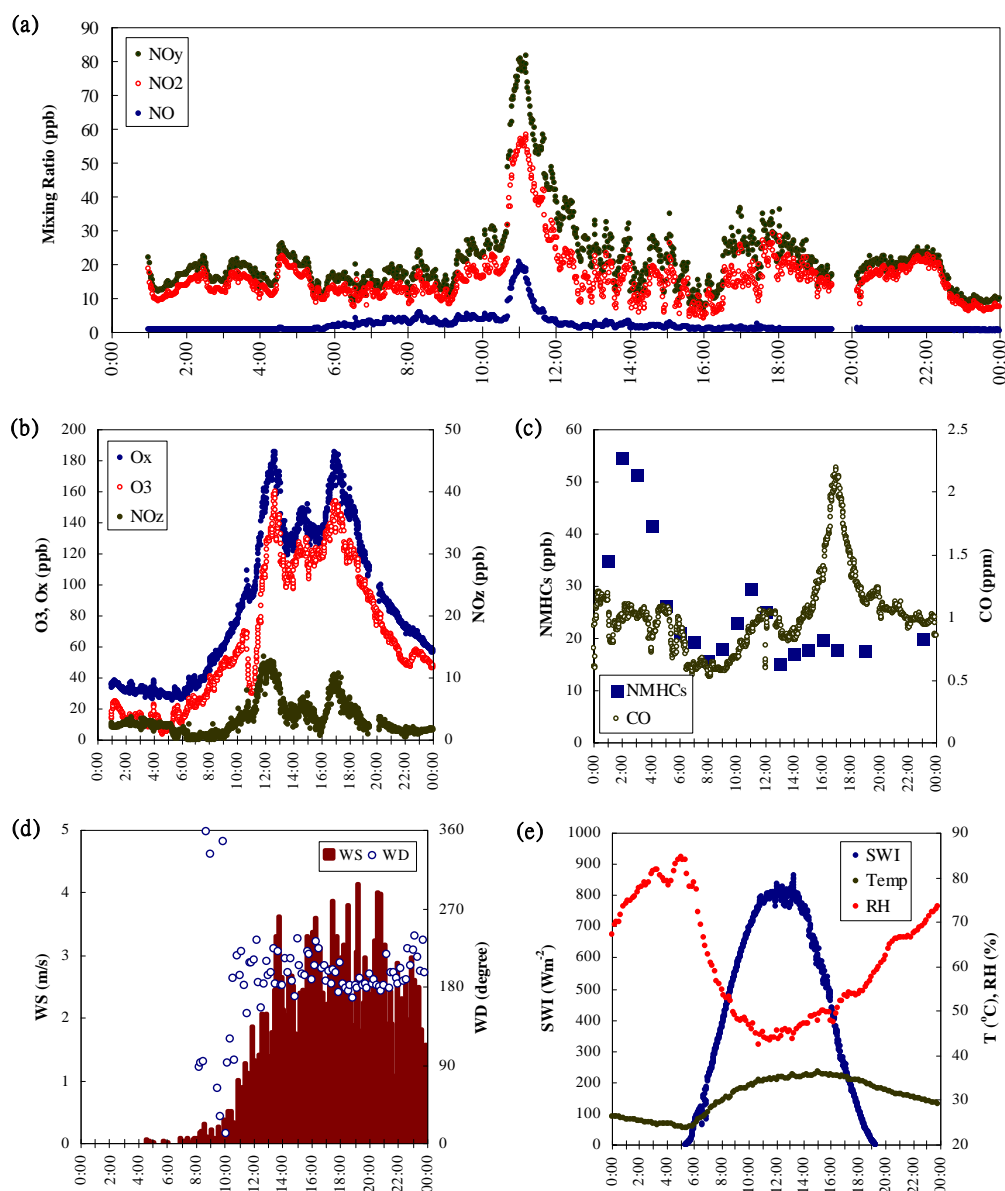


Fig. 3. Time series of the mixing ratios of trace gases and the meteorological conditions in Beijing for 3 August 2008. **(a)** NO, NO₂, and NO_y; **(b)** O_x, O₃, and NO_z; **(c)** NMHCs and CO; **(d)** wind speed and direction; **(e)** ambient temperature, RH, and SWI.

The causes of the event are not clear yet, but most likely due to some local activities. Figure 4 analyzes the data in terms of ozone production efficiency of NO_x (OPE_x) to examine the perturbation of the NO_x spike upon the O₃ production. Note that the derivation of OPE_x was following the regression method suggested by Trainer et al. (1993); however, instead of analyzing the correlation of O₃ and NO_z, here the OPE_x was derived from the slope of [O_x] vs. [NO_z]. It was revealed that the OPE_x decreased from 8.6 before the NO_x spike to 3.6 during the episode and, in turn, bound up to 7.9 mole mole⁻¹ after the event. Obviously, the NO_x injected into the atmosphere was converted to NO_z efficiently dur-

ing the episode. The enhanced NO_x-NO_z conversion should have increased the consumption of radicals and, thereby, retarded the ozone production. Figure 5 shows that the 1-min mixing ratios of O₃ (10:30–12:30) correlate linearly with the corresponding ratios of NO₂ to NO, being consistent with the photo-stationary state relation. This consistency allows approximation of the ozone production rate (P_{O₃}) following the photo-stationary state equation (Frost et al, 1998),

$$P_{O_3} = j_{NO_2} \cdot [NO_2] - k_{NO-O_3} \cdot [O_3] \cdot [NO] \quad (2)$$

Without direct measurement of the photolysis rates of NO₂, j_{NO_2} , the values of j_{NO_2} were estimated being

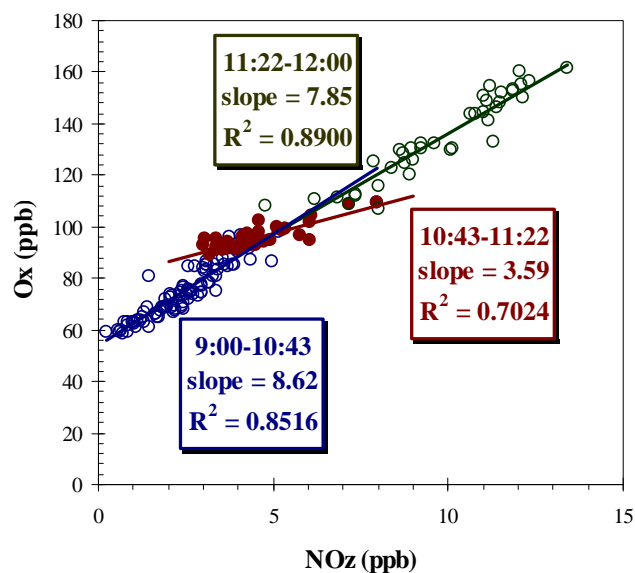


Fig. 4. Correlation between O_x and NO_z observed at the PKU observatory in the morning of 3 August 2008. The data are divided into three periods to characterize the ozone production efficiency of NO_x (OPE $_x$) before, during, and after the spiky event of primary pollutants, respectively.

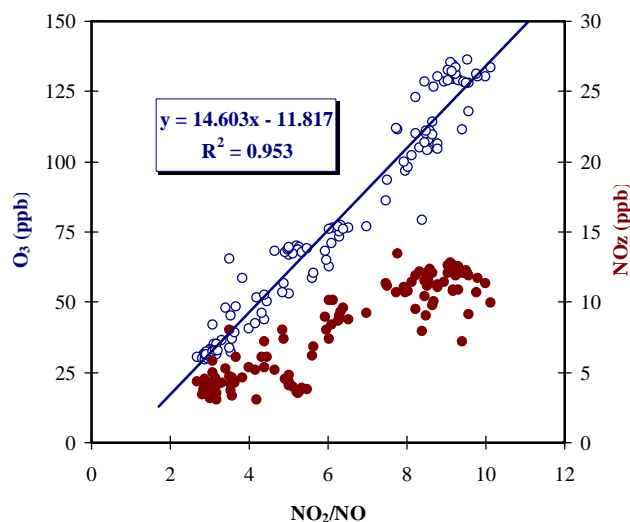


Fig. 5. Correlation of O_3 and NO_z , respectively, versus the NO_2/NO ratio for the period of 10:30–12:30, 3 August 2008. The linear regression is associated to the O_3 data. The increasing trend of NO_z with the NO_2/NO ratio is discontinued as $NO_2/NO > 8$.

0.008 s^{-1} for noontime (11:30–12:30) and 0.007 s^{-1} for late morning (10:30–11:30). The rate constant k_{NO-O_3} was calculated following Demore et al. (1997),

$$k_{O_3-NO} = 2.0 \times 10^{-12} \exp\left(\frac{-1400}{T}\right) \quad (3)$$

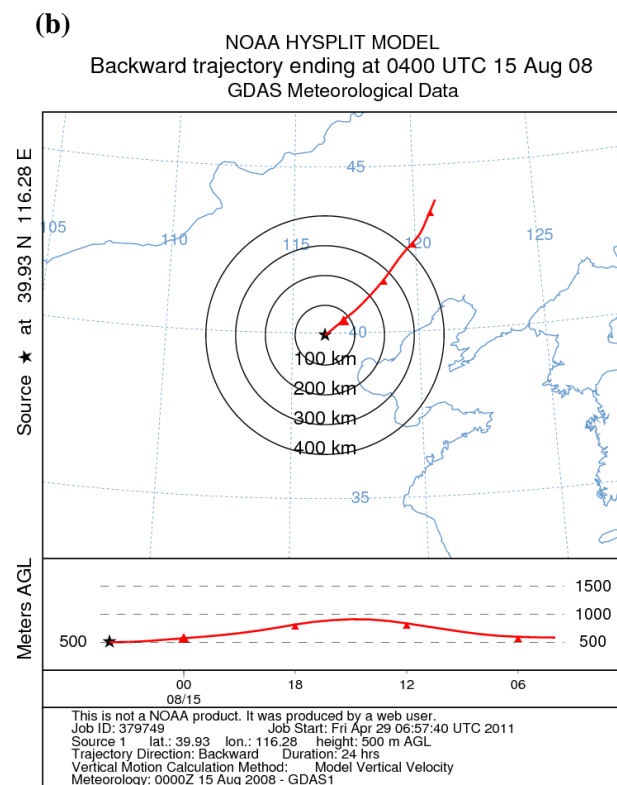
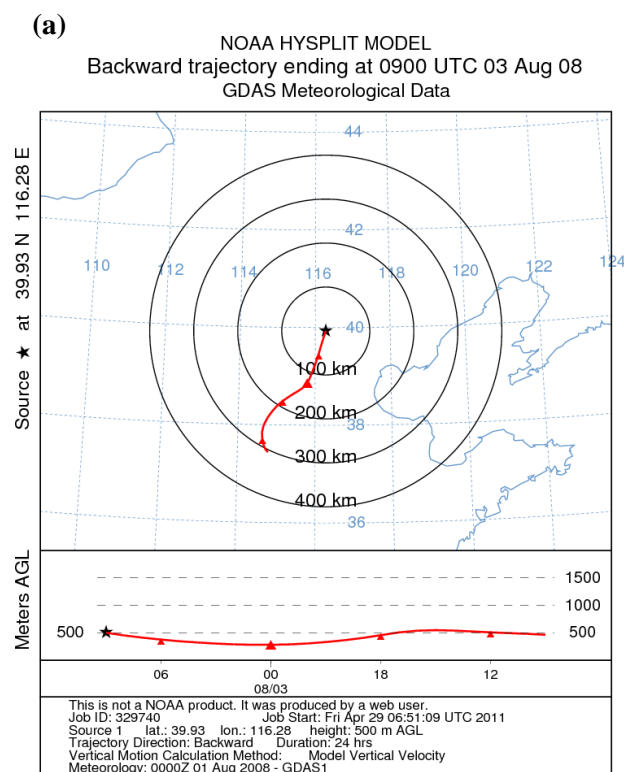


Fig. 6. Backward trajectories of air mass arriving Beijing at 17:00, 3 August (a), and at 12:00, 15 August 2008 (b). The trajectories were calculated for 24 h from an altitude of 500 m above the ground level of Beijing.

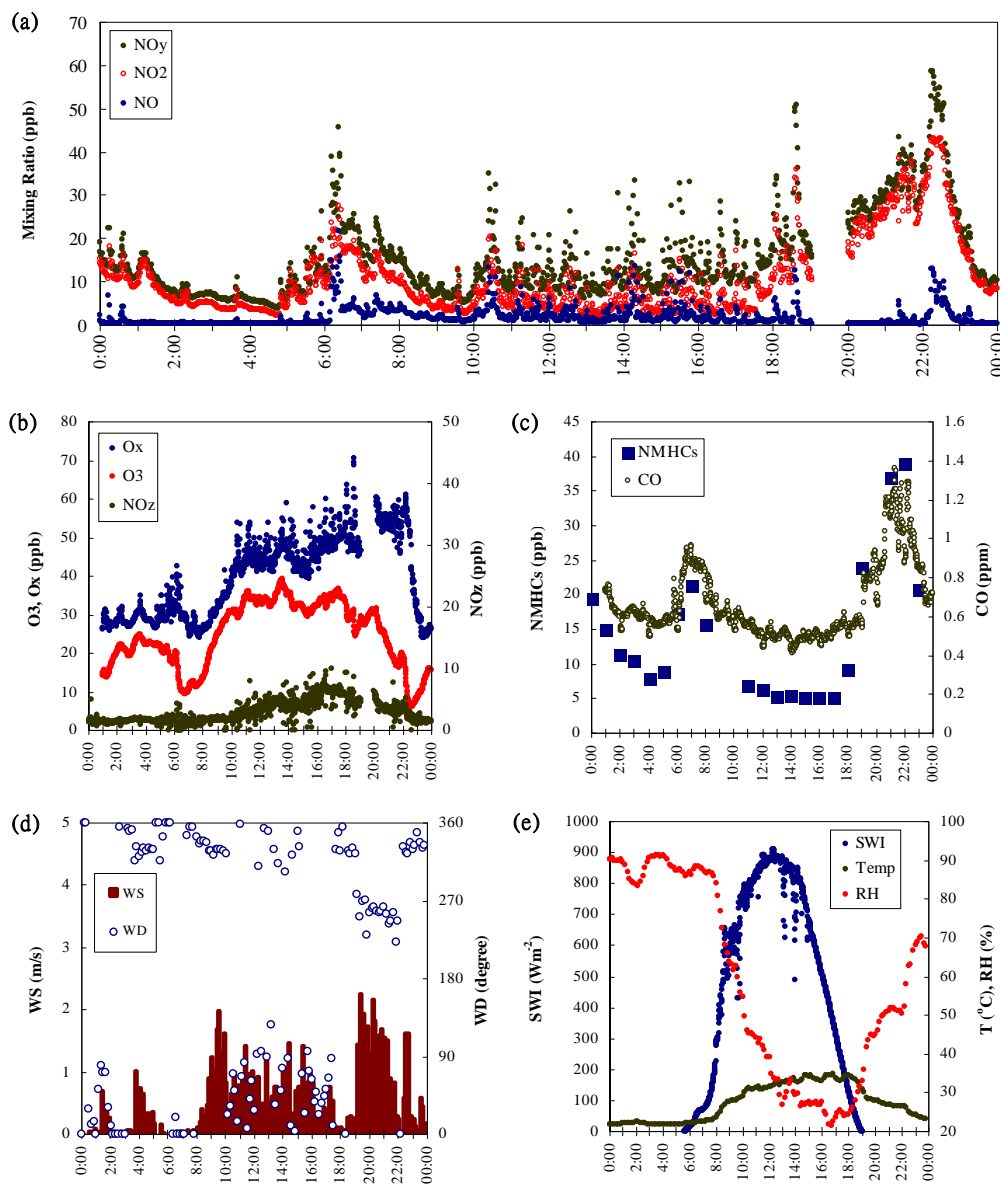


Fig. 7. Same as Fig. 3 but for 15 August 2008.

The calculation indicated that the 5-min averaged P_{O_3} was $30.7 \pm 9.2 \text{ ppb h}^{-1}$ for 10:31–10:35, and increased to $75.8 \pm 20.1 \text{ ppb h}^{-1}$ at noon time (12:26–12:30). The values of P_{O_3} are significantly higher than those observed in the US urban areas by a factor of 3–7 (Kleinman et al., 2002), and are comparable to recent observation in the Mexico City (Wood et al., 2009). Note that the range of P_{O_3} is comparable to that observed in Beijing during the summer of 2006 (Lu et al., 2010). Such a high P_{O_3} explains, at least partly, the high ozone levels observed in August 2008. The correlation between the NO_z concentration and the ratio of NO_2 to NO is also shown in Fig. 5. Along with the photochemical evolution of the air mass, it was revealed

that the ambient level of NO_z increased with NO_2/NO ratio until $NO_2/NO > 8$, whereas the mixing ratio of O_3 kept increasing. Consequently, the ratio of O_3 to NO_z increased to be above 10, indicating that the O_3 production shifted from VOC-sensitive regime to NO_x -sensitive regime (Sillman, 1995). Moreover, the leveling-off of NO_z suggests that the consumption of NO_x was getting limited. As a result, the fraction of NO_x in NO_y was significantly higher than that observed in CAREBeijing-2006 (Chou et al., 2009). Thus, in spite of the substantial reduction in NO_x emissions in Beijing during the Olympic period, particularly during the morning rush hours, the ambient levels of NO and NO_2 were not reduced as well during the midday.

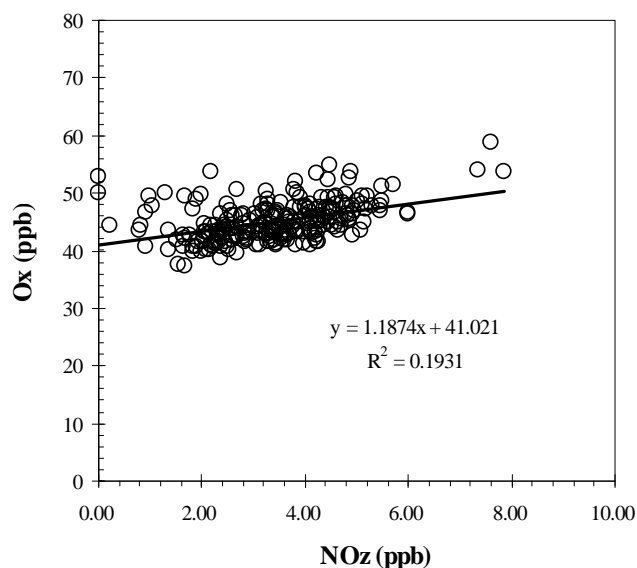


Fig. 8. Correlation between O_x and NO_z observed at the PKU observatory during the midday (10:00–14:00) of 15 August 2008. An averaged OPEX of 1.2 mole mole⁻¹ is derived from the linear regression model.

As shown in Fig. 3b, there was a second O_x peak occurred in the late afternoon of 3 August. As a result, the daily maximum 8-h mean of O_3 reached 119.2 ppbv for the period from 12:00–20:00 LST. The mixing ratios of NO_y and NO_z increased coincidentally. Unlike the midday peak, this afternoon O_x peak was associated with a strong CO peak but without significant changes in the NMHCs. The declined solar flux at that time excluded the possibility of strong in-situ photochemical production of O_3 . Thus, the most probable cause of the late afternoon episode is transport of aged air mass from surrounding urban areas, where the emissions of CO were not controlled as did in Beijing. Figure 6 illustrates the 24-h backward trajectory of the surface air mass arriving in Beijing at 17:00, which suggests that the photochemically-aged plume was associated with moderate southwesterly flows (~ 300 km per day). The influences of the southerly transported polluted air mass on the air quality in Beijing have been discussed in previous studies (e.g., An et al., 2007, Wang et al., 2010b). The point underlined in this case study is that the coupling of in-situ photochemical ozone production during midday and the transport of ozone plumes in the late afternoon could further impact the air quality, particularly in terms of the “8-h-mean” O_3 guideline (WHO, 2006).

3.3.2 Case 2: 15 August 2008

Figures 7a–e show the measurements of trace gases and meteorological parameters on 15 August 2008. Note that the northerly winds were prevailing and, as a result, the transport of polluted air mass from the southern North China Plains to

Beijing was prevented. Despite of the rains in early morning, the skies were very clear during the daytime. However, in contrast to the previous case, the mixing ratio of O_3 was kept at 30–40 ppbv during the daytime. The observed O_3 leveling-off suggests that the production and loss rates of ozone were comparable to each other. The major sinks of O_3 in the boundary layer include dry deposition and photolysis. With general conditions in urban areas, it was estimated that the maximum loss rate of O_3 could be around 10 ppb h⁻¹ only (Wood et al., 2009, Lu et al., 2010). Given the strong solar flux, the photolysis rate of NO_2 and production rate of OH on 15 August 2008 should be comparable to those on 3 August, respectively. Thus, there must be a major OH sink(s) that inhibited the formation of O_3 on 15 August.

On 15 August, the mixing ratio of NO_z was increasing from ~ 0 to ~ 10 ppbv during the daytime (as shown in Fig. 7b), implying that a substantial amount of OH radicals was consumed by reacting with NO_2 . Figure 8 illustrates the correlation between NO_z and O_x and gives an averaged OPEX of 1.2 mole mole⁻¹ for 10:00–14:00. Such a low OPEX suggests that the photochemical chain length of NO_x was very short and NO_x was the major terminator of radicals. Given that the reaction between NO_2 and OH is the primary sink of NO_x in the boundary layer, it was inferred from the low OPEX that the O_3 production was retarded by the consumption of OH for NO_2 oxidation. However, the high-end estimates of the consumption rates of OH due to reacting with NO_2 were around 3 ppb h⁻¹, which were calculated based on observed NO_2 concentrations, using $k_{NO_2-OH} = 9 \times 10^{-12}$ cm³ s⁻¹ (Donahue et al., 1997) and assuming $[OH] = 1 \times 10^7$ cm⁻³. That is evidently not enough to explain the O_3 leveling-off. Figure 7c shows that the mixing ratio of NMHCs was only 6.1 ppbv for the major photochemical time slot, i.e. 11:00–13:00, of 15 August. Comparing with 23.2 ppbv on 3 August, the concentration of NMHCs was reduced by 74%. Meanwhile, the total OH-reactivity of CO and the measured NMHCs decreased from 9.3 to 4.8 s⁻¹, or by $\sim 50\%$. The reduction in OH-reactivity of NMHCs will certainly inhibit the production of organic peroxy radicals (RO_2). Considering the recycling of OH through the reactions of peroxy radicals and NO (Hofzumahaus et al., 2009), the effects of the reduction in the OH-reactivity of NMHCs upon the O_3 production could have been amplified to a certain degree in this case.

3.3.3 Implications of the case studies

The two distinct cases discussed above demonstrate the responses of ozone production to the changes in the precursor levels, and provide important clues for further studies. In the first case (3 August), the ozone production was found being shifting from VOC-sensitive in late morning to NO_x -sensitive regime in early afternoon. Thus, the ozone production was first fueled by the substantial emissions of VOCs and, then, that shift could have inhibited the consumption of

NO_x and allowed the further increases of the O_3 mixing ratio in the early afternoon. Such a scenario could be responsible partly for the formation of high ozone episodes in Beijing, and should be considered and analyzed in more details in further modeling work. On the contrary, in case without the shift in the photochemical regime (i.e., 15 August), the photochemical production of O_3 declined substantially for the reduced OH-reactivity of VOCs during the midday. This could also explain the extremely low OPEX observed in Beijing on 15 August 2008.

4 Conclusions

During August 2008, including the period of the 29th Summer Olympic Games, an intensive atmospheric chemistry experiment was conducted at the air quality observatory of the Peking University in Beijing, China. The measurements were compared with the results of the CAREBeijing-2006, which was carried out in the summer of 2006, to infer the emission reduction in the Olympic month. Moreover, the measurements of the oxides of nitrogen were analyzed and discussed in details with implications for the photochemical ozone production in Beijing.

The monthly means of NO , NO_2 , NO_x , NO_y , and NO_z mixing ratios for August 2008 are 1.6 ± 1.9 , 13.7 ± 7.2 , 15.2 ± 8.2 , 19.7 ± 9.0 , and 4.3 ± 2.7 ppbv, respectively. As comparing with the measurements made in the summer of 2006, the overall reductions in NO_x/NO_y are 42.2/56.5%. Besides, the observations showed that the ambient levels of CO and NMHCs reduced by 27.8% and 49.7%, respectively, agreeing with the reduction in NO_x and NO_y . Thus, in line with previous modeling and observation studies, it was concluded that the emissions of primary air pollutants in Beijing were controlled successfully during the August 2008. In contrast to the primary pollutants, it was found that the mixing ratio of O_3 increased from 28.2 ± 27.2 for the CareBeijing-2006 period to 40.1 ± 25.1 ppbv for August 2008, which equals to an increase of 42.2%. The sum of O_3 and NO_2 increased by 11.8%, which means the reduced NO- O_3 titration cannot explain the contradictions between O_3 and its precursors well. Nevertheless, the levels of total oxidant ($\text{O}_x = \text{O}_3 + \text{NO}_2 + 1.5 \text{NO}_z$) indeed reduced by 21.3%, agreeing with the reduction of ozone precursors.

The photochemical responses of O_3/O_x to the reduction of the precursors were examined in two case studies with clear skies. On 3 August 2008, the hourly averages of O_3 and O_x mixing ratios reached their respective maxima, 135 and 169 ppbv, at 12:00 (local time = GMT+8:00). An ozone production rate of 75.8 ppbv h^{-1} was estimated for the midday, implying that the precursors were still enough to sustain the O_3 formation although the emissions were reduced significantly. During the course of O_3/O_x production and accumulation, there was an episode with spiky increases in the mixing ratios of CO, NMHCs, NO_x as well as NO_y . The ob-

served OPEX were 8.6 and 7.9 mole mole⁻¹ before and after the spiky event, and dropped down to 3.6 mole mole⁻¹ during the episode. The declined OPEX for increases in NO_x mixing ratio suggests that the $\text{NO}_x\text{-NO}_z$ conversion was enhanced and the photochemical condition was shifted toward VOC-sensitive regime. However, after the event, it was found that the concentrations of O_3 increased with the increasing NO_2/NO ratio, whereas the NO_z concentrations leveled off when $\text{NO}_2/\text{NO} > 8$. Consequently, the ratio of O_3 to NO_z increased to above 10, indicating the shift from VOC-sensitive regime to NO_x -sensitive regime. Such a back-and-forth shift of the photochemical regime of O_3 production necessitates further studies with sophisticated models. In contrast to the case of 3 August, the mixing ratios of O_3 remained around 30–40 ppbv on 15 August in spite of the strong solar flux. An averaged OPEX of 1.2 mole mole⁻¹ was observed for 10:00–14:00, suggesting that the OH radicals were consumed very efficiently for the oxidation of NO_x . Besides the loss of OH radicals, it was inferred that the O_3 production was inhibited by the extremely low level of NMHCs. The midday (11:00–13:00) mixing ratio of NMHCs was 6.1 ppbv on 15 August, comparing with 23.2 ppbv on 3 August. Thus, the formation of RO_2 and, in turn, the recycling of OH should have been retarded.

According to the results of this study, it was concluded that the O_3 production in Beijing should have been mitigated significantly during August 2008. The overall reduction in the mixing ratio of total oxidant was achieved for the successful control of the emissions of primary air pollutants. In particular, the reduction in NMHCs emissions was suggested to be the major cause of the mitigated O_3 production during midday. On the other hand, as comparing with the summer of 2006, apparently higher mixing ratios of O_3 were observed in August 2008. In addition to the declined $\text{O}_3\text{-NO}$ titration, changes in the composition of “total oxidant” were observed and suggested to be responsible for the contradictions between the O_3 and O_x mixing ratios.

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