Nitrogen dioxide measurement by cavity attenuated phase shift spectroscopy (CAPS) and implications in ozone production efficiency and nitrate formation in Beijing, China

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[1] Nitrogen dioxide (NO2) is a key species in studying photochemical smog and formation mechanisms of nitrate in fine particles. However, the conventional commercially available chemiluminescence (CL)-based method often has uncertainties in measuring NO2 because of interferences with other reactive nitrogen species. In this study, an Aerodyne Cavity Attenuated Phase Shift Spectroscopy (CAPS) NO2 monitor that essentially has no interferences with nitrogen containing species was deployed in Beijing for the first time during August 2012. The CAPS NO2 monitor is highly sensitive with a detection limit (3σ) of 46.6 ppt for 1 min integration. The NO2 measured by CAPS shows overall agreement with that from CL, yet large differences up to 20% were also observed in the afternoon. Further, the discrepancies of NO2 measurements between CAPS and CL appear to be NO2 dependent with larger differences at higher NO2 concentrations (e.g., > 14 ppb). As a result, the ozone production efficiency of NOx (OPEz) derived from the correlations of O3–NOx with the CL NO2 can be overestimated by 19–37% in Beijing. The daily OPEz calculated with the CAPS NO2 ranges from 1.0 to 6.8 ppb/ppb with an average (±1σ) of 2.6 (±1.3) for the entire study. The relatively low OPEz and the relationship between OPEz and NOx suggest that ozone production chemistry is VOC sensitive during summer in Beijing. Two case studies further show that high concentrations of NOx can significantly enhance the formation of nitrate in fine particles in the presence of high O3 and favorable meteorological conditions.


1. Introduction

[2] Air pollution is a great concern in China in recent years. The roles of megacities in regional air pollution, such as photochemical smog and haze, have been extensively investigated in previous works [Guttikunda et al., 2003, 2005; Kanakidou et al., 2011; Lawrence et al., 2007; Madronich, 2006; Molina et al., 2010; Molina and Molina, 2006; Shao et al., 2006]. Beijing, one of the largest cities in China and one of the top 25 world megacities, has a resident population of more than 20 million in 2012 (http://www.bjstats.gov.cn/nj/main/2012-tjnj/index.htm). The dense population and rapid economic growth have resulted in a substantial increase of anthropogenic pollutants in Beijing and regions in its vicinity, which contributes significantly to the air pollution in Beijing [Hao et al., 2005; Shao et al., 2006; Wang et al., 2006]. It was estimated that ~74% of the ground level NOx in Beijing is due to vehicular emissions, whereas power plants and industrial sources contribute only 2% and 13%, respectively [Hao et al., 2005]. Although photochemical smog is a major air pollution issue in Beijing, the mechanisms of the formation of surface O3 are not well known for this area; specifically with respect to the formation mechanisms of O3 in urban versus rural areas of Beijing. Wang et al. [2006] found that O3 formation in a mountainous area in the north of Beijing was limited by NOx; however, a VOC-controlled ozone formation mechanism was dominant at the urban sites in Beijing [Wang et al., 2010b]. Similarly, Chou et al. [2009] found that reduction of NOx emission appeared not to be effective toward reducing O3 concentration at an urban site in Beijing.
Previous studies [Chameides et al., 1992; Kleinman et al., 1994, 2000; Sillman, 1999] have shown that the surface O₃ is primarily formed from photochemical reactions of VOCs and NOₓ. NOₓ not only plays the role of catalyst in the chain reactions for O₃ production but also is a major terminator of free radicals, which has the potential to limit the formation of O₃ in the atmosphere [Sillman, 1999; Roberts et al., 1995; Seinfeld and Pandis, 2006]. Since the oxidants of NOₓ can be removed from the O₃-production-reaction system, Liu et al. [1987] defined the number of molecules of O₃ formed per NOₓ, O₃/NOₓ, not only plays the role of catalyst in the chain reactions for O₃ production but also is a major terminator of free radicals, which has the potential to limit the formation of O₃ in the atmosphere.

It is widely accepted that the OPE, derived from the commercially standard chemiluminescence-based (called CL hereafter) instruments often has large uncertainties and represents an upper limit, especially in the photochemically aged air [Ge et al., 2010]. For example, Dunlea et al. [2007] reported an overestimation of 22% of NOₓ measured by the CL monitors compared with the collocated spectroscopic measurements in Mexico City. Such uncertainties are expected to be enlarged in the downwind areas of megacities where the production of NOₓ, such as PAN and HNO₃, in the total reactive nitrogen species is more significant in comparison to urban cities.

To improve the accuracy of NOₓ measurements, a NOₓ monitor utilizing Cavity Attenuated Phase Shift Spectroscopy (CAPS) was recently developed [Kebabian et al., 2005, 2008]. The CAPS NO₂ monitor directly measures the absorption of NO₂ at the wavelength of 450 nm and requires no conversion of NOₓ to other species. Compared to the standard commercially available CL-based NOₓ analyzer, the CAPS NO₂ monitor shows much enhanced performance in terms of sensitivity, accuracy, and baseline stability [Kebabian et al., 2005]. In particular, the CAPS NO₂ has essentially no interferences from other nitro containing species, although small spectral interferences from 1,2-dicarbonyl compounds, such as glyoxal and methylglyoxal, are possible due to the ±20 nm band-pass centered at 440 nm [Kebabian, et al., 2008]. Commercially available CL analyzers are the standard type of instrument employed at surface monitoring network stations for ambient measurements of atmospheric NOₓ. Ambient NO₂ analyzers employing the same CL detection scheme, yet utilizing UV photolysis with high power LEDs to convert NO₂ to NO prior to CL detection, are also commonly utilized in field research. Similar to the Aerodyne CAPS instrument, photolysis-chemiluminescence (P-CL) instruments have higher sensitivity and chemical selectivity for NO₂ than the standard commercially available NOₓ CL analyzer [Ryerson et al., 2000; Pollack et al., 2010; Sadanaga et al., 2010]. These P-CL systems are the current recommended standard for ambient measurements of NOₓ by the Global Atmospheric Watch (GAW). Considering the above mentioned advantages of the commercially available Aerodyne CAPS NO₂ monitor compared to the standard commercial CL analyzer, evaluation of the Aerodyne CAPS NO₂ instrument as a potential resource for future NOₓ measurements has significant implications for future surface monitoring networks, especially for monitoring sites with low concentrations of NO₂ and/or where photochemical production of NO₂ is intense.

In this work, an Aerodyne CAPS NO₂ monitor was first deployed at an urban site in Beijing, China for in situ measurement of ambient gaseous NO₂. Here we report the results from 1 month measurement campaign during August 2012. We first evaluate the performance of the CAPS NO₂ monitor by comparing with a standard, commercial CL-based NOₓ analyzer (Thermo Scientific, Model 42i). Then, we explore the impact of NO₂ measurement on the derivation of OPE. Further, the implications of OPE in O₃-NOₓ VOCs chemistry and the strategies for ozone pollution control in Beijing are discussed. Finally, two high-O₃ episodes are used to elucidate the roles of O₃ and NO₂ in the formation of secondary particulate nitrate.

2. Experimental

2.1. Sampling Site and Meteorology

The ambient gaseous species including NO, NOₓ, and O₃ were simultaneously measured by a NO/NO₂/NOₓ analyzer (Thermo Electron Corporation, 42i) at site B, which is approximately 50 m apart. The CAPS NO₂ monitor was deployed on the roof of a two story building (~8 m above the ground) at site A. Collocated gaseous species including NO, NOₓ, and O₃ were simultaneously measured by a NO/NOₓ analyzer (Thermo Scientific, 42CY) and an Ozone Analyzer (Thermo Scientific, 49iC), respectively. In addition, NO, NO₂, and NOₓ were measured by a CL NO/NOₓ analyzer (Thermo Electron Corporation, 42CTL) at site B. The detailed descriptions of the sampling sites are given in Sun et al. [2012]. The meteorological variables including temperature (T), relative humidity (RH), precipitation, solar radiation (SR), wind speed (WS) and wind direction (WD) were obtained from the meteorology tower of IAP, which is approximately 30 m away from site A and ~20 m from site B.

2.2. Cavity Attenuated Phase Shift Spectroscopy NOₓ Monitor

The CAPS NO₂ monitor determines NO₂ by directly measuring optical absorption of NO₂ at 450 nm in the blue region of electromagnetic spectrum [Kebabian et al., 2005, 2008]. Unlike standard CL monitors, the CAPS measures the average time that the light spends within the sample cell and requires no conversion of NO₂ to other species, and thus is not sensitive to other nitro containing species (such as HNO₃, nitrate, PAN, etc.). The CAPS NO₂ system contains three major parts including a blue light emitting diode (LED) as the light source, a sample cell with two high reflectivity mirrors centered at 450 nm, and a vacuum photodiode detector. The detailed principles of the CAPS system have been described elsewhere [Kebabian et al., 2005, 2008]. In brief, a square wave modulated LED light is input into
In addition to the gaseous species measurements, an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) was used to measure the mass concentration and chemical composition of nonrefractory submicron aerosol species including organics, sulfate, nitrate, ammonium, and chloride at a time resolution of ~15 min at the site A. The detailed descriptions of ACSM measurements can be found in Sün et al. [2012, 2013]. In addition, all the data in this study are reported at Beijing local time which equals Coordinated Universal Time (UTC) plus 8 h.

3. Result and Discussion

3.1. Intercomparison

[11] A time series of NO and NO2 measured by the CAPS and CL instruments is presented in Figure 2. The NO measured by 42CY at site A and 42CTL at site B track each other well ($r^2 = 0.94$, Figure 3a). However, the regression slope of 0.91 suggests that the NO measured at site A appears to be systematically lower than that observed at site B, which is likely due to the calibration errors. Also, note that the differences at the two sites are larger at low ambient levels (<1 ppb). For example, while the minimum of NO at site A is approximately 0.4 ppb, which is close to the detection limit of 0.4 ppb for 1 min average, the NO at site B however can go down to 0.2 ppb.

[12] The NO2 measured by the CAPS NO2 monitor also tracks tightly with that measured by the CL-based analyzers ($r^2 = 0.91$, slope = 0.999, Figure 3b), yet noticeable differences in particular during afternoon were observed. Figure 3b shows that the differences between the CAPS and CL appear to be NO2 dependent. While the discrepancies are within ~10% when NO2 is below 8 ppb, large differences up to ~30% at high NO2 levels (> 14 ppb, Figure 3c) were observed between CAPS and CL because of the interferences of other reactive nitrogen species on CL NO2 measurement. This is due to the well known sensitivity of the CL-based NO2 measurements to organic nitrates and HNO3, which depends upon inlet configuration and thermal operation region of a molybdenum or stainless steel converter [Winer et al., 1974; Parrish et al., 1990; Murphy et al., 2007; Keabian et al., 2008; Steinbacher et al., 2007]. At low NO2 levels (< 2 ppb), the CAPS NO2 shows slightly higher values than that from CL. Although the band of 440 nm is essentially interference free, the 1,2-dicarbonyl compounds, e.g., glyoxal and methyl glyoxal can affect the accuracy of CAPS NO2 measurements by absorbing in the same spectral region. Such interferences might be significant when the ratio of glyoxal to NO2 is high. However, based on previous measurements of glyoxal and NO2 at both urban and rural sites [Volkamer et al., 2005; Li et al., 2013], the interferences of glyoxal on the measurement of ambient NO2 are generally less than 10%.

[13] Figure 4b shows the diurnal variation of NO2 measured by the CAPS and CL for the entire study. While the NO2 from two methods agree reasonably with each other at nighttime, large differences up to 20% were observed during daytime, mostly between 12:00 and 16:00. The large discrepancies in the afternoon are likely due to the overestimation of CL NO2 because of the interferences of abundant reactive nitrogen species. In addition, the different sampling sites might also contribute to the observed differences in NO2.
measurements. We also note that the CAPS NO2 sometimes shows higher concentration than the CL NO2 at nighttime, which might be due to the interferences of some nitrogen containing species, e.g., peroxyacyl nitrates (PANs) and N2O5, which are not thermally stable and can decompose to NO2 in the CAPS system [Kebabian et al., 2008]. However, the discrepancies at nighttime (3.7%) are much smaller compared to those observed during daytime (17.4%).

3.2. Time Series and Diurnal Variations

[14] The time series of NO, NO2, NOy, NOz, O3, Oxyz, and particulate NO3/C0 in submicron aerosols, and solar radiation (SR) are shown in Figure 2. The NO shows regular and prominent peaks in the early morning due to the traffic emissions in the morning rush hour. This is evident from the diurnal cycle of NO (Figure 4a), which shows a pronounced morning peak. The NO concentration peaks between 7:00 and 8:00 (~17 ppb) and then gradually decreases to a low ambient level (~ 1 ppb) due to the titration of NO by O3, and also the rising boundary layer during the daytime [Lin et al., 2008, 2011].

[15] The gaseous NO2 also presents a pronounced diurnal cycle, yet the highest concentration occurs in the early morning and the lowest values appear between 14:00 and 15:00 (Figure 4b). The low concentration of NO2 in the afternoon is due to the deep boundary layer [Quan et al., 2013] and also the oxidation to NOz, e.g., nitric acid, PAN, etc., consistent with the pronounced NO2 peak in the afternoon (Figure 5).

Figure 1. (a) Time series of NO2 concentration (1 s data) measured from NO2-free air every 1 h for the entire study, (b) Gaussian distribution of NO2 in Figure 1a. The two solid lines in Figure 1a indicate the 10th and 90th percentiles of the data points.

Figure 2. Time series of gaseous NO, NO2, NOy, O3, Oxyz, and NO2, particulate NO3− in submicron aerosols, and solar radiation (SR). The NO2,CL and Oxyz,CL are [NO2] − [NO] − CL [NO2] and [O3] + CL [NO2], respectively, while The NO2,CAPS and Oxyz,CAPS are [NO2] − [NO] − CAPS [NO2] and [O3] + CAPS [NO2], respectively.
Figure 3. (a) Comparison of NO measured at site A and B; (b) Comparison of NO2 measured by the CL NOx analyzer at Site B and the CAPS NO2 monitor at Site A; (c) NO2 deviation between CAPS and CL versus NO2. The data points are color coded with the NO2 concentration in Figures 3a and 3b. Also, the data points in Figure 3b are averaged according to NO2 concentration with 2 ppb increment (solid circles).

Figure 4c shows the diurnal cycles of NO2 and NOx. Again, the diurnal profile of NOx and NO2 shows a large gap during daytime with the max difference of ~15 ppb at ~14:00, clearly indicating the photochemical production of NO2. The photochemical formation of NO2 is strongly associated with solar radiation and O3 mixing ratio. For example, the high O3 pollution episodes, e.g., 9–10, 15–16, 19–26, and 28–29 August, show evident noon peaks, indicating the photochemical production of NO2. However, the days with weak solar radiation (< 300 W m−2) and low O3, e.g., 1, 7–8, 12, 17–18, and 27 August, show correspondingly low production of NO2. The relationship between O3 and NO2 will be further discussed in section 3.2.

Figure 5 shows the diurnal variations of O3,CAPS (=[O3]+CAPS[NO2]) and NO2,CAPS (=[NO2]−[NO]−CAPS [NO2]), as well as the O3,CL (=[O3]+CL[NO2]) and NO2,CL (=[NO2]−[NO]−CL[NO2]). The diurnal cycle of O3 is similar to NO2 with higher values appearing during the afternoon and lower ones at night and early morning. In addition to the photochemical production, regional transport might be another reason for the daytime peaks. For example, Wang et al. [2010b] found that regional pollution sources could contribute ~34–88% to the peak ozone at the urban site in Beijing. In this study, the average concentration of O3 for the second peak (15:00–18:00) was 79.4 and 54.4 ppb, respectively, from the air masses in the east-southwest, overall consistent with the results from Wang et al. [2010b].

3.3. Ozone Production Efficiency (OPEx)

[17] The OPEx is an important indicator to evaluate O3-NOx-VOCs sensitivity and to make effective O3 control strategies in urban areas [Couach et al., 2004; Rickard et al., 2002; Shiu et al., 2007; Sillman, 1999; Xu et al., 2009; Zaveri et al., 2003]. The OPEx can be derived from the regression slopes of correlations between O3 and NOx [Kleinman et al., 1994; Trainer et al., 1993]. Therefore, the accuracy of NO2 measurement plays an important role in the calculation of OPEx by influencing the quantification of O3 and NO2. Using the same approach, the OPEx,CAPS and OPEx,CL were obtained from the correlation analysis of [O3,CAPS] and [O3,CL] versus [NO2,CAPS] and [NO2,CL], respectively in this study. Hourly averaged data between 7:00 and 17:00 are used for the correlation analysis. In addition, only slopes with correlation coefficients R > 0.6 (significant level at 95%) and intercept > 0 (the background O3 concentration) are considered to be effective daily OPEx,CAPS/OPEx,CL for this study. Given the general overestimation of CL NO2 [Steinbacher et al., 2007], the OPEx,CL calculated from the NO2 and NOx measured by 42CTL analyzer would represent an upper limit of OPEx, especially in the photochemically aged air [Ge et al., 2010].

[18] Figure 6 shows the calculated daily OPEx,CAPS and OPEx,CL using 1 h average data for the entire study. It should be noted that some OPEx values were missed in Figure 6 because the correlations of O3 versus NO2 in these days did
not meet the requirements for calculation of OPE$_x$ in this study. The daily OPE$_x$\textsubscript{CAPS} varies from 1.0 to 6.8 ppb/ppb with an average ($\pm 1\sigma$) of 2.6 ($\pm 1.3$) for the entire study. As a comparison, the OPE$_x$\textsubscript{CAPS} is generally higher than OPE$_x$\textsubscript{CL}, ranging from 0.9 to 8.1. The average of OPE$_x$\textsubscript{CL} for the entire study is 3.4, which is ~30% higher than that of OPE$_x$\textsubscript{CAPS}. The higher OPE$_x$\textsubscript{CL} is primarily due to the overestimation of the CL NO$_2$, leading to an over prediction of [O$_x$\textsubscript{CL}]. As a result, the OPE$_x$\textsubscript{CL} calculated from the relationship between [O$_x$\textsubscript{CL}] and [NO$_x$\textsubscript{CL}] is overestimated. The discrepancies between OPE$_x$\textsubscript{CAPS} and OPE$_x$\textsubscript{CL} vary day by day, and the overestimation of OPE$_x$\textsubscript{CL} ranges from 19–37% depending on photochemical production of NO$_x$ and the differences of NO$_2$ between CAPS and CL. Our results suggest that the previously reported OPE$_x$ calculated from the CL measurements [Xu et al., 2009; Ge et al., 2012] might have been overestimated by 30% on average.

![Figure 4](image_url) **Figure 4.** Mean diurnal cycles of (a) NO, (b) NO$_2$, and (c) NO$_x$ and NO$_3$ based on the entire measurement period. Another reason might be related to the well-known phenomenon commonly referred to as the “weekend ozone effect” or “holiday effect” [Fujita et al., 2003; Pollack et al., 2012; Yarwood et al., 2003]. In these cases, Chou et al. [2011] and Sun et al. [2011] observed that enhancements in ozone are caused by reductions in NO$_x$ emissions on weekends that lead to enhancements in VOC/NO$_x$ ratio and ozone production efficiency. Although the high OPE$_x$ values observed during the 2008 Olympics also coincided with weekends, the observed enhancements likely reflect changes in ozone precursors due to the short-term, but strict control policies implemented for this event. Note that the OPE$_x$ varies differently among different O$_3$ episodes. Figure 7 shows the correlations of [O$_3$] versus [NO] during four O$_3$ episodes (hourly maximum O$_3$ > 100 ppb), i.e., 9–10, 15–16, 19–20, and 23–26 August. Although the daily OPE$_x$ during every episode is similar, the average OPE$_x$ for four episodes is quite different, for example, the highest OPE$_x$ of 3.6 ppb/ppb is observed during the episode of 23–26 August, which is more than twice higher than 1.5 ppb/ppb during the episode of 15–16 August.

[20] The daily OPE$_x$ in this study is always lower than the value suggested for O$_3$-VOC sensitivity (OPE$_x$ < 7, [Sillman, 1995]), indicating that the ozone production in summer in Beijing is VOC-limited. Therefore, measures to control VOC emissions in Beijing would be effective to reduce O$_3$ levels. To further support this, we plot the daily OPE$_x$ versus the peak of NO$_x$ in early morning ([NO$_x$]$_0$, a surrogate of NO$_x$ emissions from local traffic) in Figure 8. Similar to that reported by Chou et al. [2009] during the CAREBeijing-2006 campaign, the daily OPE$_x$ presents a negative relationship with [NO$_x$]$_0$, suggesting that reduction of NO$_x$ emissions appears not to be helpful for mitigation of O$_3$ pollution. The decrease of OPE$_x$ as a function of [NO$_x$]$_0$ also supports the potential O$_3$-VOC sensitivity under the current ambient level of NO$_x$ in Beijing. This is because that increase of Δ[NO$_x$] will not result in a corresponding increase of O$_3$ since high [NO$_x$]$_0$ is associated with high value of Δ[NO$_x$]. [NO$_x$]/[NO]$_0$ is used to indicate the photochemical age by a number of studies [e.g., Dommen et al., 1999; Ge et al., 2012; Kleinman et al., 2000; Nunnermacker et al., 1998; Olszyna et al., 1994]. The variations of daily OPE$_x$ as a function of [NO$_x$]/[NO]$_0$ are shown in Figure 8b. The OPE$_x$ shows a concentration generally would lead to the high OPE$_x$ values (Figure 8). Another reason might be related to the well-known phenomenon commonly referred to as the “weekend ozone effect” or “holiday effect” [Fujita et al., 2003; Pollack et al., 2012; Yarwood et al., 2003]. In these cases, Chou et al. [2011] and Sun et al. [2011] observed that enhancements in ozone are caused by reductions in NO$_x$ emissions on weekends that lead to enhancements in VOC/NO$_x$ ratio and ozone production efficiency. Although the high OPE$_x$ values observed during the 2008 Olympics also coincided with weekends, the observed enhancements likely reflect changes in ozone precursors due to the short-term, but strict control policies implemented for this event. Note that the OPE$_x$ varies differently among different O$_3$ episodes. Figure 7 shows the correlations of [O$_3$] versus [NO] during four O$_3$ episodes (hourly maximum O$_3$ > 100 ppb), i.e., 9–10, 15–16, 19–20, and 23–26 August. Although the daily OPE$_x$ during every episode is similar, the average OPE$_x$ for four episodes is quite different, for example, the highest OPE$_x$ of 3.6 ppb/ppb is observed during the episode of 23–26 August, which is more than twice higher than 1.5 ppb/ppb during the episode of 15–16 August.

![Figure 5](image_url) **Figure 5.** Mean diurnal cycles of O$_3$\textsubscript{CAPS}, O$_3$\textsubscript{CL}, NO$_2$\textsubscript{CAPS}, and NO$_2$\textsubscript{CL} for the entire study. The shaded areas in the figure refer to nighttime.
positive correlation with [NO$_3$]/[NO$_2$] ($r^2 = 0.38$, $p < 0.05$), indicating that the OPE, at the urban site of Beijing increases simultaneously with the aging of air parcels. This result is consistent with that observed at Peking University (near 4th North Ring of Beijing) during CAREBeijing-2006 [Chou et al., 2009] and also in agreement with those at various urban sites, e.g., Houston and Tennessee, USA [Daum et al., 2003; Zaveri et al., 2003]. However, the correlation between OPE$_i$ and [NO$_3$]/[NO$_2$] is contrary to that observed at a rural site (SDZ) in Beijing, where ~75% of O$_3$ pollution is from regional transport rather than local photochemical production [Ge et al., 2012].

### 3.4. Case Studies

[21] Our previous study frequently observed high concentration of nitrate in summer, which played an important role in particulate matter pollution in Beijing [Sun et al., 2012]. Similarly, several episodes with high concentration of nitrate were also observed in this study (Figure 2). The formation of nitrate is mainly driven by three different processes, i.e., daytime photochemical production (R1), gas-particle partitioning (R2), and nighttime heterogeneous reactions (R3–R5). It appears that high concentration of NO$_3^–$ is closely linked to the high O$_3$ and NO$_2$, which are two key precursors in the formation of nitrate particles. Here two high-O$_3$ episodes were chosen to further elucidate the roles of precursors of O$_3$ and NO$_2$ in the nitrate formation.

\[
\begin{align*}
\text{NO}_2 + \text{OH} + \text{M} &\rightarrow \text{HNO}_3(g) + \text{M} \quad \text{(R1)} \\
\text{HNO}_3(g) + \text{NH}_3(g) &\leftrightarrow \text{NH}_4\text{NO}_3(s) \quad \text{(R2)} \\
\text{NO}_2 + \text{O}_3 &\rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R3)} \\
\text{NO}_2 + \text{NO}_3 + \text{M} &\rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R4)} \\
\text{N}_2\text{O}_3 + \text{H}_2\text{O} (aq) &\rightarrow 2\text{HNO}_3 \quad \text{(R5)}
\end{align*}
\]

[22] The first high-O$_3$ episode (Ep1) occurred between 9–10 August (Figure 9). The daily maximum of O$_3$ showed a large enhancement from ~60 ppb on 8 August to ~100 ppb on 9–10 August, indicating the strong photochemical processing during the 2 days. Although the OPE$_x$ values were similar, 2.6 and 2.5 ppb/ppb, respectively, the variations of nitrate in aerosol particles were quite different. The concentration of NO$_3^–$ remained consistently low ($< 7$ μg m$^{-3}$) on 9 August, yet exhibited a large enhancement associated with a pronounced diurnal cycle on 10 August. The increase of NO$_3^–$ on 10 August showed a corresponding decrease of NO$_2$ and NO. While the NO$_3^–$ concentration was enhanced by a factor of more than 6 from ~6 μg m$^{-3}$ to 38 μg m$^{-3}$ in 6 h (6:00–12:00), the NO$_2$ and NO decreased by ~53% and

### Table 1. A Summary of the OPE$_x$ Reported in Beijing and Surrounding Regions

<table>
<thead>
<tr>
<th>Location</th>
<th>OPE$_x$</th>
<th>Method</th>
<th>NO$_2$ Instrument</th>
<th>Date</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, Mountain area</td>
<td>3–6</td>
<td>[O$_3$] versus [NO$_x$]</td>
<td>P-CL</td>
<td>July 2005</td>
<td>Wang et al. [2006]</td>
</tr>
<tr>
<td>Beijing, Mountain area</td>
<td>3.0</td>
<td>[O$_3$] versus [NO$_x$]</td>
<td>P-CL</td>
<td>Summer 2008</td>
<td>Wang et al. [2010b]</td>
</tr>
<tr>
<td>Beijing, Urban</td>
<td>3.7–9.7</td>
<td>[O$_3$] + [NO$_x$] versus [NO$_x$]</td>
<td>P-CL</td>
<td>Summer 2008</td>
<td>Chou et al. [2009]</td>
</tr>
<tr>
<td>Beijing, Urban</td>
<td>8</td>
<td>[O$_3$] + [NO$_x$] versus [NO$_x$]</td>
<td>P-CL</td>
<td>Summer 2008</td>
<td>Chou et al. [2011]</td>
</tr>
<tr>
<td>Beijing, Rural area</td>
<td>1–6.8</td>
<td>[O$_3$] versus [NO$_x$]</td>
<td>CAPS</td>
<td>Summer 2012</td>
<td>This study</td>
</tr>
<tr>
<td>Urban plume</td>
<td>4.0</td>
<td>[O$_3$] versus [NO$_x$]</td>
<td>CL</td>
<td>Summer 2008</td>
<td>Ge et al. [2012]</td>
</tr>
<tr>
<td>Rural plume</td>
<td>5.3</td>
<td>[O$_3$] versus [NO$_x$]</td>
<td>CL</td>
<td>Summer 2008</td>
<td>Ge et al. [2012]</td>
</tr>
</tbody>
</table>

*P-CL represents the photolysis-chemiluminescence instruments.*
85% to 47 and 9 ppb, respectively. It is very likely that the NO$_3^-$ plume was due to the rapid photochemical production from the reactions of NO$_2$ and OH, followed by the formation of nitrate particles. In addition, the relatively low ambient temperature and high RH also facilitates the partitioning of HNO$_3$ to nitrate particles. After 12:00, the NO$_3^-$ started to decrease rapidly mainly because of the evaporative loss of NH$_4$NO$_3$ at high ambient temperature, and also the deeper PBL. Although the variations of O$_3$ and meteorological variables were similar, the concentration of nitrate however was much lower on 9 August than on 10 August, which was likely due to the consistently low levels of NO$_2$ limiting the daytime photochemical production of nitrate from the reaction of NO$_2$ with OH.

Beijing experienced another high-O$_3$ episode during 23–26 August (Ep2, Figure 10). During the 4 day episode, the variations of wind, RH and temperature were rather similar day by day, and the precursors of O$_3$ and NO$_2$ remained at high levels. The average OPE$_x$, 3.4 ppb/ppb is among the highest values throughout this study, suggesting the strong photochemical processing during this episode. Indeed, the daily maximum of O$_3$ is up to 130 ppb, which is the highest value observed in this study. To better elucidate the formation of nitrate, we calculate the photochemical production rate of HNO$_3$ using NO$_2$ × UV as a surrogate during daytime and the equilibrium constant of $K_p$ for the reaction R2 (higher $K_p$ indicates more stable NH$_4$NO$_3$) [Seinfeld and Pandis, 2006]. The time series of NO$_2$ × UV and $K_p$ is shown in Figure 11.

The NO$_3^-$ presented two peaks occurring in the early morning and around noon, and it appeared that the evolution of NO$_3^-$ was separated into two stages, i.e., from midnight to 3:00–4:00, and from ~5:00–6:00 to noon. During the first stage, the increase of NO$_3^-$ was associated with a synchronous increase of NO$_2$ and a corresponding decrease of O$_3$.

**Figure 7.** Correlations between O$_x$,CAPS and NO$_2$,CAPS (red dots), and O$_x$,CL and NO$_2$,CL (black dots) during four high-O$_3$ episodes: (a) 9–10 August, (b)14–15 August, (c)19–20 August, and (d) 23–26 August. The regression slopes refer to the average OPE$_x$,CAPS (red dots) and OPE$_x$,CL (black dots) determined for each episode.

**Figure 8.** Correlations of (a) OPE$_x$ versus [NO$_x$]$_0$, and (b) OPE$_x$ versus [NO$_3$]/[NO$_2$]. [NO$_x$]$_0$ is the maximum of NO$_x$ in early morning representing the relative traffic emission of 1 day. [NO$_3$]/[NO$_2$] indicates the photochemical age of the air, and higher values suggest more aged air.
While the NO was low, the NO\textsubscript{2} and O\textsubscript{3} remained at a considerable level, which facilitated the formation of the NO\textsubscript{3} radical and dinitrogen pentoxide (R\textsubscript{3}–R\textsubscript{4}), and hence the heterogeneous formation of HNO\textsubscript{3} under high RH conditions. This is consistent with the continuous increase of the equilibrium constant of $K_p$ for ammonium nitrate formation. Although the low boundary layer height might have played a role in the enhancement of NO\textsubscript{3}\textsuperscript{−} concentration, the first peak at ~3:00–4:00 was more likely due to the heterogeneous reaction associated with the removal of NO\textsubscript{y} at nighttime. The formation of NO\textsubscript{3} was then slowed down because the precursor of O\textsubscript{3} was almost completely consumed during this period. The NO\textsubscript{3}\textsuperscript{−} started to increase again at ~5:00–6:00 and peaked between ~10:00–12:00. The increase of NO\textsubscript{3}−
Figure 11. Time series of particulate NO₃⁻, equilibrium constant of $K_p$, for ammonium nitrate formation, and NO₂ × UV, a surrogate of photochemical production rate of HNO₃ during daytime.

exactly corresponded to the start of daytime photochemical processing (NO₂ × UV in Figure 11). Meanwhile, the $K_p$ gradually decreased counteracting the formation of nitrate. Therefore, the second increase of NO₃⁻ suggests the photochemical production dominates over the evaporative loss processes during this stage. The photochemical production reached a maximum at noon time when the NO₃⁻ concentration peaked as well. After that, the NO₃⁻ rapidly decreased to the lowest level of the day in ~2–3 h, due to the reduced photochemical production rate and significantly enhanced evaporative loss.

4. Conclusions

[25] The ambient nitrogen dioxide (NO₂) was measured in situ by an Aerodyne Cavity Attenuated Phase Shift NO₂ monitor in August 2012 at an urban site in Beijing. The CAPS is highly sensitive with the detection limit an order of magnitude lower than the standard, commercially available CL-based NOₓ analyzer, and also a wide linear response range of 15 ppt–1 ppm. The NO₂ measured by the CAPS and CL shows overall agreement; however, large discrepancies up to ~20%, in particular during the afternoon, were also observed due to the interferences with reactive nitrogen species on CL measurements. The discrepancies therefore were NOₓ dependent with larger differences associated at higher NOₓ levels.

[26] The daily OPEₓ was derived from the correlation of Oₓ versus NOₓ. The average OPEₓ for the entire study was 2.6 (1–6.8) ppb/ppb, which is comparable to the values previously reported in Beijing. Our results showed that the OPEₓ derived from the CL NO₂ can be overestimated by 19–37% due to the interferences with reactive nitrogen species. The overestimation is expected to be more significant in rural and remote areas where the contribution of NOₓ to the total NOₓ is much higher than urban cities. The generally low OPEₓ and the negative correlation between OPEₓ and [NOₓ]₀ implied the VOC-limited ozone production in summer in Beijing. In addition, the OPEₓ increased as a function of photochemical age, [NO₂]/[NOₓ], which is in contrast to that observed at rural sites, indicating the different sources and photochemical processing of Oₓ between urban and rural areas in and around Beijing.

[27] Two case studies during 9–10 August and 23–26 August 2012 revealed that high concentrations of precursors of Oₓ and NOₓ are of importance for the formation of nitrate particles. A detailed analysis of the evolution of gaseous species, nitrate, and meteorological conditions suggest that the variations of nitrate in fine particles are caused by the competing effects of different formation mechanisms, including daytime photochemical production, gas-particle partitioning equilibrium, and nighttime heterogeneous reactions. Overall, high concentrations of NO₂ and Oₓ with favorable meteorological conditions, e.g., high RH and low temperature, will greatly facilitate the formation of nitrate particles and increase the air pollution levels in the cities.

References


