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 (NOₓ and NOᵧ), 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 NOₓ, NOᵧ, 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 (Oₓ = O₃+NO₂+1.5NOᵧ) and NOᵧ were reduced by 21.3 and 77.4 %, respectively. The contradictions between Oₓ and O₃ were further examined in two case studies. Ozone production rates of 30–70 ppbv h⁻¹ and OPEx 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 NOᵧ mixing ratio leveled off when NO₂/NO > 8. Consequently, the ratio of Oₓ to NOᵧ increased to above 10, indicating the shift from VOC-sensitive regime to NOₓ-sensitive regime. However, in the other case, it was found that the Oₓ production was inhibited significantly due to substantial reduction in the NMHCs. According to the observations, it was suggested that the Oₓ and/or Oᵧ 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 Oₓ levels increased due to a decline in the NO-Oₓ titration, and the midday Oₓ peak levels were elevated because of the shift in the photochemical regime and the inhibition of NOᵧ 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),
nitrogen oxides (NO\textsubscript{x}), and particulate matters (PM\textsubscript{10}) were reduced by \sim50\% from their respective normal levels in Beijing (Zhou et al., 2010; Wang et al., 2010c). The estimates of NO\textsubscript{3} reduction are consistent with previous reports based on satellite observations, which indicated a reduction of \sim40–60\% in the column density of NO\textsubscript{2} over Beijing during the Olympic Games (Miyling 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\textsubscript{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\textsubscript{3} for August 2008 was reduced by \sim20\%, 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\textsubscript{3} (Wang et al., 2010b). The increases in the O\textsubscript{3} mixing ratio were not consistent with the decreases in the emissions of precursors, i.e. NO\textsubscript{x} and VOCs. In particular, the ozone formation potentials (OFFs) 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 NO\textsubscript{x} titration, which was a result of the reduction in NO\textsubscript{y} emissions. Wang et al. (2009b) suggested that the high O\textsubscript{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\textsubscript{3} in Beijing downtown. To date, the high O\textsubscript{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\textsubscript{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\textsubscript{3} level to a drastic reduction in the emissions of precursors. In this study, the measurements of O\textsubscript{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\textsubscript{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\textsubscript{2}), and total reactive nitrogen (NO\textsubscript{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\textsubscript{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 \sim66\% throughout the campaign, which was determined with gas titration method. A NO\textsubscript{y} converter (ECO Physics) was employed to reduce the NO\textsubscript{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\textsubscript{y}. The efficiency of this converter was \sim100\%, which was checked by HNO\textsubscript{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\textsubscript{2}, and NO\textsubscript{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 \sim170°C. Air sample was drawn through the cryo-trap at a rate of 12 mL min\textsuperscript{-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 m \times 0.32 mm; df = 5.0 µm) 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.

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

* Species measured in the CAREBeijing-2006.

60 m×0.32 mm; df = 1.0 μm) 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 °C min⁻¹, to 140 °C at 5 °C min⁻¹, and ends at 180 °C for 9.5 min.

In addition to the NO/NOx 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 O3 from the station will be included in the following analysis and discussion. Besides, the total short-wave irradiance, SWI, (0.3–3.0 µm) was measured using an Eppley precision spectral pyrometers (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, NO2, NOx, O3, O3, CO, and NMHCs) measured at the PKU station during August 2008. Here NOx is defined as the differences between NOx and NO (NO−NOx), which are the oxidation products of NOx. Note that the “total oxidant” (O3) is defined following Levy et al. (1985), O3=O3+O(3P)+O(1D)+0.5·OH+0.5·HO2+H2O2 (1) +NO2+2·NO3+3·N2O5+1.5·HNO3.

Given that the mixing ratios of radicals, oxygen atoms, H2O2 and N2O5 are rather low in the atmosphere, the right hand side of Eq. (1) is dominated by O3, NO2, and HNO3. Further, because HNO3 is usually the predominant component of NOx in an urban area, the mixing ratio of O3 was estimated by [O3+NO2+1.5·NO2] in this study.

In the first week of August 2008, just before the Olympic Games, Beijing experienced an episode of high O3/Ox. The hourly [O3] and [Ox] reached their respective maxima, 135 and 169 ppbv, at 12:00 (local time = GMT + 08:00) on 3 August. The maximal levels of NOx, Ox, and NMHCs were observed at 11:00, i.e. 1 h prior to the peaks of O3 and Ox. Note that there was another O3/Ox 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 O3 declined gradually since 6 August and remained below 100 ppbv, in spite of the daily NOx/NOy spikes, during the Olympic Games. Apparently, the emission of NOx did not contribute efficiently to the formation of O3 in Beijing during the Olympics. The reduced photochemical activity was also indicated by the absence of NO2 peaks, as shown in the NO2 time series. The mitigation of O3/Ox 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 O3 was not enhanced significantly on some days (e.g., 15–16 August) with strong solar flux. Thus the mechanisms for the observed reduction in O3 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, O3, O3, 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; NOx, NOy, 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.
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 $28.2 \pm 27.2$ ppbv to $40.1 \pm 25.1$ ppbv, or by 42 %. Meanwhile, the sum of $O_3$ and NO$_2$ mixing ratios increased from $48.2 \pm 24.5$ ppbv to $53.9 \pm 25.0$ 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 $O_3$ decreased from $76.6 \pm 28.7$ ppbv to $60.3 \pm 26.9$ ppbv, which is equivalent to a reduction of 21 %. Among the components of $O_3$, the mixing ratios of NO$_z$ decreased most significantly. The campaign average of NO$_z$ mixing ratio decreased from $19.0 \pm 6.3$ ppbv to $4.3 \pm 2.7$ 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 report 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 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 ±1σ are indicated by the error bars associated with the hourly means or shaded for the 1-min. data. (a) NO; (b) NO₂; (c) NOₓ; (d) NO₃; (e) CO; (f) NMHCs; (g) O₃; (h) Oₓ.
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 OX, respectively. The mixing ratio of O3 was higher during the 2008 campaign, whereas OX 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 noon time are comparable in the two campaigns; meanwhile the OX 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 OX. In terms of monthly average, the daily peak level of 1-h O3 (O3_max) in August 2008 increased by 4.9 % than during the 2006 campaign, whereas the OX_max (daily peak level of 1-h OX) was reduced by 20.1 % (shown in Table 2). The inconsistency between O3 and OX 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 OX.

### 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.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>NO (ppb)</td>
<td>6.9 (11.3)</td>
<td>1.6 (1.9)</td>
<td>76.8</td>
</tr>
<tr>
<td>NO2 (ppb)</td>
<td>19.5 (10.2)</td>
<td>13.7 (7.2)</td>
<td>29.7</td>
</tr>
<tr>
<td>NOX (ppb)</td>
<td>26.3 (17.5)</td>
<td>15.2 (8.2)</td>
<td>42.2</td>
</tr>
<tr>
<td>NOy (ppb)</td>
<td>45.3 (21.5)</td>
<td>19.7 (9.0)</td>
<td>56.5</td>
</tr>
<tr>
<td>NOz (ppb)</td>
<td>19.0 (6.3)</td>
<td>4.3 (2.7)</td>
<td>77.4</td>
</tr>
<tr>
<td>NMHC* (ppb)</td>
<td>29.0 (17.0)</td>
<td>14.6 (8.0)/23.3 (11.9)</td>
<td>49.7</td>
</tr>
<tr>
<td>CO (ppb)</td>
<td>1173 (623)</td>
<td>847 (275)</td>
<td>27.8</td>
</tr>
<tr>
<td>O3 (ppb)</td>
<td>28.2 (27.2)</td>
<td>40.1 (25.1)</td>
<td>-42.2</td>
</tr>
<tr>
<td>O3 +NO2 (ppb)</td>
<td>48.2 (24.5)</td>
<td>53.9 (25.0)</td>
<td>-11.8</td>
</tr>
<tr>
<td>OX (ppb)</td>
<td>76.6 (28.7)</td>
<td>60.3 (26.9)</td>
<td>21.3</td>
</tr>
<tr>
<td>O3_max (ppb)**</td>
<td>69.9 (33.9)</td>
<td>73.3 (25.3)</td>
<td>-4.9</td>
</tr>
<tr>
<td>OX_max (ppb)**</td>
<td>120.8 (42.3)</td>
<td>96.5 (29.1)</td>
<td>20.1</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>25.8 (4.8)</td>
<td>27.4 (4.1)</td>
<td>-6.2</td>
</tr>
<tr>
<td>RH (%)</td>
<td>64.3 (19.9)</td>
<td>68.8 (17.2)</td>
<td>-7.0</td>
</tr>
<tr>
<td>Wind Speed (m s⁻¹)</td>
<td>1.4 (1.3)</td>
<td>0.9 (0.8)</td>
<td>35.7</td>
</tr>
</tbody>
</table>

* 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.

* O3_max and OX_max denote the daily peak levels of O3 and OX, respectively.

### 3.3 Ozone production efficiency of NOX: 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 NOX (OPEX) is among the key parameters of NOX-O3 chemistry, which is defined as the number of ozone molecules produced by one NOX molecule in the NOX-catalyzed photochemical reactions (Liu et al., 1987). In the followings, two distinct cases will be presented in the context of OPEX. 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 NOx/NOy 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, OX, and NO2 increased drastically from ∼09:00 to ∼12:00. Note the spikes of NO/NO2/NOy peaking at ∼11:00, which resulted in the titration dip in O3.
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 NOx (OPE_x) to examine the perturbation of the NOx 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 NO2, here the OPE_x was derived from the slope of [O3] vs. [NO2]. It was revealed that the OPE_x decreased from 8.6 before the NOx spike to 3.6 during the episode and, in turn, bound up to 7.9 mole mole^{-1} after the event. Obviously, the NOx injected into the atmosphere was converted to NO2 efficiently during the episode. The enhanced NOx-NO2 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),

\[ P_{O3} = j_{NO2} \cdot [NO2] - k_{NO-O3} \cdot [O3] \cdot [NO] \] (2)

Without direct measurement of the photolysis rates of NO2, \( j_{NO2} \), the values of \( j_{NO2} \) 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 $NO_x$ (OPEx) before, during, and after the spiky event of primary pollutants, respectively.

$y = 14.603x - 11.817$
$R^2 = 0.953$

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 $NO_2$ with the $NO_2$/NO ratio is discontinued as $NO_2$/NO $> 8$.

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

$$k_{O_3-NO} = 2.0 \times 10^{-12} \exp\left(-\frac{1400}{T}\right)$$  (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±9.2 ppb h$^{-1}$ for 10:31–10:35, and increased to 75.8±20.1 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$_2$ 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$_2$ 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$_2$ 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$_2$ 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.
As shown in Fig. 3b, there was a second \( O_3 \) 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 \( NO_x \) and \( NO_z \) increased coincidently. Unlike the midday peak, this afternoon \( O_3 \) 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 \( NO_2 \) 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 \( NO_2 \) and \( O_3 \), 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 \( NO_3 \) 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 \( k_{NO_2-OH} = 9 \times 10^{-12} \text{cm}^3\text{s}^{-1} \) (Donahue et al., 1997) and assuming \([OH] = 1 \times 10^7 \text{cm}^{-3}\). 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 ~50 %. The reduction in \( OH \)-reactivity of NMHCs will certainly inhibit the production of organic peroxo radicals (RO\(_2\)). Considering the recycling of \( OH \) through the reactions of peroxo 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\textsubscript{x} and allowed the further increases of the O\textsubscript{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\textsubscript{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\textsubscript{2}, NO\textsubscript{x}, NO\textsubscript{y}, and NO\textsubscript{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\textsubscript{x}/NO\textsubscript{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\textsubscript{y} and NO\textsubscript{z}. 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\textsubscript{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\textsubscript{3} and NO\textsubscript{2} increased by 11.8 %, which means the reduced NO-NO\textsubscript{2} titration cannot explain the contradictions between O\textsubscript{3} and its precursors well. Nevertheless, the levels of total oxidant (O\textsubscript{x} = O\textsubscript{3}+NO\textsubscript{2}+1.5 NO\textsubscript{y}) indeed reduced by 21.3 %, agreeing with the reduction of ozone precursors.

The photochemical responses of O\textsubscript{3}/O\textsubscript{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\textsubscript{3} and O\textsubscript{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\textsuperscript{-1} was estimated for the midday, implying that the precursors were still enough to sustain the O\textsubscript{3} formation although the emissions were reduced significantly. During the course of O\textsubscript{3}/O\textsubscript{x} production and accumulation, there was an episode with spiky increases in the mixing ratios of CO, NMHCs, NO\textsubscript{x} as well as NO\textsubscript{y}. The observed OPEX were 8.6 and 7.9 mole mole\textsuperscript{-1} before and after the spiky event, and dropped down to 3.6 mole mole\textsuperscript{-1} during the episode. The declined OPEX for increases in NO\textsubscript{x} mixing ratio suggests that the NO\textsubscript{x}-NO\textsubscript{2} 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\textsubscript{3} increased with the increasing NO\textsubscript{2}/NO\textsubscript{z} ratio, whereas the NO\textsubscript{z} concentrations leveled off when NO\textsubscript{2}/NO\textsubscript{z}>8. Consequently, the ratio of O\textsubscript{3} to NO\textsubscript{2} increased to above 10, indicating the shift from VOC-sensitive regime to NO\textsubscript{x}-sensitive regime. Such a back-and-forth shift of the photochemical regime of O\textsubscript{3} production necessitates further studies with sophisticated models. In contrast to the case of 3 August, the mixing ratios of O\textsubscript{3} remained around 30–40 ppbv on 15 August in spite of the strong solar flux. An averaged OPEX of 1.2 mole mole\textsuperscript{-1} was observed for 10:00–14:00, suggesting that the OH radicals were consumed very efficiently for the oxidation of NO\textsubscript{x}. Besides the loss of OH radicals, it was inferred that the O\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{3} production during midday. On the other hand, as comparing with the summer of 2006, apparently higher mixing ratios of O\textsubscript{3} were observed in August 2008. In addition to the declined O\textsubscript{3}/NO\textsubscript{2} titration, changes in the composition of “total oxidant” were observed and suggested to be responsible for the contradictions between the O\textsubscript{3} and O\textsubscript{x} mixing ratios.

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References


