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 SO_2, O_3, NO_x, NO_y 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 (O_3) 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 (OPE_x) for the urban plume and background condition was 4.0 and 5.3, respectively. Based on these OPE_x values and the NO_z values for the respective conditions, the contribution of in-situ production in the urban plume to the level of O_3 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 O_3 rather than in-situ photochemistry contributes mainly to the summer elevation of the level of O_3 at SDZ.

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

1. Introduction

Ozone (O_3) is one of the most important oxidants and the dominant precursor of radicals (OH and NO_3) in the atmospheric troposphere. As one of the greenhouse gases, O_3 plays a significant role in climate change and atmospheric chemistry (Akimoto, 2003). Elevated concentration of surface O_3 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 O_3 is because of the increased concentration of its precursors (i.e. NO_x, 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-O_3 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 O_3 in these air masses. For example, transport of polluted air masses are believed to elevate O_3 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 SO_2, NO_x 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).

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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 NO_2, CO and SO_2 and may increase the transport distance of gaseous pollutants. Wang et al. (2006) also reported a high O_3 pollution case in a mountainous area north of Beijing and attributed the high O_3 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 O_3 at SDZ has been one of the topics that deserve a careful study. Initial measurements show that the hourly mean concentration of surface O_3 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 O_3 at SDZ, Lin et al (2008) investigated the contributions of pollutants from the NCP to the background level of surface O_3 at SDZ and found that such contributions accounted for about 28.9 ppb in summer during 2004–2006. Ozone production efficiency (OPE_x), which is defined as the number of molecules of O_3 formed per NO_x removed from atmospheric O_3-forming oxidation cycles [i.e. $P(O_3)/P(NO_x)$] (Liu et al., 1987) and is calculated from observations of NO_y and NO_x (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 O_3, NO_x, NO_y, 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 O_3 at a background site can come from the transport of O_3 (including O_3 formed during transport), in-situ photochemical production by the transported O_3 precursors and pseudo natural O_3 background.

The study of Lin et al. (2008) only shows the total impact of urban plume on the level of surface O_3 at SDZ. The OPE study of Ge et al. (2010) cannot differentiate contribution of the in-situ photochemical reactions from O_3 transported to the site. Therefore, the roles of different factors influencing the O_3 formation and OPE_x at the site are still not very clear. In this article, we present the variation characteristics of O_3 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 O_3 at SDZ. The OPE_x 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 O_3 (49C), $NO/NO_2/NO_x$ (42CTL), NO/NO_y (42CY), CO (48CTL) and SO_2 (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 SO_2, NO and CO. More frequent zero checks (every
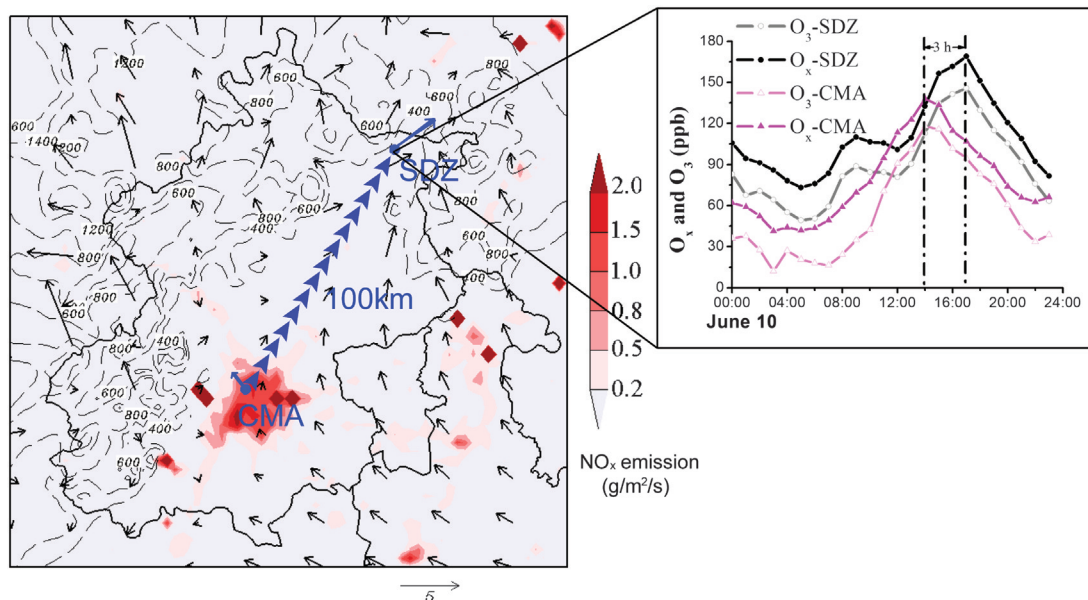
Fig. 1. Locations of the CMA and SDZ sites and the topography around them. The contour lines with number indicate the height of terrain; the red-colour shaded areas show the intensity of NO_x emission during 2006 from Wu et al. (2011). Wind vectors with blue colour indicate the observations at 15:00 on 10 June 2008, and in black the MM5-simulated data at the same time. The figure on the right shows the diurnal patterns of O_x and O_3 at SDZ and CMA on 10 June 2008 and the postponement of 3 h of the concentration peaks at SDZ (reproduced with permission from B.Z. Ge).

6 h) 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_y, 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 $O_x^*(\equiv O_3 + NO_2)$ as the total oxidant at SDZ, the O_x ($\equiv O_3 + NO_2 + NO_z$) 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, Wang et al., 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_x 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
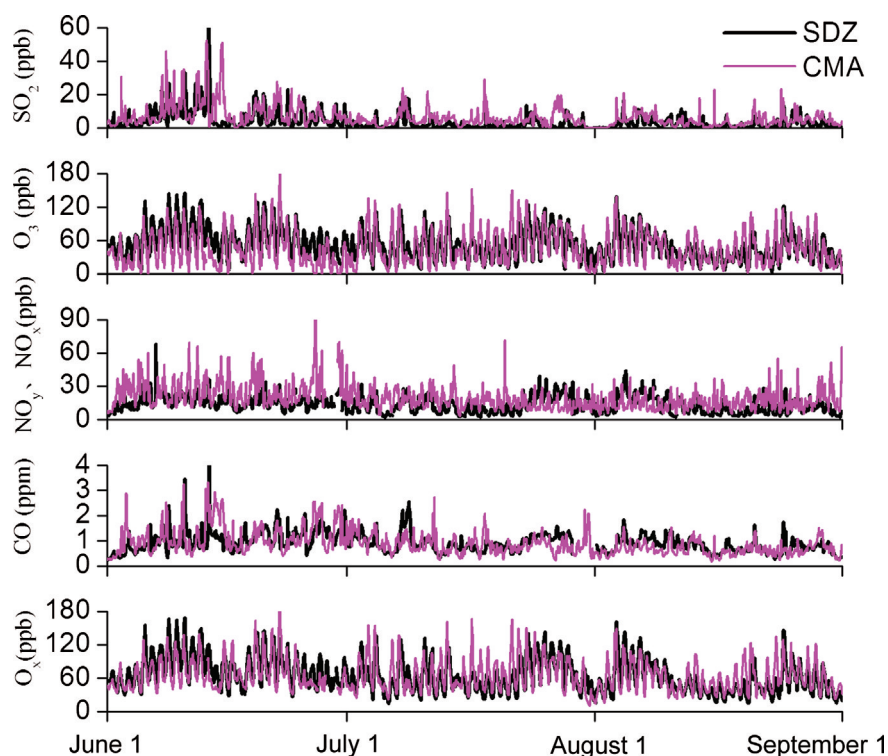
Fig. 2. Time series of SO₂, NOₓ, NOᵧ, CO, O₃ and Oₓ at SDZ and CMA during summer 2008 (reproduced with permission from B.Z. Ge).

92.6 ppb at SDZ). Besides, the O_x peak at CMA was 3 h earlier (at 14:00) than that at SDZ (at 17:00). This example shows that, as the high-O_3 events (daily maximal mixing ratio of 1 h averaged O_x 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 O_x between SDZ and CMA may be attributable to the difference in the O_3 concentrations in the previous night. At the urban site, the higher NO_x level because of vehicle emissions causes larger consumption of O_3 during the night. In fact, out of the 39 high-O_3 days, 28 (about 72%) days showed higher peak of O_x at SDZ than at CMA and 68% of these days showed higher concentration of O_x in

the previous evening at SDZ and 74% of the days showed similar daily amplitude of O_x in these two sites during the observation periods (see Table 1) . Figure 3 shows the scatter plot of the daily amplitude of O_x 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 signifi-cantly correlated ($R = 0.78$, $P < 0.01$) and the slope of the fitted line, 1.15 (close to 1), suggests similar daily amplitudes of O_x at both sites.

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

Table 1. Differences of daily maximal and minimal mixing ratio of O_x and O_3 between SDZ and CMA during high-ozone days

	A	B	C	D
O_x (days)	39	28	19	29
($O_3 + NO_2$) (days)	34	21	12	23
O_3 (days)	29	17	14	20
Fraction O_x (%)	–	72	68	74
Fraction ($O_3 + NO_2$) (%)	–	62	57	68
Fraction O_3 (%)	–	59	82	69

A: high-ozone days; B: days with peak value of O_x, ($O_3 + NO_2$) and O_3 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 O_x is the fraction of three scenes in high-ozone days. For comparing, ($O_3 + NO_2$) was also calculated at both sites.

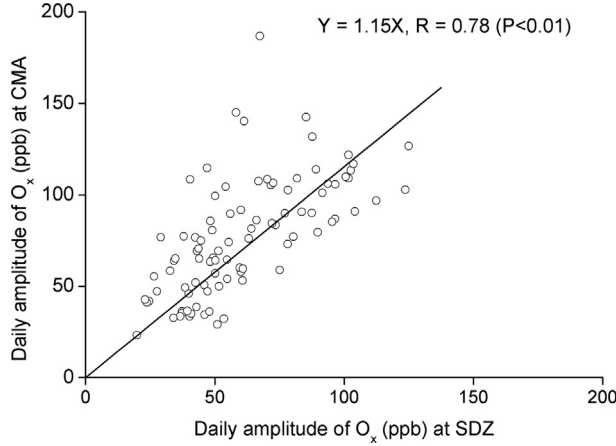*Fig. 3.* Scatter plot of daily amplitude of O_x at SDZ and CMA (reproduced with permission from B.Z. Ge).

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.

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

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
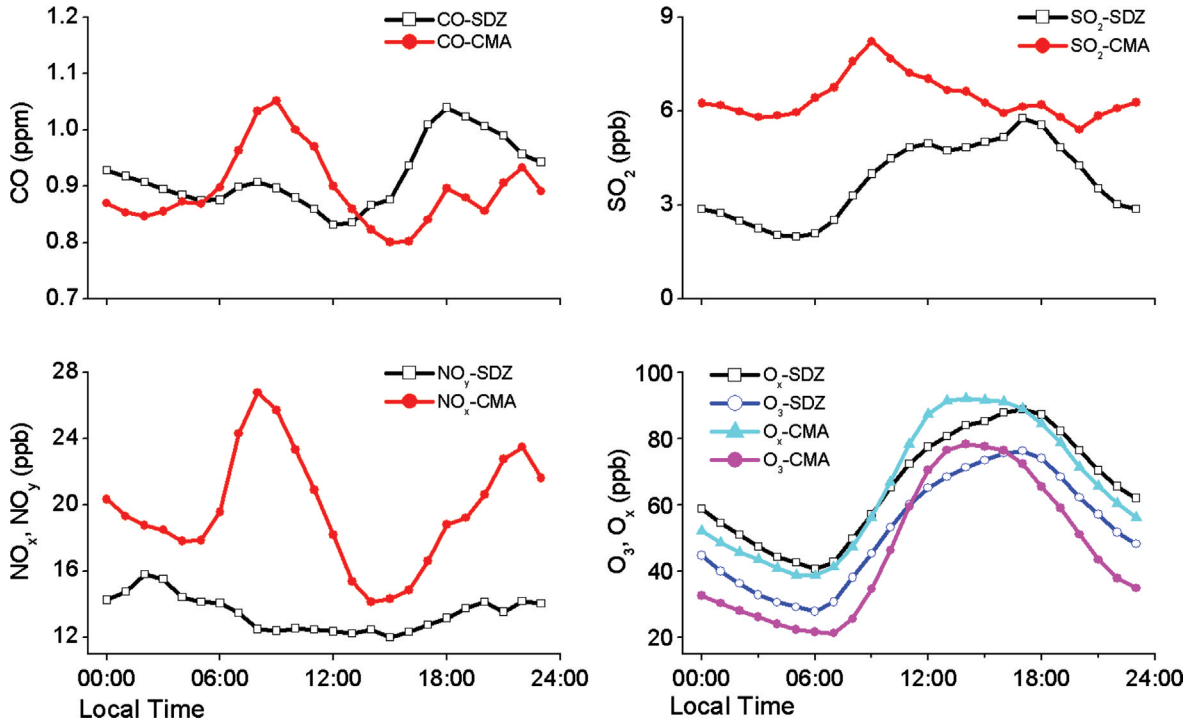

Fig. 4. Average diurnal cycles of CO, SO_2, NO_x/NO_y and O_3/O_x at SDZ and CMA in summer 2008 (reproduced with permission from B.Z. Ge).
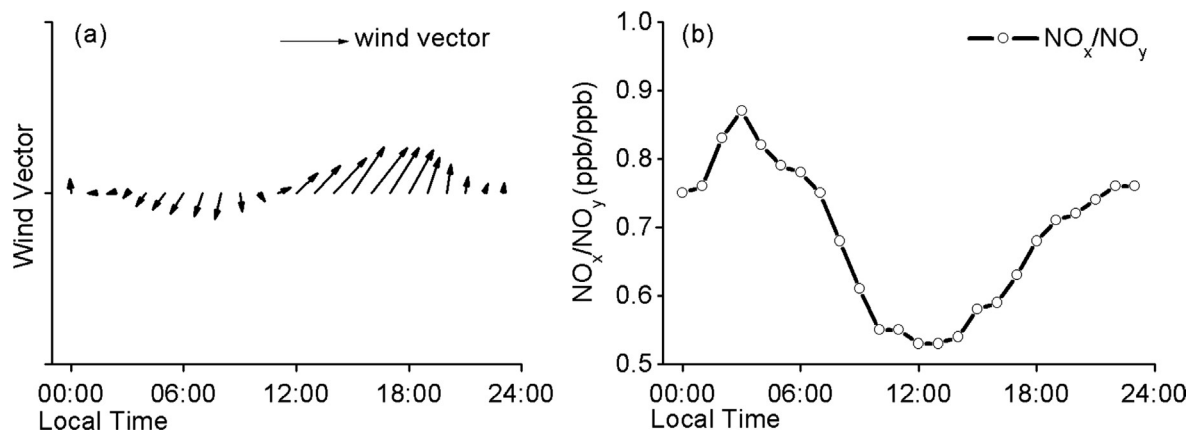
Fig. 5. Average diurnal cycles of wind vector (a) and the ratio NO_x/NO_y (b) at SDZ in summer 2008 (reproduced with permission from B.Z. Ge).

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, CO, 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,

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_y-SDZ	O_x-SDZ	NO_x-SDZ	CO-CMA	SO_2-CMA	NO_x-CMA
SO_2-SDZ	1.00							
CO-SDZ	0.65	1.00						
NO_y-SDZ	0.46	0.63	1.00					
O_x-SDZ	0.57	0.46	0.52	1.00				
NO_x-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	0.59	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.
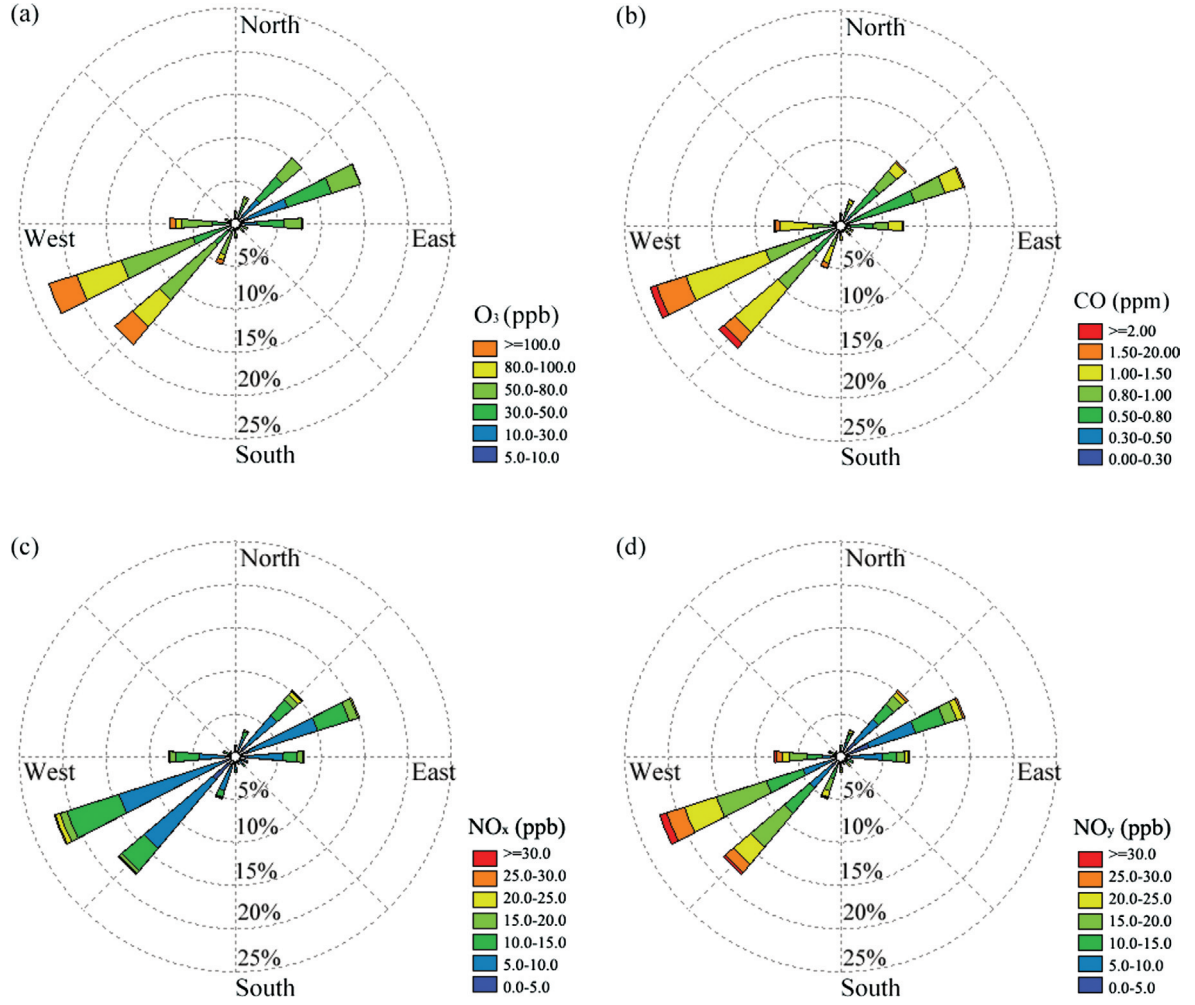
Fig. 6. Rose distributions of the average concentrations of O_3 (a), CO (b), NO_x (c) and NO_y (d) over summer 2008 at SDZ (reproduced with permission from B.Z. Ge).

a result similar to that based on the 2004–2008 measurements (Lin et al., 2008).

The impacts of urban plume on the O_x concentration at SDZ may be decomposed as

$$[O_{x \text{ trans\_impacts}}] = [O_{x \text{ trans}}] + [O_{x \text{ trans\_production}}] + [O_{x \text{ in–situ\_production}}] \quad (1)$$

where ($O_{x\text{trans\_impacts}}$) represents the total impacts of urban plume on the O_x concentration at SDZ, and ($O_{x\text{trans}}$), ($O_{x\text{trans\_production}}$) and ($O_{x\text{in-situ\_prodution}}$) are the O_x increases due to transport of O_x already formatted in urban area, transport of O_x formatted during air travelling to SDZ and in-situ O_x 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 O_x production will be quantified and analysed.

As can be seen in Fig. 6, the differences in the NO_y and CO concentrations were also large between the SW–NE directions, with 6.95 ± 1.19 ppbv for NO_y and 360 ± 80 ppbv for CO. However, the average concentration of 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 NO_x in the SW plume. Larger emissions of VOCs in the polluted sector may favour the production of O_3, transform NO_x into NO_z and increase the concentration of NO_z (Xu et al., 2011). In addition, few NO_x transformed to NO_z during night and early morning, when the wind from NE sector is dominant, may result in smaller difference of NO_x between the SW–NE directions.

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) ($O_3 + NO_2 + NO_z$) versus (NO_z) ($NO_y - NO_x$) 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), Olszyna 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
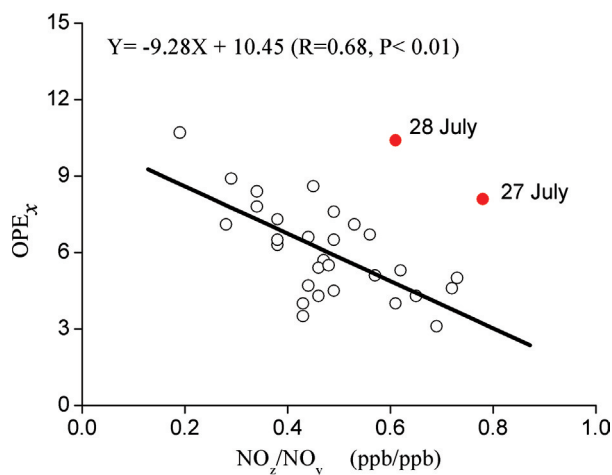

Fig. 7.   The correlation between the daily OPE_x and (NO_z)/(NO_y). The red-solid points indicate outliers of 27 and 28 July and are not included in the regression. The winds on these 2 days were always from SW with no direction change and hence are not considered as normal conditions (reproduced with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

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_z/NO_y. Besides, the increased concentration of O_x 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_z 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_z in the SW and NE wind conditions, with results of linear regressions. The slopes of the (O_x) – (NO_z) 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_z) correlation for the SW wind (0.63) is
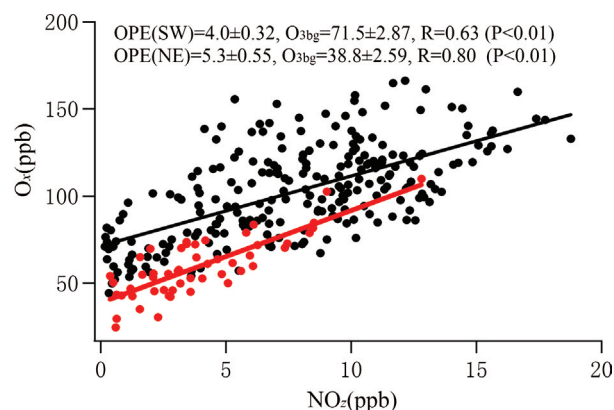

Fig. 8.   Scatter plot of O_x versus NO_z at SDZ during the summer of 2008. The black points show data under SW wind conditions and the red ones show those under NE wind conditions (reproduced with permission from B.Z. Ge).

smaller than that for the NE wind (0.80). This may be attributable to the impact of the pollutants' transport (O_3 and NO_x) from the polluted sector on the local concentrations of O_x and NO_z at SDZ, as under the SW transport conditions, larger parts of variances of the O_x and NO_z concentrations are not related to local photochemistry, on which the (O_x)–(NO_z) correlation is based. The impact of the SW transport is particularly important during afternoon as mentioned in Section 3.1.

Factually, the OPE_x-NE could be used as the in-situ OPE_x as the aged air parcel (NO_x/NO_y below 0.25) from rural background area and the OPE_x-SW as the OPE_x of the urban plume (NO_x/NO_y above 0.40). Factually, the value of OPE_x-SW is similar to that for Beijing urban area (An, 2006) if considering the (O_x) as $(O_3 + NO_2)$ instead $(O_3 + NO_2 + NO_z)$, and is in the OPE_x range of 3.9–9.7 obtained by Chou et al. (2009) using the same method. Therefore, the in-situ O_x production enhanced by urban plume can be calculated as following:

$$In-situPro\,\bar{O}_x = OPE_{sw} \times \alpha \times \Delta\overline{NO_z} \qquad (2)$$

$$\Delta\overline{NO_z} = \overline{NO_z}_{\,SW} - \overline{NO_z}_{\,SWTransport} - \overline{NO_z}_{\,NE} \qquad (3)$$

where α is the correcting coefficient (0.53) for correcting NO_z loss during the transport of pollutants from the source region to the observation point according to Ge et al. (2010) and the $\Delta\overline{NO_z}$ can be considered as the average additional NO_z produced by urban plume at SDZ. However, according to a previous study (Ge et al., 2010), the photochemical production of NO_z in SW direction has been lost by more than a half owing to dry deposition during transport, $\overline{NO_z}_{\,SWTransport}$ could be small and is assumed to be zero. The $\overline{NO_z}_{\,SW}$ and $\overline{NO_z}_{\,NE}$ are 7.8 and 3.9, respectively. We obtained the upper limit level of $\Delta\overline{NO_z}$ as 3.9 ($7.8 - 3.9 = 3.9$). The O_x 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_x at SDZ. This indicates that in-situ O_x production enhanced by urban plume is not the dominant factor for O_x 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 CBMZ-OBM (observation based cbm-z model) model. In this case, the hourly maximum of O_3 concentration reached 124.5 ppbv at 17:00 on 23 July. For the model calculation, we used the hourly observations of VOCs, NO_x and daily minimum of O_3 (instead of O_x for eliminating the hourly $NO_2 + NO_z$ observation impact) concentration as well as hourly meteorological data. The modelled and observed O_3 concentrations agree well with each other (not shown). The O_3 accumulations caused by in-situ photo-

chemistry 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_3 level, which is consistent with the above result.

3.4. The source analysis of NO_y at rural site

Although the NO_y–CO and NO_y–SO_2 correlations during summer at SDZ are less significant than those during winter at CMA and Gucheng (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_y share some common sources with CO and SO_2 during summer at SDZ. Usually, stationary sources (mainly coal-burning) emit much more SO_2 than CO, whereas mobile sources emit much more CO than SO_2. Both types of sources emit NO_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_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_y at CMA, an urban site of Beijing. To see the differences in NO_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_y at the SDZ site. Suppose that NO_y at SDZ can be calculated using the multilinear model

$$NO_y = \alpha1 \times SO_2 + \alpha2 \times CO + \beta \qquad (4)$$

where $\alpha1$ and $\alpha2$ represent the fitted coefficients of SO_2 and CO, and β is the intercept. Based on the regression, $\alpha1$, $\alpha2$ and β 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_2, CO and NO_y in summer 2008 and the coefficients $\alpha1$ and $\alpha2$ are used to calculate the relative contributions of the stationary and mobile sources to NO_y. On average, the relative contributions of the stationary and mobile sources to NO_y at SDZ during summer are estimated to be 4 ± 1 and $68 \pm 28\%$, respectively. The relative contribution of mobile sources to NO_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
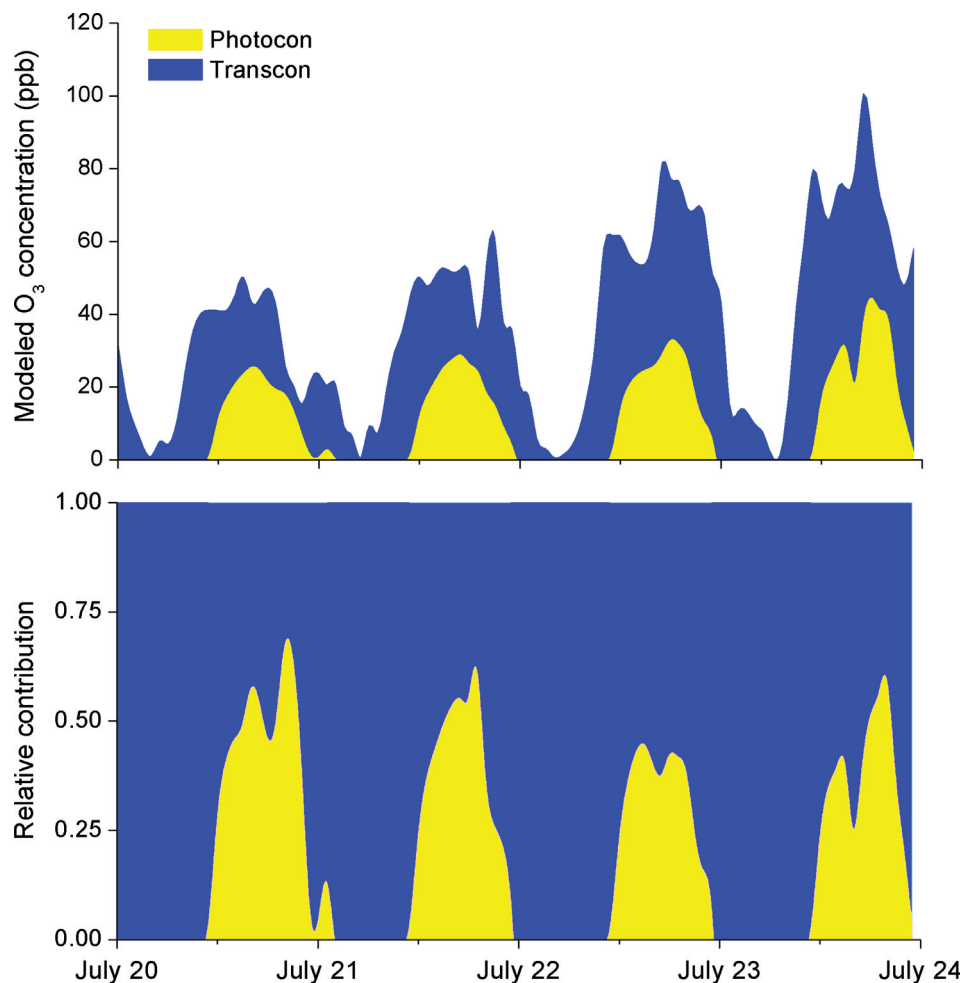
Fig. 9. The impacts of in-situ photochemistry and urban plume transport on the concentration of O₃ at SDZ (a) and the relative contributions of the two factors (b) (reproduced with permission from B.Z. Ge).

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_y–CO and NO_y–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_x peak at the rural site than at the urban site and more than half of these days showed higher concentrations of O_x at SDZ in the previous nights and similar daily amplitudes of O_x for both sites. The diurnal variation of O_x showed similar patterns at SDZ and CMA, but with the peak of the O_x 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

rural site, SDZ, are strongly influenced by urban plumes of Beijing. A total impact of urban plume transport on the average concentrations of O_3 at SDZ is estimated to be 33.4 ± 0.4 ppbv for the summer of 2008.

The daily OPE_x value was derived from the daytime measurements of O_x and NO_z and found to be negatively correlated with the photochemical age of air parcel. The OPE_x for the SW and NE plumes were estimated to be 4.0 and 5.3, respectively. From these values and the NO_z values for the SW and NE plumes, the contribution of in-situ production in the urban plume to the level of O_3 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 O_x at SDZ and direct transport of O_3 makes a major contribution under the condition of urban plume transport.

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