Impact of the regional transport of urban Beijing pollutants on downwind areas in summer: ozone production efficiency analysis

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ABSTRACT

Ambient measurements of SO₂, O₃, NOₓ, NO₃, and CO were made at Shangdianzi (SDZ), a rural site in the northeast (NE) of Beijing, and urban Beijing (China Meteorological Administration) from 1 June 2008 to 31 August 2008. The pollutants at SDZ showed very different levels under different wind conditions, with the levels under the southwest (SW) wind being much higher than those under the NE wind. The SW wind facilitates the transport of urban plume to SDZ, whereas the NE wind provides a background condition. At SDZ, the Ozone (O₃) concentration in air masses from urban Beijing was found to be 33.4 ± 0.4 ppbv higher than that from clean regions in summer. The ozone production efficiency (OPEₓ) for the urban plume and background condition was 4.0 and 5.3, respectively. Based on these OPEₓ values and the NOₓ values for the respective conditions, the contribution of in-situ production in the urban plume to the level of O₃ at SDZ is estimated to be 8.6 ppbv, corresponding only to 25.7% of the total impact of urban plume transport. This suggests that direct transport of O₃ rather than in-situ photochemistry contributes mainly to the summer elevation of the level of O₃ at SDZ.

Keywords: regional transport, O₃, NOₓ, ozone production efficiency (OPEₓ), sources

1. Introduction

Ozone (O₃) is one of the most important oxidants and the dominant precursor of radicals (OH and NO₃) in the atmospheric troposphere. As one of the greenhouse gases, O₃ plays a significant role in climate change and atmospheric chemistry (Akimoto, 2003). Elevated concentration of surface O₃ is of great concern because of its adverse impacts on human health and ecosystems (Mills et al., 2011). Most studies show that the elevated concentration of surface O₃ is because of the increased concentration of its precursors (i.e. NOₓ, CO and VOCs), which originate mainly from anthropogenic sources (Chameides et al., 1992; Bowman and Seinfeld, 1994; Finlayson-Pitts and Pitts, 1997; Tang et al., 2010). This is true in cities, especially in megacities (Wang et al., 2000; Molina and Molina, 2004; Shao et al., 2006; Chan and Yao, 2008; Ran et al., 2009; Yan et al., 2011). However, frequent high-O₃ events occur not only in cities but also in rural or remote areas, where local emission of anthropogenic pollutants is not important. This phenomenon is usually caused by transport of polluted air masses and photochemical formation of O₃ in these air masses. For example, transport of polluted air masses are believed to elevate O₃ levels at Chinese regional background sites (Chan et al., 2003; Lin et al., 2008; Xu et al., 2008) or even global background sites (Li et al., 2009).

Beijing is one of the megacities in Asia and the major population centre in the city cluster of Beijing–Tianjin–Tangshan region in North China, where the regional air pollution is characterised by high concentrations of both primary and secondary pollutants (Shao et al., 2006). The emissions of SO₂, NOₓ and VOCs are mainly related to fuel burning from industry, power plants, domestic heating, vehicles and solvent use in urban Beijing (Hao et al., 2005).
These pollutants may strongly influence the air quality of the downwind areas of Beijing. This view is supported by an early study of Yang et al. (2005), who showed high similarity in aerosol mass and elements between Beijing downtown and suburb areas. Li et al. (2011) reported that the aerosol in urban Beijing has large impact on the lifetimes of NO₂, CO and SO₂ and may increase the transport distance of gaseous pollutants. Wang et al. (2006) also reported a high O₃ pollution case in a mountainous area north of Beijing and attributed the high O₃ pollution to a polluted plume from urban Beijing.

To monitor the long-term changes of atmospheric compositions and related properties over North China, a regional background station was established in the early 1980s at the north edge of the North China Plain (NCP). This station, called Shangdianzi (SDZ), has been one of the Global Atmosphere Watch (GAW) stations. Located between the heavily polluted and fairly clean areas, SDZ is a very interesting site for atmospheric chemistry studies. In the past few years, a number of studies (Yang et al., 2005; Lin et al., 2008; Meng et al., 2009; Ge et al., 2010; Stohl et al., 2010; Shen et al., 2011) have been done at this site, focusing on different topics. Surface O₃ at SDZ has been one of the topics that deserve a careful study. Initial measurements show that the hourly mean concentration of surface O₃ at SDZ can be much higher than 100 ppb (Meng et al., 2009), indicating that photochemical smog can occur at this background site. To better understand the origin of surface O₃ at SDZ, Lin et al. (2008) investigated the contributions of pollutants from the NCP to the background level of surface O₃ at SDZ and found that such contributions accounted for about 28.9 ppb in summer during 2004–2006. Ozone production efficiency (OPE), which is defined as the number of molecules of O₃ formed per NO₃ removed from atmospheric O₃-forming oxidation cycles [i.e. P(O₃)/P(NO₃)] (Liu et al., 1987) and is calculated from observations of NO₂ and NO₃ (Kleinman et al., 1994), is one of the useful indicators in the study of photochemical pollution. A few studies have paid attention to OPE in Beijing’s urban and rural areas. Based on measurements made at a Peking University site, Chou et al. (2009) obtained OPE values ranging from 3.9 to 9.7. An (2006) modelled OPE in the Beijing urban areas and reported a value of about 3.0. Based on in-situ measurements of O₃, NOₓ, NOₓ, and so on, Ge et al. (2010) estimated the OPE at SDZ to be in the range of 0.2–21.1, with an average of 4.9. All these OPE values are within the range of the OPE values found in America and Europe (Rickard et al., 2002; Xu et al., 2009).

Generally, surface O₃ at a background site can come from the transport of O₃ (including O₃ formed during transport), in-situ photochemical production by the transported O₃ precursors and pseudo natural O₃ background. The study of Lin et al. (2008) only shows the total impact of urban plume on the level of surface O₃ at SDZ. The OPE study of Ge et al. (2010) cannot differentiate contribution of the in-situ photochemical reactions from O₃ transported to the site. Therefore, the roles of different factors influencing the O₃ formation and OPE at the site are still not very clear. In this article, we present the variation characteristics of O₃ and its precursors in Beijing’s urban and rural areas (SDZ) in the summer of 2008, study the contributions of in-situ photochemical production and transport from southwestern plume (Beijing city and the NCP) to the afternoon enhancement of O₃ at SDZ. The OPE from southwestern and northeast (NE) plume and the correlation with daily photochemical age is also presented in this article.

2. Measurements

2.1. Observation sites

The measurements were made at an urban Beijing site and a regional background site in North China. The urban site is located on the rooftop of a building in China Meteorological Administration (CMA: 39°95′N, 116°32′E, 96 m a.s.l.) in Beijing city, whereas the background site, SDZ (40°39′N, 117°07′E, 293.9 m a.s.l.), is located 100 km NE of Beijing city and is one of the WMO/GAW regional background stations in China. Figure 1 shows the locations of the two sites and the surrounding topography. More details about the sites are given in Lin et al. (2008, 2011).

As indicated in a previous study (Lin et al., 2008), the valley topography facilitates the transport of pollutants from the NCP to SDZ. In summer, the prevailing winds are southwest (SW) from afternoon to early evening and NE during night and morning. Therefore, pollutants from the urban area of Beijing and its surrounding areas may be transported to SDZ during afternoon and be cleaned up as the NE wind (clean air masses from rural area) blows at night.

2.2. Instruments and data

Commercial instruments from Thermo Electron Corporation, USA were used to measure O₃ (49C), NO/NO₂/NOₓ (42CTL), NO/NOₓ (42CY), CO (48CTL) and SO₂ (43CTL) at CMA and SDZ. All instruments were housed in an air-conditioned rooftop room of the building (38 m above ground level) at CMA and an air-conditioned bungalow at SDZ, and the air inlets were installed 1.8 m above the roofs. Daily zero/span checks were automatically done using dynamic gas calibrators (Model 146C) combined with zero air suppliers (Model 111) and standard gas mixtures for SO₂, NO and CO. More frequent zero checks (every
6h) for CO analysers were carried out. The multipoint calibrations of CO, SO\(_2\), NO\(_x\), and NO\(_y\) analysers were made every month at CMA and every season at SDZ using the standard gases, which were compared against National Institute of Standards and Technology (NIST) traceable standards (Scott Specialty Gases, USA). An O\(_3\) calibrator (49C PS) was used to calibrate the O\(_3\) analysers at the sites. The calibrator is traceable to the Standard Reference Photometer maintained by WMO World Calibration Centre in Switzerland (EMPA). High-resolution data (5 or 1 min averages) were recorded and hourly average values are presented and analysed in this article.

3. Results and analysis

3.1. Characteristics of air pollutants

Figure 2 shows the time series of SO\(_2\), NO\(_x\), CO, O\(_3\), and O\(_x\) at SDZ and of SO\(_2\), NO\(_x\), CO, O\(_3\), and O\(_x\) at CMA in summer (1 June to 31 August 2008). Instead of using O\(_x\) (≡O\(_3\) + NO\(_2\)) as the total oxidant at SDZ, the O\(_x\) (≡O\(_3\) + NO\(_2\) + NO\(_y\)) in this study includes more important odd nitrogen oxidants other than NO\(_2\), particularly HNO\(_3\) (Chou et al., 2009), and it was 4 ppb in daytime and 1.4 ppb in nighttime higher than O\(_x\) during summer time, which took up 7 and 3% of the mean concentration of O\(_x\) during daytime and nighttime, respectively. However, the observation of NO\(_y\) was absent at the CMA site, the total oxidant for this site is given by O\(_x\) as before (St John et al., 1998) and might be underestimated by 20% during high-O\(_3\) episodes according to Chou et al. (2009). Significant day-to-day variations of pollutants were observed during the period. These variations are caused by many factors, such as emissions from local and outside, meteorological parameters and atmospheric chemistry (Li et al., 2007; Meng et al., 2009). It is worth to mention that the mixing ratios of all species at both sites were lower in August when the 2008 Beijing Olympic Games were held than those in the other 2 months during the observation period and did not exceed the values of the Grade-II standards of Chinese Ambient Air Quality. Much stricter emission reduction measures were implemented during the Olympic Games and the air quality was improved greatly, as reported in many studies (Witte et al., 2009; Huang et al., 2010; Wang et al., 2010a, 2010b; Yang et al., 2010; Yu et al., 2010; Zhang et al., 2011). However, the level of O\(_3\) at SDZ did not show month-to-month differences exceeding those found in the summer months of the normal years, for example, those reported by Lin et al. (2008). Moreover, the calculated monthly OPE for the SW plume was nearly stable. Therefore, in this study, we do not treat the data during the Olympic Games separately.

The hourly maximal O\(_3\) level at CMA and SDZ reached 138 and 169 ppb, respectively, on 10 June 2008 with almost similar daily amplitude of O\(_x\) (95.8 ppb at CMA and
92.6 ppb at SDZ). Besides, the O₃ peak at CMA was 3 h earlier (at 14:00) than that at SDZ (at 17:00). This example shows that, as the high-O₃ events (daily maximal mixing ratio of 1 h averaged O₃ over 100 ppb) occur, the daily increase of total oxidant at SDZ may be similar to that at the urban site. The difference in the peak values of O₃ between SDZ and CMA may be attributable to the difference in the O₃ concentrations in the previous night. At the urban site, the higher NOₓ level because of vehicle emissions causes larger consumption of O₃ during the night. In fact, out of the 39 high-O₃ days, 28 (about 72%) days showed higher peak of O₃ at SDZ than at CMA and 68% of these days showed higher concentration of O₃ in the previous evening at SDZ and 74% of the days showed similar daily amplitude of O₃ in these two sites during the observation periods (see Table 1). Figure 3 shows the scatter plot of the daily amplitude of O₃ at CMA against that at SDZ during the summer of 2008. As can be seen in the figure, the daily amplitudes at both sites are significantly correlated ($R = 0.78$, $P < 0.01$) and the slope of the fitted line, 1.15 (close to 1), suggests similar daily amplitudes of O₃ at both sites.

The diurnal patterns of CO, SO₂ and NOₓ at SDZ look very different from those at CMA, whereas O₃ and Oₓ show similar diurnal patterns at both sites (Fig. 4). The CO and NOₓ concentrations at CMA show similar diurnal

**Table 1.** Differences of daily maximal and minimal mixing ratio of Oₓ and O₃ between SDZ and CMA during high-ozone days

|       | A   | B   | C   | D   |
|-------|-----|-----|-----|-----|
| O₃ (days) | 39  | 28  | 19  | 29  |
| (O₃ + NO₂) (days) | 34  | 21  | 12  | 23  |
| Oₓ (days) | 29  | 17  | 14  | 20  |
| Fraction Oₓ (%) | –   | 72  | 68  | 74  |
| Fraction (O₂ + NO₂) (%) | –   | 62  | 57  | 68  |
| Fraction O₃ (%) | –   | 59  | 82  | 69  |

A: high-ozone days; B: days with peak value of Oₓ, (O₃ + NO₂) and O₃ at SDZ higher than that at CMA; C: days with daily minimal at SDZ higher than CMA among B; D: similar daily amplitude (daily amplitude lower than $± 20$ ppb) between SDZ and CMA. Fraction Oₓ is the fraction of three scenes in high-ozone days. For comparing, (O₃ + NO₂) was also calculated at both sites.
patterns, with elevated concentration during the night, a peak around 8:00 and a valley in the afternoon, fairly consistent with those at the same site in winter (Lin et al., 2011). At SDZ, the peaks of CO and SO$_2$ occur in late afternoon (around 17:00), similar to those of O$_3$ and O$_x$. The late occurrences of these pollutant peaks may be attributed to the transport of urban plume to the SDZ site, which causes enhanced concentrations of air pollutants in the afternoon. Figure 5 may help to clarify the impact of the transport of urban plume. As indicated by the wind vectors in Fig. 5a, the wind direction changes around noon from northeasterly (from the clean rural sector) to southwesterly (from the urban and polluted rural sector). The wind directions in the entire afternoon favour the transport of urban plume to SDZ, which can inevitably elevate the concentrations of pollutants, such as CO, NO$_x$, and SO$_2$. The fact that the concentrations of O$_3$ and O$_x$ at SDZ peaked 3 h later than those at CMA also support the idea of the transport of urban plume towards SDZ. Another evidence of the transport is the diurnal variation of the ratio of NO$_x$/NO$_y$, which shows a continuous increase after 12:00 (Fig. 5b) and suggests that air with more freshly emitted NO$_x$ from urban sector replaces gradually more or less aged air over SDZ. In the following section, we will quantify the influence of such air transport.

3.2. Impacts of precursors from the urban area on the O$_3$ concentration at SDZ

To investigate the relationships among SO$_2$, CO, O$_x$ and NO$_y$ at SDZ and CMA, Pearson correlations are calculated from the hourly concentrations of trace gases and meteorological parameters and are listed in Table 2. Compared to the study of the winter measurements from Gucheng (Lin et al., 2009) and the CMA site (Lin et al., 2011), the

Fig. 3. Scatter plot of daily amplitude of O$_x$ at SDZ and CMA (reproduced with permission from B.Z. Ge).

Fig. 4. Average diurnal cycles of CO, SO$_2$, NO$_x$/NO$_y$, and O$_3$/O$_x$ at SDZ and CMA in summer 2008 (reproduced with permission from B.Z. Ge).
summer concentrations of the primary pollutants at SDZ are less significantly correlated among each other, like those concentrations of primary pollutants at Gucheng (Lin et al., 2009). This phenomenon may indicate that the concentrations of primary pollutants in summer are more influenced by some processes other than emission and transport than in winter. Such processes can be photochemical reactions, wet and dry depositions (Pan et al., 2010).

The concentrations of the pollutants at SDZ are significantly correlated with those at CMA, especially those of SO$_2$, CO and O$_x$, with $R = 0.60$, 0.53 and 0.72, respectively, suggesting close relationships between pollutants in urban plume and those at SDZ. To quantify the effect of the transport of urban pollutants on O$_x$ formation at SDZ, the rose distributions of average concentrations of O$_3$, NO$_x$, and NO$_y$ at SDZ are plotted in Fig. 6. Among the gases, O$_3$, NO$_x$, and NO$_y$ are subjected to stronger influences of chemical reactions, whereas CO is not and hence can be used as a marker. In summer, the frequency of wind direction is the highest from SW (46.0%) and then from NE (28.6%). This indicates that the urban plumes from SW, containing more pollutants, exert much stronger influences on the levels of ambient pollutants at SDZ than the clean air masses from NE. A difference of 33.4 ± 0.4 ppbv between the average concentrations of O$_3$, 33.5 ± 0.4 ppbv between those of O$_x$, not shown in Fig. 6, from SW and NE plume can be calculated from the statistics, suggesting that urban plumes from SW may elevate the concentration of O$_x$ at SDZ by 33.5 ± 0.4 ppbv,

![Figure 5](image)

**Fig. 5.** Average diurnal cycles of wind vector (a) and the ratio NO$_x$/NO$_y$ (b) at SDZ in summer 2008 (reproduced with permission from B.Z. Ge).

### Table 2. The correlation coefficients of the correlations among the trace gas concentrations and meteorological parameters at SDZ and CMA ($N = 1946$)

|            | SO$_2$-SDZ | CO-SDZ | NO$_x$-SDZ | O$_x$-SDZ | NO$_y$-SDZ | CO-CMA | SO$_2$-CMA | NO$_x$-CMA | T | RH | WS |
|------------|------------|--------|------------|-----------|------------|--------|------------|------------|---|----|----|
| SO$_2$-SDZ | 1.00       |        |            |           |            |        |            |            |   |    |    |
| CO-SDZ     | 0.65       | 1.00   |            |           |            |        |            |            |   |    |    |
| NO$_x$-SDZ | 0.46       | 0.63   | 1.00       |           |            |        |            |            |   |    |    |
| O$_x$-SDZ  | 0.57       | 0.46   | 0.52       | 1.00      |            |        |            |            |   |    |    |
| NO$_y$-SDZ | 0.21       | 0.26   | 0.43       | -0.10     | 1.00       |        |            |            |   |    |    |
| CO-CMA     | 0.42$^a$   | 0.53$^a$| 0.40$^a$   | 0.25$^a$  | 0.11       | 1.00   |            |            |   |    |    |
| SO$_2$-CMA | 0.60$^a$   | 0.42$^a$| 0.47$^a$   | 0.48$^a$  | 0.13       | 0.59   | 1.00       |            |   |    |    |
| NO$_x$-CMA | 0.34$^a$   | 0.23$^a$| 0.23$^a$   | 0.21      | 0.21       | 0.59   | 0.27       | 1.00       |   |    |    |
| O$_x$-CMA  | 0.30$^a$   | 0.16$^a$| 0.30$^a$   | 0.72$^a$  | -0.02      | 0.20   | -0.16      |            |   |    |    |
| T          | 0.21       | 0.13   | 0.13       | 0.57      | -0.34      |        |            |            |   |    |    |
| RH         | -0.27      | 0.21   | 0.07       | -0.55     | 0.30       |        |            |            |   |    |    |
| WS         | 0.32       | 0.09   | 0.57       | -0.28     |            |        |            |            |   |    |    |

All the correlation coefficients are significant at 99% level.$^a$Data based on 12 h smooth to minimise the impacts of transport delay for air masses from the urban area to SDZ.
a result similar to that based on the 2004–2008 measurements (Lin et al., 2008).

The impacts of urban plume on the \( \text{O}_3 \) concentration at SDZ may be decomposed as

\[
|O_{x\text{ trans impacts}}| = |O_{x\text{ trans}}| + |O_{x\text{ trans production}}| + |O_{x\text{ in-situ production}}| \tag{1}
\]

where \( O_{x\text{ trans impacts}} \) represents the total impacts of urban plume on the \( \text{O}_3 \) concentration at SDZ, and \( O_{x\text{trans}} \), \( O_{x\text{trans production}} \), and \( O_{x\text{in-situ production}} \) are the \( \text{O}_3 \) increases due to transport of \( \text{O}_x \) already formatted in urban area, transport of \( \text{O}_x \) formatted during air travelling to SDZ and in-situ \( \text{O}_3 \) production enhanced by precursors transported to SDZ from urban area, respectively. According to the above result, \( O_{x\text{trans impact}} \) is 33.5 ± 0.4 ppbv. In the following section, the effects of regional transport and the enhancement of in-situ \( \text{O}_3 \) production will be quantified and analysed.

As can be seen in Fig. 6, the differences in the \( \text{NO}_x \) and CO concentrations were also large between the SW–NE directions, with 6.95 ± 1.19 ppbv for \( \text{NO}_y \) and 360 ± 80 ppbv for CO. However, the average concentration of \( \text{NO}_x \) from SW is similar to that from NE, with a difference of only 0.25 ± 0.16 ppbv between both directions. This may be caused by more intensive photochemical losses of \( \text{NO}_x \) in the SW plume. Larger emissions of VOCs in the polluted sector may favour the production of \( \text{O}_3 \), transform \( \text{NO}_x \) into \( \text{NO}_y \) and increase the concentration of \( \text{NO}_x \) (Xu et al., 2011). In addition, few \( \text{NO}_x \) transformed to \( \text{NO}_y \) during night and early morning, when the wind from NE sector is dominant, may result in smaller difference of \( \text{NO}_x \) between the SW–NE directions.

**Fig. 6.** Rose distributions of the average concentrations of \( \text{O}_3 \) (a), CO (b), \( \text{NO}_x \) (c) and \( \text{NO}_y \) (d) over summer 2008 at SDZ (reproduced with permission from B.Z. Ge).
3.3. Impacts of photochemical production

It is shown in Section 3.2 that pollutants in the SW plume could increase the concentration of O$_x$ at SDZ by 30 ppbv. However, the detailed contributions from the transport of pollutants and from the enhancement of the in-situ O$_3$ production at SDZ are unknown (see Eq. 1). Here, we estimate the contributions by using the OPE$_x$ of different plumes. In this study, linear regressions are applied to (O$_x$) (O$_3$/C$_27$NO$_2$/C$_27$NO$_x$) versus (NO$_z$/C$_1$NO$_x$) data and the slopes of the regression lines are taken as daily OPE$_x$ (Chou et al., 2009). Data during 6:00–19:00 are used for the regressions. Only slopes of the regression lines with higher correlation coefficients ($R^2 > 0.6$) and positive intercepts (the background O$_x$ concentration) are considered to be effective daily OPE$_x$ for this study. In order to study the O$_3$ formation characteristics at SDZ, the daily OPE$_x$ as a function of chemical ageing calculated by (NO$_z$/NO$_y$) is plotted in Fig. 7. As clearly shown in this figure, there is a significant negative correlation between OPE$_x$ and (NO$_z$/NO$_y$), indicating that the OPE$_x$ at SDZ decreases significantly with the ageing of air parcels. This result is consistent with that of Marion et al. (2001), Olzyna et al. (1994) and Trainer et al. (1995) and indicates a reduction of OPE with the increase of precursor emissions. Model simulations by Lei et al. (2008) show that the O$_3$ production rate decreases with the increase of chemical age parameter for downwind areas of Mexico City. However, the study by (Chou et al., 2009) shows a positive correlation between OPE$_x$ and (NO$_z$/NO$_y$) for the urban site, Peking University. The different correlation between OPE$_x$ and (NO$_z$/NO$_y$) often exist among urban and its downwind areas and this may be attributed to the transport of urban plume to its downwind site. According to this study, more specifically, the air with freshly emitted NO$_x$ from urban sector replaces the aged air over SDZ and decreases the ratios of NO$_2$/NO$_x$. Besides, the increased concentration of O$_3$ at SDZ would not be produced by the local photochemical production because the air parcel is fresh, but strongly might be the daily transported from high O$_3$ concentration area, such as Beijing downtown and the NCP.

The relationship between O$_x$ and NO$_2$ can be very different under different wind conditions. Here, we use the method of Nunnermacker et al. (1998) to obtain OPE values representing the urban plume and background. Fig. 8 shows the scatter plot of the concentrations of O$_x$ and NO$_2$ in the SW and NE wind conditions, with results of linear regressions. The slopes of the (O$_x$)–(NO$_2$) line for the SW and NE winds are 4.0 ± 0.32 and 5.3 ± 0.55 ppb/ppb$^{-1}$, respectively. These values are in the range of those (3.9–9.7) based on the measurements from the Peking University site during high-O$_3$ episodes (Chou et al., 2009) and those (2–8) simulated for the Pearl River Delta region (Wang et al., 2010c) and consistent with the value in previous study for SDZ (average 4.3 for clear days) (Ge et al., 2010). The OPE$_x$ value for the NE wind (OPE$_x$-NE) is higher than that for the SW plume (OPE$_x$-SW), suggesting that air masses from the clean sector produce O$_3$ more efficiently than those from the polluted sector. This result is consistent with those reported in other studies (Carpenter et al., 2000; Kleinman et al., 2002; Rickard et al., 2002; Lin et al., 2009; Thielmann et al., 2002). It is noteworthy that the correlation coefficient of the (O$_x$)–(NO$_2$) correlation for the SW wind (0.63) is

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**Fig. 7.** The correlation between the daily OPE$_x$ and (NO$_z$/NO$_y$). The red-solid points indicate outliers of 27 and 28 July and are not included in the regression. The winds on these 2 days were always from SW with no direction change and hence are not considered as normal conditions (reproduced with permission from B.Z. Ge).

**Fig. 8.** Scatter plot of O$_x$ versus NO$_2$ at SDZ during the summer of 2008. The black points show data under SW wind conditions and the red ones show those under NE wind conditions (reproduced with permission from B.Z. Ge).
smaller than that for the NE wind (0.80). This may be attributable to the impact of the pollutants’ transport (O\textsubscript{3} and NO\textsubscript{y}) from the polluted sector on the local concentrations of O\textsubscript{3} and NO\textsubscript{y} at SDZ, as under the SW transport conditions, larger parts of variances of the O\textsubscript{3} and NO\textsubscript{y} concentrations are not related to local photochemistry, on which the (O\textsubscript{3})-(NO\textsubscript{2}) correlation is based. The impact of the SW transport is particularly important during afternoon as mentioned in Section 3.1.

Factually, the OPE\textsubscript{c}-NE could be used as the in-situ OPE\textsubscript{c} as the aged air parcel (NO\textsubscript{y}/NO\textsubscript{z} below 0.25) from rural background area and the OPE\textsubscript{c}-SW as the OPE\textsubscript{c} of the urban plume (NO\textsubscript{y}/NO\textsubscript{z} above 0.40). Factually, the value of OPE\textsubscript{c}-SW is similar to that for Beijing urban area (An, 2006) if considering the (O\textsubscript{3}) as (O\textsubscript{3} + NO\textsubscript{2}) instead (O\textsubscript{3} + NO\textsubscript{2} + NO\textsubscript{y}), and is in the OPE\textsubscript{c} range of 3.9-9.7 obtained by Chou et al. (2009) using the same method. Therefore, the in-situ O\textsubscript{3} production enhanced by urban plume can be calculated as following:

\[
\text{In-situ \overline{O}_3} = \text{OPE}_{\text{SW}} \times \alpha \times \Delta \text{NO}_y (2)
\]

\[
\Delta \text{NO}_z = \text{NO}_z^{\text{SW}} - \text{NO}_z^{\text{SW Transport}} - \text{NO}_z^{\text{NE}} (3)
\]

where \(\alpha\) is the correcting coefficient (0.53) for correcting NO\textsubscript{y} loss during the transport of pollutants from the source region to the observation point according to Ge et al. (2010) and the \(\Delta \text{NO}_y\) can be considered as the average additional NO\textsubscript{y} produced by urban plume at SDZ. However, according to a previous study (Ge et al., 2010), the photochemical production of NO\textsubscript{y} in SW direction has been lost by more than a half owing to dry deposition during transport. \(\text{NO}_z^{\text{SW Transport}}\) could be small and is assumed to be zero. The \(\text{NO}_z^{\text{SW}}\) and \(\text{NO}_z^{\text{NE}}\) are 7.8 and 3.9, respectively. We obtained the upper limit level of \(\Delta \text{NO}_z\) as 3.9 (7.8-3.9 = 3.9). The O\textsubscript{3} elevation due to in-situ production enhanced by urban plume is estimated to be 8.6 ppbv, corresponding to about 25.7% of the total impact (about 33 ppbv) of the SW plume on the level of O\textsubscript{3} at SDZ. This indicates that in-situ O\textsubscript{3} production enhanced by urban plume is not the dominant factor for O\textsubscript{3} pollution at SDZ and contributes only to one-fourth of the total impact from transport of urban pollutants.

To support this view, we calculated the in-situ photochemical production at SDZ during 20–23 July 2008 using the CMBZ-OBM (observation based cbm-z model) model. In this case, the hourly maximum of O\textsubscript{3} concentration reached 124.5 ppbv at 17:00 on 23 July. For the model calculation, we used the hourly observations of VOCs, NO\textsubscript{y} and daily minimum of O\textsubscript{3} (instead of O\textsubscript{3} for eliminating the hourly NO\textsubscript{y} + NO\textsubscript{z} observation impact) concentration as well as hourly meteorological data. The modelled and observed O\textsubscript{3} concentrations agree well with each other (not shown). The O\textsubscript{3} accumulations caused by in-situ photochemistry and transport are estimated from the model result and observational data (Fig. 9). The in-situ photochemistry contributed 26.3% on average and about 50% during afternoon to the observed O\textsubscript{3} level, which is consistent with the above result.

### 3.4. The source analysis of NO\textsubscript{y} at rural site

Although the NO\textsubscript{y}-CO and NO\textsubscript{y}-SO\textsubscript{2} correlations during summer at SDZ are less significant than those during winter at CMA and Guicheng (see Section 3.2) with the correlation coefficients of 0.46 and 0.63, respectively, the correlations are statistically significant at \(P = 0.01\) (Table 2). This indicates that NO\textsubscript{y} share some common sources with CO and SO\textsubscript{2} during summer at SDZ. Usually, stationary sources (mainly coal-burning) emit much more SO\textsubscript{2} than CO, whereas mobile sources emit much more CO than SO\textsubscript{2}. Both types of sources emit NO\textsubscript{y} (Lin et al., 2009, Lin et al., 2011). Stehr (2000) and Tong et al. (2005) used the multilinear regression method to estimate the relative contributions of different types of sources to NO\textsubscript{y} at the shore of Chesapeake Bay, Maryland, and in two national parks of the United States, respectively. The same method was applied by Lin et al. (2011) to estimate the relative contributions of stationary and mobile sources to NO\textsubscript{y} at CMA, an urban site of Beijing. To see the differences in NO\textsubscript{y} sources between the CMA and SDZ sites, we follow the same approach to obtain the relative contributions of stationary and mobile sources to NO\textsubscript{y} at the SDZ site.

Suppose that NO\textsubscript{y} at SDZ can be calculated using the multilinear model

\[
\text{NO}_y = x1 \times \text{SO}_2 + x2 \times \text{CO} + \beta (4)
\]

where \(x1\) and \(x2\) represent the fitted coefficients of SO\textsubscript{2} and CO, and \(\beta\) is the intercept. Based on the regression, \(x1, x2\) and \(\beta\) are 0.147, 0.01 and 3.48, respectively, and the multiple regression coefficient is 0.62 (\(P = 0.01\)). The condition index is 6.83 (<30) and the variance inflation factor is 1.69 (<10), suggesting the regression is statistically significant and the collinearity of independents is not significant.

The average concentrations of SO\textsubscript{2}, CO and NO\textsubscript{y} in summer 2008 and the coefficients \(x1\) and \(x2\) are used to calculate the relative contributions of the stationary and mobile sources to NO\textsubscript{y}. On average, the relative contributions of the stationary and mobile sources to NO\textsubscript{y} at SDZ during summer are estimated to be 4 ± 1 and 68 ± 28%, respectively. The relative contribution of mobile sources to NO\textsubscript{y} is comparable to those from the other studies, such as 47% in 2006 in Beijing city based on the emission data (Zhang et al., 2009) and 66% at a urban site in Beijing during winter (Lin et al., 2011). However, the
relative contribution of stationary sources is significantly smaller than that of 40% for the CMA site in Beijing during winter of 2007–2008 (Lin et al., 2011). This may be caused by the emission control imposed for the Olympic Games 2008, which was implemented mainly in summer 2008 and reduced emissions from power plants and other industrial sources more efficiently in Beijing and surrounding areas. Another reason for the high contribution of stationary sources in the study of Lin et al. (2011) may be more emission of SO$_2$ in winter time due to house heating.

It should be noted that the less significant NO$_x$–CO and NO$_x$–SO$_2$ correlations for SDZ may cause large uncertainties in the results from the application of the multilinear model to the SDZ data. On the other hand, the results may still be reliable as the air at the regional background site is well mixed and less directly influenced by local sources.

4. Conclusions

Ground-based measurements of trace gases SO$_2$, CO, NO/NO$_x$/NO$_y$ and O$_3$ were made at a rural (SDZ) and an urban (CMA) site in the summer of 2008. Statistical analysis of the daily peaks of O$_3$ at SDZ and CMA reveals that about 72% of the high-O$_3$ days show higher O$_3$ peak at the rural site than at the urban site and more than half of these days showed higher concentrations of O$_3$ at SDZ in the previous nights and similar daily amplitudes of O$_3$ for both sites. The diurnal variation of O$_3$ showed similar patterns at SDZ and CMA, but with the peak of the O$_3$ concentration at SDZ (17:00) 3 h later than that at CMA (14:00). The peaks of other pollutants (CO and SO$_2$) at SDZ also occurred at around 17:00, suggesting that urban plume transport after wind direction change (at about 12:00) is the main reason for the elevated concentrations of pollutants. Significant correlations of the pollutants between SDZ and CMA indicate that air pollutants at the

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**Fig. 9.** The impacts of in-situ photochemistry and urban plume transport on the concentration of O$_3$ at SDZ (a) and the relative contributions of the two factors (b) (reproduced with permission from B.Z. Ge).
rural site, SDZ, are strongly influenced by urban plumes of Beijing. A total impact of urban plume transport on the average concentrations of O₃ at SDZ is estimated to be 33.4 ± 0.4 ppbv for the summer of 2008.

The daily OPE₃ value was derived from the daytime measurements of O₃ and NOₓ and found to be negatively correlated with the photochemical age of air parcel. The OPE₃ for the SW and NE plumes were estimated to be 4.0 and 5.3, respectively. From these values and the NOₓ values for the SW and NE plumes, the contribution of in-situ production in the urban plume to the level of O₃ at SDZ, averaged over the summer of 2008, was estimated to be 8.6 ppbv, corresponding to 25.7% of the total impact of urban plume transport. This suggests that the in-situ photochemistry plays only a small role in the elevation of O₃ at SDZ and direct transport of O₃ makes a major contribution under the condition of urban plume transport.

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