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Evolution of surface O_3 and $PM_{2.5}$ concentrations and their relationships with meteorological conditions over the last decade in Beijing

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HIGHLIGHTS

- $PM_{2.5}$ (O_3) concentrations decreased (increased) in Beijing over the last decade.
- Meteorological factors play important role in the daily variability of pollutants.
- Hazy days are a major manifestation of air pollution in Beijing.

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ABSTRACT

In this study, hourly and daily records since 2005 and correlation, regression and composite methods were used to analyze the long-term evolution of surface O_3 and $PM_{2.5}$ concentrations at the rural station of Shangdianzi (SDZ) and urban station of Baolian (BL) over Beijing and their relationships with meteorological conditions. The results show that the mean concentrations of $PM_{2.5}$ (O_3) decreased (increased) at the urban and rural stations over the last decade. The linear trends of the annual mean concentrations of $PM_{2.5}$ at BL and SDZ were -31.8 ug/m^3/10yr (-4.3%/yr) ($p < 0.01$) and -13.3 ug/m^3/10yr (-2.9%/yr) ($p < 0.05$), respectively. In winter, the mean wind speed (W_s) and relative humidity (RH) were the most closely correlated with O_3 at both stations, whereas RH and sunshine hours (S) were most closely correlated with $PM_{2.5}$. The correlation coefficients and explained variances in spring and autumn were generally less than those in winter and greater than those in summer. Moreover, increase in precipitation can significantly reduce the $PM_{2.5}$ concentration in both urban and rural areas in Beijing, whereas trace and light precipitation more effectively decreases the O_3 concentration. Concentrations of $PM_{2.5}$ (O_3) on haze days increased by 114% (3%) and 162% (20%) compared with that on non-haze days at the urban and rural stations, respectively. This result suggests that haze is a major manifestation of air pollution in Beijing.

1. Introduction

Beijing is the capital and one of the largest cities of China, with approximately 20 million residents. The rapid economic growth and urbanization have increased the level of air pollution in recent decades (Streets et al., 2007; Chan and Yao, 2008). Beijing and northern China have frequently suffered from severe haze or smog days in recent years. For example, the continuously haze days in January 2013 greatly threatened human health and traffic safety (Kang et al., 2013; Wang et al., 2013). Generally, air pollution is caused by two factors: pollutant emissions to the lower atmosphere from fossil fuel combustion or construction and favorable meteorological conditions. Meteorological conditions are controlling factors for the occurrence of haze or heavy pollution (Wu, 2012; Zhang et al., 2013b). Specifically, weather conditions play an essential role in the daily fluctuation of air pollutant

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concentrations. To date, many studies have focused on the physical and chemical properties of pollutants in Beijing and other cities or countries (Feng et al., 2006; Yu et al., 2011; Zhao et al., 2011; Xu et al., 2013; Zhang et al., 2013a; Zhao et al., 2013). Because of the lack of long-term and widespread air pollutant records in Beijing, a number of studies have focused on the features of air pollutants and their relationships with weather conditions over a short time or at specific times, particularly before, during, and after the 2008 Beijing Olympics (Streets et al., 2007; Wang et al., 2009, 2010; Zhang et al., 2009; Gao et al., 2011). Few studies have quantitatively explored the relationships between air pollutant concentrations and meteorological conditions for long time periods in Beijing.

Previous studies elucidated the formation and chemical composition of air pollutants on haze days or during heavy pollution in Beijing and its adjacent areas. However, unresolved issues remain. For example, although observations have shown that the PM_{10} concentration has been reduced since 2003 (Chan and Yao, 2008), pollution levels appear to have been more severe in recent years because of a series of heavy pollution events. Ozone (O_3) and fine particulate matter ($PM_{2.5}$) are the two major urban air pollutants in most of the cities, especially $PM_{2.5}$ in Chinese cities, and they are of great concern because of their adverse effects to public health, visibility, vegetation and other pollution problems (Carlo et al., 2007; Hyslop, 2009; Fann et al., 2012). These pollutants are indicators for air quality and can be easily understood by the non-scientific community. In addition, O_3 and $PM_{2.5}$ provide continuous and long-term pollutant data, especially the hourly O_3 and $PM_{2.5}$ and meteorological datasets since 2005 (2006 for O_3) from two stations in Beijing. Generally, it is feasible and necessary to further re-examine the general characteristics of the evolution of O_3 and $PM_{2.5}$ concentrations and their relationships with meteorological conditions over last decade in Beijing. Therefore, the goal of this study is to examine (i) the long-term trends of O_3 and $PM_{2.5}$ concentrations over the last decade; (ii) the quantitative links between the variability of pollutant concentrations and meteorological variables on the synoptic time scale; (iii) the differences between the concentrations on haze days and non-haze days and in urban and rural areas.

2. Data and methods

2.1. Site, instruments and observations

The hourly environmental and meteorological data were provided by Beijing Meteorological Bureau. The O_3 and $PM_{2.5}$ concentrations were monitored at an urban station of Baolian (BL) and rural station of Shangdianzi (SDZ) (Fig. 1). The distance from BL to nearby major roads is approximately 400 m, and the regions surrounding this site are mostly residential districts without obvious point source of $PM_{2.5}$, thus providing a good representation of an urban area. The SDZ station is one of the regional Global Atmosphere Watch (GAW) stations in China and located in the northern North China Plain and Miyun County of Beijing (a mountainous area that is approximately 100 km to the city center). Only a limited number of populated small villages and insignificant anthropogenic emission sources lie within 30 km of the site (Zhao et al., 2009).

At both the BL and SDZ stations, an R&P model 1400a Tapered Element Oscillating Microbalance (TEOM) instrument with a 2.5 μm cyclone inlet, inlet humidity control system, and dedicated sampling line was used to obtain 5-min averaged time particulate mass concentrations. The two TEOMs have operated as real-time $PM_{2.5}$ monitors since 2004, and each is housed in an air-conditioned room and operated at 26 °C with a hydrophobic filter material to reduce the humidity of the incoming sampled air. The sample stream is preheated to 50 °C before entering the mass transducer, and hence semi-volatiles such as ammonium nitrate and water are not measured. Additional information on the site and instruments can be found in Zhao et al. (2009).

Throughout the period from 2005 to 2013 (beginning in January 2006 for O_3), the hourly missing data rates of pollutant records for the BL and SDZ stations were 1.2% and 1.5%, respectively, thus exhibiting good continuity of the monitoring operations. It should be noted that the SDZ station is also a conventional meteorological observatory, whereas the BL station monitors air pollutants only. Thus, meteorological data from the nearest conventional meteorological station (Haidian Station, which is 4 km from BL Station) were used for comparisons with the pollutants at BL. The hourly and daily meteorological datasets of the two stations were used in the analysis, including the mean wind speed (marked as W_s), daily maximum wind direction (W_d), daily mean temperature (T), relative humidity (RH), surface pressure (P), the daily precipitation amount (R) and sunshine hours (S). According to the observation standard released by the Chinese Meteorological Administration, days with daily mean visibility <10 km and daily mean $RH \leq 90\%$ were defined as haze days; otherwise, a non-haze day was recorded in this study.

2.2. Analysis methods

Commonly used statistical methods, such as composite analyses and Pearson correlation analyses with a two-tailed Student's t-test, were employed in this research. The linear trends of time series were derived from the least squares regression method, and the explained variance of the meteorological factors upon the daily variation of pollutant concentrations was evaluated by the multiple regression method. A high-frequency correlation was also inspected for each correlation analysis to determine whether the daily correspondence of air pollutants and meteorological factors was stable, because it could better reflect the response of air pollutants to synoptic scale disturbances without the influence of long-term trends and annual or seasonal cycles (Gong and Luterbacher, 2008). All of the time series were high-pass filtered using a Butterworth filter with a window of 10 during the high-frequency correlation analysis.

3. Results

3.1. Long-term trends of the concentrations of O_3 and $PM_{2.5}$

We first examined the general features of the annual mean concentration of O_3 and $PM_{2.5}$ at the BL and SDZ stations over the last decade (Fig. 2). The concentration of O_3 at the BL station was much lower than that at the SDZ station, whereas the concentration of $PM_{2.5}$ was much higher at BL than at SDZ. The mean concentration of O_3 at SDZ over the entire period was 36.0 ug/m^3 and approximately 1.59 times than that of BL (22.6 ug/m^3), whereas the mean concentrations of $PM_{2.5}$ at BL over the entire period was 73.4 ug/m^3 and approximately 1.67 times than that of SDZ (44.0 ug/m^3). According to the long-term records, the mean $PM_{2.5}$ concentrations in urban areas were obviously lower than that reported in the previous studies that sampled early time periods over short time intervals, including the annual average of 101 ug/m^3 observed in 2000 by Zheng et al. (2005) and monthly mean $PM_{2.5}$ concentrations of 80 ug/m^3 to 140 ug/m^3 observed in 2006 by Liu et al. (2008) in Beijing. Compared to that of the early period, the annual mean concentration of $PM_{2.5}$ in urban areas of Beijing in recent decades had reduced by 10%–30% at least. A similar result was also found at the rural station, with the annual mean concentrations reducing by 19% relative to the period from 2005 to 2007 according to Zhao et al. (2009). This result may be attributed to the reduced

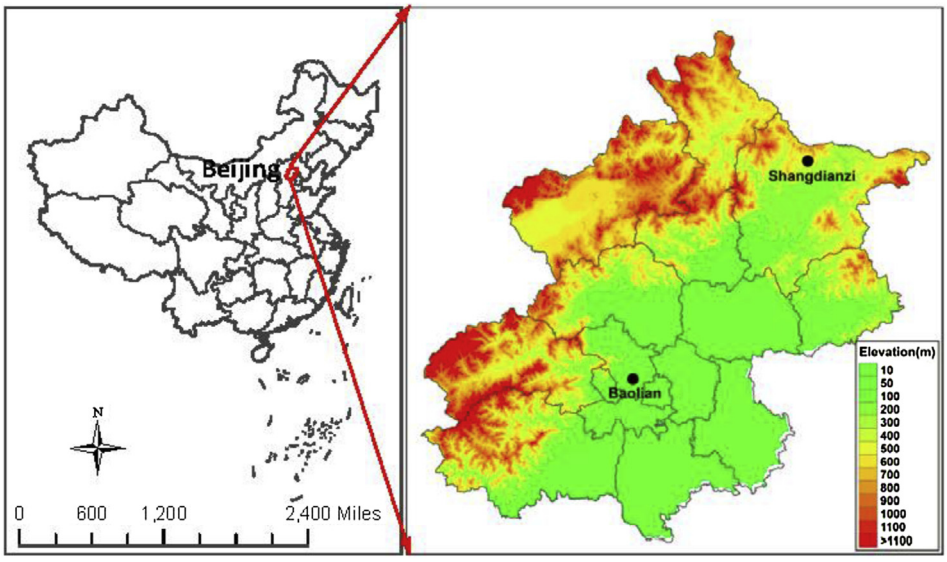

Fig. 1. Locations of the urban station of Baolian (BL) and rural station of Shangdianzi (SDZ).

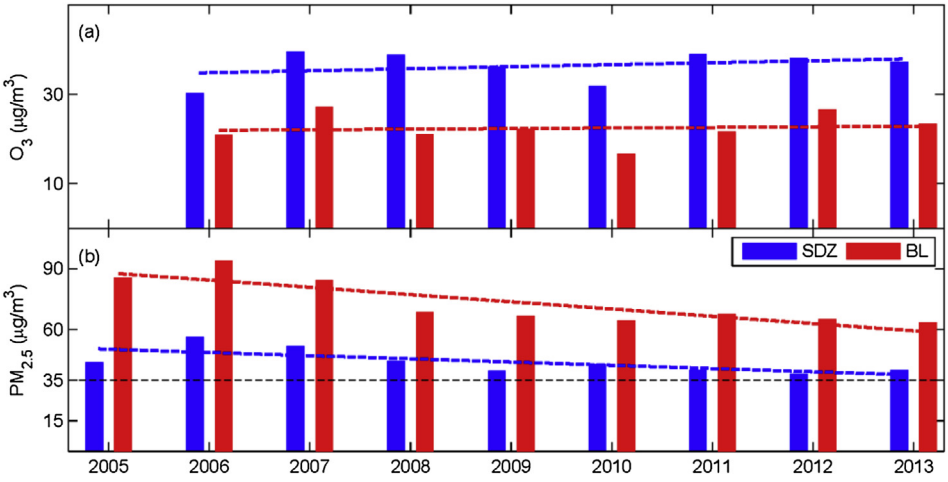

Fig. 2. Annual mean concentrations of O_3 (a) and $PM_{2.5}$ (b) at SDZ and BL stations (Long-term trends are shown as dotted lines; the black dashed lines in (b) indicated the $PM_{2.5}$ at the minimum safe level for the residential areas).

atmospheric pollutant emissions in Beijing and its adjacent areas around the 2008 Beijing Olympics. However, both the urban and rural $PM_{2.5}$ concentrations still exceeded the minimum safe level of $PM_{2.5}$ (annual mean < 35 ug/m^3) for residential areas according to the ambient air quality standards of China's National Standard.

Moreover, Fig. 2 shows that the annual mean concentrations of $PM_{2.5}$ at both urban and rural stations decreased over the period from 2005 to 2013, especially at BL. The linear trends of the annual mean concentrations of $PM_{2.5}$ at BL and SDZ were −31.8 ug/m^3/10yr (−4.3%/yr) ($p < 0.01$) and −13.3 ug/m^3/10yr (−2.9%/yr) ($p < 0.05$), respectively. Furthermore, the trends for different seasons were also calculated (Table 1). The decreasing linear trends at BL in spring (March, April and May), summer (June, July and August) and autumn (September, October and November) were statistically significant at the 0.01 or 0.05 confidence level. Although a decreasing trend was observed in winter (December, January and February), it was not significant. As for the seasonal trends of $PM_{2.5}$ concentration at SDZ, they also showed decreasing trends in all seasons except for winter, and the decreasing trend in spring and summer were statistically significant ($p < 0.05$). In contrast, the annual mean concentrations of O_3 increased over the period from 2006 to 2013, especially at SDZ. The increasing trends of the annual mean concentrations of O_3 at BL and SDZ were 1.8 ug/m^3/10yr and 3.5 ug/m^3/10yr, respectively. Furthermore, the concentrations increased in spring and summer and decreased slightly in winter and autumn at both BL and SDZ stations. However, none of the

Table 1
Linear trends of concentrations over the period 2005–2013 (unit is ug/m^3/10yr, the values in brackets are the trend magnitude in unit of %/yr).

		Annual	Winter	Spring	Summer	Autumn
$O_3^{\#}$	BL	1.8[0.8]	−1.1[−1.4]	4.3[1.7]	3.2[0.8]	−1.8[−1.3]
	SDZ	3.5[1.0]	−0.7[−0.4]	8.0[1.9]	7.4[1.4]	−2.2[−1.3]
$PM_{2.5}$	BL	−31.8 [−4.3]**	−15.7[−2.0]	−31.4 [−4.6]*	−29.9 [−4.1]**	−50.6[−6.7]**
	SDZ	−13.3 [−2.9]*	8.0[2.4]	−26.1 [−5.8]*	−16.9 [−3.3]*	−5.9[−1.1]

$^{**}p < 0.01$, $^{*}p < 0.05$, based on a two-tailed Student's t-test; $^{\#}$ the period is 2006–2013 for O_3.

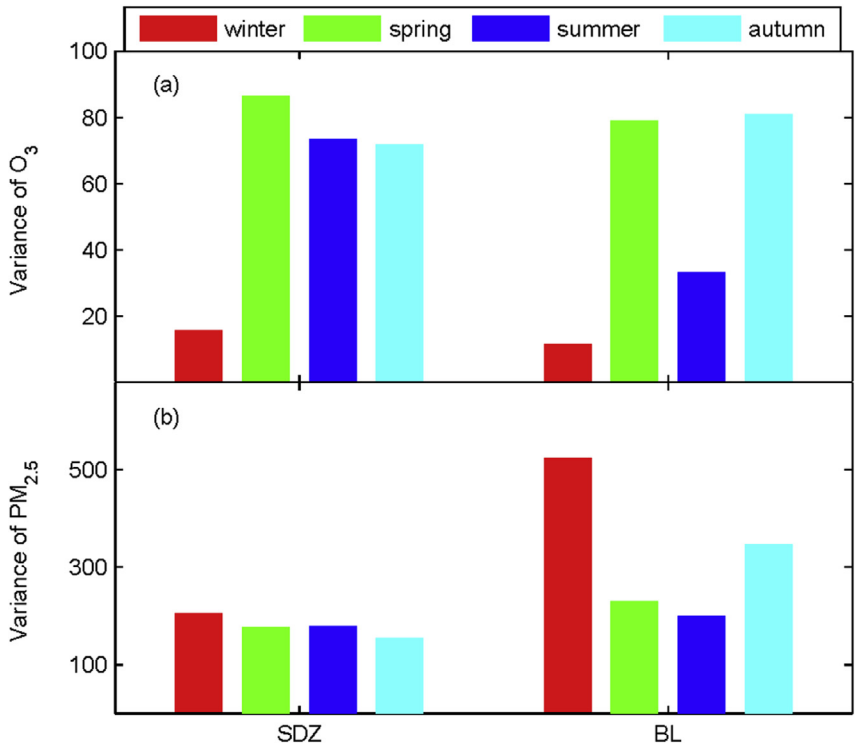

Fig. 3. Variances of the average daily variability of O_3 (a) and $PM_{2.5}$ (b) in the different seasons for the two stations.

linear trends of O_3 were statistically significant, and the increasing rate of O_3 was much lower than that in July to September over period from 2001 to 2006, which was approximately 2.2 ± 1.0 ug/m3/yr (Tang et al., 2009). Generally, the decreases of $PM_{2.5}$ could be attributed to the reduced emissions of pollutants in Beijing, although they slightly increased again over the last three years. The

Table 2
Correlation coefficients of the daily O_3 concentration and meteorological factors in different seasons.

		W_s	W_d	T	RH	P	R	S
Winter	SDZ	0.60[0.61]	-0.29[-0.34]	-0.09[-0.05]	-0.56[-0.62]	0.27[0.39]	-0.11[-0.14]	0.45[0.48]
	BL	0.62[0.71]	0.35[0.37]	-0.02[0.10]	-0.53[-0.59]	0.14[0.27]	-0.06[-0.04]	0.46[0.47]
Spring	SDZ	0.12[0.23]	0.09[-0.03]	0.65[0.34]	-0.06[-0.20]	-0.35[0.00]	-0.03[-0.11]	0.27[0.22]
	BL	0.13[0.43]	0.09[0.16]	0.54[0.27]	-0.12[-0.37]	-0.30[0.12]	0.01[-0.10]	0.31[0.44]
Summer	SDZ	0.37[0.28]	0.30[0.29]	0.27[0.35]	-0.25[-0.11]	-0.10[-0.08]	-0.11[-0.09]	0.04[0.08]
	BL	0.14[0.14]	0.12[0.04]	0.41[0.51]	-0.42[-0.42]	-0.08[-0.07]	-0.22[-0.21]	0.44[0.50]
Autumn	SDZ	0.11[0.22]	0.21[0.11]	0.60[0.34]	0.20[-0.01]	-0.39[-0.08]	0.06[-0.05]	0.16[0.07]
	BL	0.19[0.41]	0.09[0.16]	0.62[0.32]	-0.08[-0.34]	-0.45[-0.04]	0.01[-0.03]	0.32[0.38]

(SDZ and BL indicate the stations of Shangdianzi and Baolian, respectively. W_s, W_d, T, RH, P, R and S denote the mean wind speed, daily wind direction of the maximum wind speed, daily mean temperature, relative humidity, surface pressure, the daily precipitation amount and sunshine hours, respectively. The values in brackets denote the high frequency (<10 days) correlations. The numbers of samples are much greater than 100 for all correlations, so the correlation coefficients for the confidence levels of 0.05 and 0.01 are ±0.20 and ±0.25, respectively; the significance values at $p<0.05$ are shaded.)

Table 3
Correlation coefficients of the daily $PM_{2.5}$ concentration and meteorological factors in different seasons.

		W_s	W_d	T	RH	P	R	S
Winter	SDZ	-0.39[-0.35]	0.34[0.26]	0.42[0.34]	0.65[0.50]	-0.43[-0.38]	0.12[-0.03]	-0.57[-0.52]
	BL	-0.44[-0.41]	-0.30[-0.21]	0.23[0.21]	0.66[0.49]	-0.33[-0.42]	0.03[-0.03]	-0.50[-0.43]
Spring	SDZ	0.01[-0.07]	0.33[0.29]	0.26[0.31]	0.35[0.43]	-0.34[-0.41]	-0.01[-0.01]	-0.36[-0.41]
	BL	-0.28[-0.39]	-0.23[-0.18]	0.23[0.24]	0.35[0.42]	-0.37[-0.48]	-0.04[-0.04]	-0.23[-0.30]
Summer	SDZ	-0.02[-0.09]	0.35[0.28]	0.26[0.34]	0.24[0.33]	0.03[-0.05]	-0.03[-0.05]	-0.40[-0.44]
	BL	0.02[-0.12]	0.00[0.01]	0.26[0.33]	0.13[0.24]	-0.07[-0.17]	-0.06[-0.04]	-0.10[-0.34]
Autumn	SDZ	-0.25[-0.29]	0.33[0.26]	0.16[0.29]	0.43[0.58]	-0.24[-0.42]	-0.05[-0.03]	-0.38[-0.41]
	BL	-0.17[-0.27]	-0.17[-0.12]	-0.02[0.07]	0.41[0.58]	-0.11[-0.34]	-0.11[-0.07]	-0.28[-0.37]

(Same as Table 2)

2008 Olympic Games in Beijing influenced the Chinese government to reduce atmospheric pollutant emissions from the combustion of fossil fuel and construction over northern China (An et al., 2007; Zhang et al., 2010). However, pollutant emissions rebounded slightly in recent years, especially in the areas surrounding Beijing. Thus, the atmospheric pollution in Beijing increased in recent years to some extent, whereas downward trends dominated the entire time series. The increase in O_3, which was also demonstrated in previous studies, may be attributed to the reduction of NOx emissions and elevated non-methane hydrocarbon (NMHCs) emissions (Sicard et al., 2009; Tang et al., 2009).

3.2. Daily variability of O_3 and $PM_{2.5}$ and relationship to meteorological factors

In addition to the obvious annual cycle, daily variability (day-to-day changes) is common for meteorological factors and air pollutants. The variances of the average daily O_3 and $PM_{2.5}$ concentrations at BL and SDZ stations over the four seasons are shown in Fig. 3. Distinct differences can be observed in the variances of the different pollutants, stations and seasons. Generally, the daily variability of O_3 concentration is most intense in spring, summer and autumn, with the exception of weak O_3 variability in summer at the urban station. However, the daily variability of $PM_{2.5}$ concentration is most intense (weak) in winter (summer), especially in the urban areas.

Unlike long-term changes or annual and diurnal variations, the daily fluctuations of air pollutant concentrations may primarily depend on synoptic-scale weather conditions, assuming that the pollutant emissions remained nearly constant every day for most of the period. To quantitatively investigate the relationships between daily fluctuations of air pollutant concentrations and meteorological factors, the correlation coefficients between the daily O_3 (Table 2) and $PM_{2.5}$ (Table 3) concentrations and meteorological factors for winter, spring, summer, and autumn were calculated.

Consistent coefficients between the raw and high-frequency correlations suggest that stable relationships occurred between the variability of air pollutants and meteorological factors. Of these significant meteorological factors, W_s and RH (followed by S, W_d and P) were the most closely correlated with O_3 at both the SDZ and BL stations, and RH and S (followed by W_s, P, W_d and T) were the most closely correlated with the $PM_{2.5}$. The significant positive or negative correlations should be a reflection of the physical response mechanisms. For example, the significant negative correlations with W_s suggest that the concentrations of $PM_{2.5}$ decrease with increasing wind speed because high wind speeds are conducive to the spread and elimination of air pollutants. Similarly, the significant negative correlations with S show that the concentrations of $PM_{2.5}$ decrease with increasing sunshine hours. A day with more sunshine hours often indicates good weather with little cloud cover or strong winds, which are favorable for the diffusion and elimination of air pollutants (Yang et al., 2009; Sanchez-Romero et al., 2014). For RH, the significant positive correlations with $PM_{2.5}$ are associated with windless, cloudy and weak sunshine days, which encourage the accumulation and chemical reaction of pollutants (Kang et al., 2013; Csavina et al., 2014). The significant negative correlations between $PM_{2.5}$ and P are caused by the close association between pressure variability and changes in other meteorological factors, e.g., a stronger pressure gradient that is accompanied by an increase in wind speed, which reduces the concentration of air pollutants, especially at a synoptic time scale (Tian et al., 2014). Compared with $PM_{2.5}$, the correlations between O_3 and meteorological factors were generally opposite, e.g., significantly positively correlated with W_s, S, P and W_d and significantly negatively correlated with RH. This phenomenon is straightforward due to the intrinsic chemical properties of O_3 (it is consumed quickly by the chemical reactions between O_3 and NO), and meteorological factors that are conducive for the accumulation of NO_x reduce the concentration of O_3 due to the simultaneous chemical reactions between O_3 and NO (Wallace and Hobbs, 2006). However, strong winds can transport O_3 from other regions or even from the middle-upper troposphere and may also contribute to the strong positive relationships between the daily variability of O_3 and W_s.

An interesting phenomenon occurs for the raw and high-frequency correlation coefficients between pollutants (O_3 and $PM_{2.5}$) and W_d at the urban and rural stations, with positive or negative correlations at BL showing opposite conditions to those at SDZ. This result may partially reflect the differences in transport and accumulation of air pollutants and emission sources between

Table 4
Explained variances of the seven meteorological factors upon the daily variability of O_3 and $PM_{2.5}$ in the different seasons.

		Winter	Spring	Summer	Autumn
O_3	SDZ	52%	48.1%	29.2%	41.0%
	BL	45%	38.0%	29.3%	50%
$PM_{2.5}$	SDZ	59%	34.8%	37.5%	32.3%
	BL	50%	28.8%	22.8%	29.1%

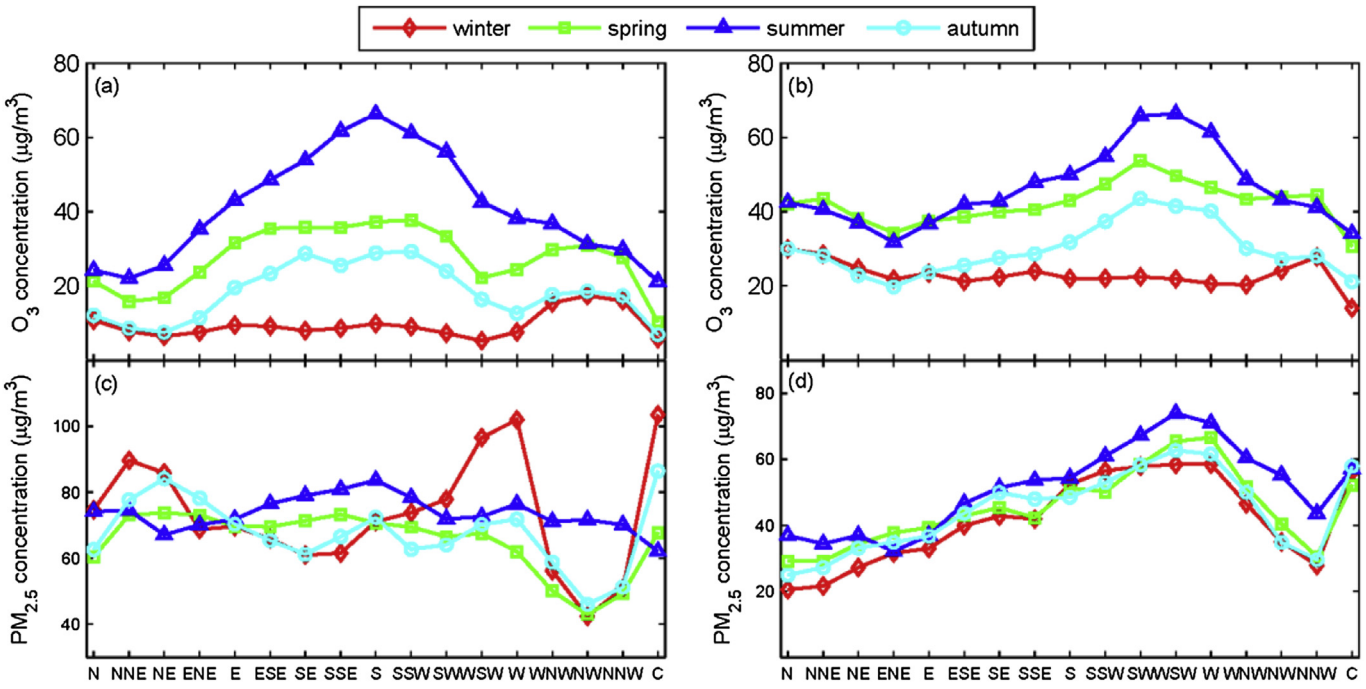

Fig. 4. Distribution of seasonal average concentrations of O_3 (a, b) and $PM_{2.5}$ (c, d) at BL (left) and SDZ (right) stations in 16 directions (C denotes the concentrations on calm days).

urban and rural areas. We also examined the correlations between pollutants and the most frequent daily wind direction, and the results showed that the correlations between pollutants and maximum wind direction were generally similar to the correlations with the most frequent daily wind direction. However, correlation coefficients cannot quantify the influence of wind direction on air pollutants (Carlo et al., 2007), although it is important for air pollutant concentrations. Thus, the relationship between O_3 and $PM_{2.5}$ concentrations and W_d are specifically evaluated in a later section using a composite analysis. Moreover, the correlations between pollutants and R at all stations were not significant, which suggests that the links between pollutants and precipitation on a daily time scale were weak. However, precipitation usually plays an important role in the wet deposition of various pollutants. Thus, the links between precipitation and pollutants are also discussed in a later section.

In spring, summer and autumn, the absolute values of the correlation coefficients between O_3 and $PM_{2.5}$ and meteorological factors were generally lower than those in winter (except for T with O_3), although many of them were significant at $p < 0.05$ (Tables 2 and 3). More precisely, the correlation coefficients in spring and autumn were generally stronger than those in summer and weaker than those in winter. Compared with the results from winter, significantly positive correlations were observed between T and O_3 at the urban and rural stations in spring, summer and autumn because higher temperatures can promote photochemical reactions and generate abundant ozone in summer half years. Moreover, S was significantly and positively correlated with O_3 most of the time, which suggests that additional sunshine can also promote the formation of O_3, especially in urban areas. For $PM_{2.5}$, significantly negative correlations with W_s were still observed in spring and autumn, suggesting that increases in wind speed can depress the accumulation and reduce the concentrations of pollutants. Moreover, T, RH and S were significantly correlated with $PM_{2.5}$ at the BL and SDZ stations, although the absolute values of the coefficients were much lower than those in winter.

Furthermore, the explained variance of the seven meteorological factors (W_s, W_d, T, RH, R, P and S) upon the daily variability of O_3 and $PM_{2.5}$ concentrations in the different seasons were examined by using a multiple regression method (Table 4). The seven meteorological factors together can explain 50% (45%) and 59% (52%) variances of the winter daily $PM_{2.5}$ (O_3) concentrations at BL and SDZ stations, respectively, which suggests that meteorological factors play essential roles in the daily fluctuations of pollutants in winter. Similar to the correlation coefficients, the explained variances in spring and autumn were generally lower than that in winter and greater than that in summer. In addition, a series of experiments were performed to inspect differences in the explained variances when different meteorological factors were used. The results showed that if only four factors (W_s, W_d, T and RH) were used, the explained variances were close to the values derived from the seven factors (only slight decrease). Moreover, the explained variances showed little variation when R was used or not.

3.3. Concentrations of O_3 and $PM_{2.5}$ for different wind directions and precipitation conditions

To better understand the influence of wind direction on the air pollutant concentrations, the seasonal average pollutant concentrations in 16 directions were examined using a composite analysis (Fig. 4). Intuitively, limited differences were observed for the seasonal distribution patterns of O_3 and $PM_{2.5}$ concentrations at the SDZ and BL stations. At SDZ, the O_3 concentration was greatest in the SW, WSW and W directions in all seasons (Fig. 4a), whereas the O_3 concentrations were highest in summer for all directions. However, the O_3 concentration maximized in E to SW (clockwise) at BL, particularly peaked in the SSE, S and SSW directions in summer (Fig. 4b). In addition, the O_3 concentrations in calm weather conditions were much lower than those in other conditions, which indicated that windless conditions can depress the formation of O_3 at both the urban and rural stations. The $PM_{2.5}$ concentration at SDZ was greatest in the W, WSW and SW directions (greater than 60 ug/m^3) and lowest in the N to E directions (less than 40 ug/m^3), especially in summer. The $PM_{2.5}$ concentration in calm weather

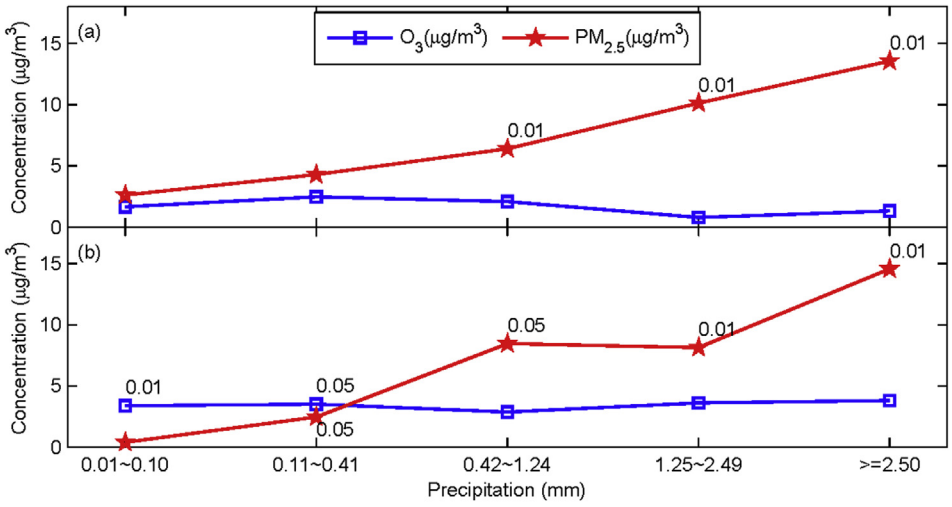

Fig. 5. Average hourly concentration differences of O_3 and $PM_{2.5}$ between pre- and post-precipitation for each category of precipitation at the SDZ (a) and BL (b) stations (values shown in the figure denote the significance level of the differences).

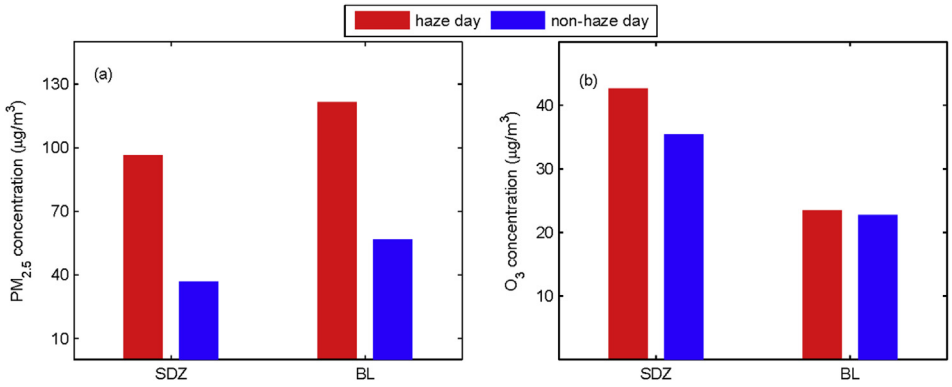

Fig. 6. Average daily concentrations of $PM_{2.5}$ (a) and O_3 (b) on haze day and non-haze day (all of the differences were significant at the 0.01 confidence level).

conditions ranged from 52.2 to 59.7 ug/m^3. At the BL station, the $PM_{2.5}$ concentrations were greatest in the NNE, NE, W, and WSW directions (close to or large than 80 ug/m^3), and lowest in the WNW, NW and NNW directions (less than 60 ug/m^3), and distributed somewhat evenly in the other directions (70–75 ug/m^3). The $PM_{2.5}$ concentrations at BL in calm weather conditions in winter and autumn were approximately 44% and 30% higher than the mean values, respectively. Generally, the concentrations of $PM_{2.5}$ and O_3 at BL peaked in the southwest and northeast directions, whereas they peaked in the southwest direction at SDZ. Based on the spatial locations of the stations, the high pollutant concentrations in calm weather conditions suggest that local emissions are a crucial source of pollutants in Beijing and the pollutants at SDZ are mainly attributed to the transport of pollutants from urban areas of Beijing and south-central region of Hebei Province with southwesterly winds. The findings derived from the long-term records generally support the results from previous studies based on early or short time sampling (Liu et al., 2008; Zhao et al., 2009).

Although significant statistical correlations were not observed between precipitation (rainfall and snowfall) and pollutant concentrations on a daily basis in the previous correlation analyses, precipitation is often important for the wet deposition of atmospheric pollutants (Connan et al., 2013; Tsai et al., 2014). Thus, we examined the possible links between air pollutant changes and precipitation using the concentration differences between pre- and post-precipitation, i.e., rain occurring at 7 and 8 o'clock, and the difference between $PM_{2.5}$ concentrations at 6 o'clock and $PM_{2.5}$ concentrations at 9 o'clock indicate differences in concentrations associated with precipitation. In addition, five precipitation categories (according to the national standard of the People's Republic of China) were used: 0.01–0.10 (trace), 0.11–0.41 (light), 0.42–1.24 (moderate), 1.25–2.49 (heavy) and greater than 2.50 mm/h (rainstorm). The results were displayed in Fig. 5. The mean concentration differences were greater than 0, suggesting that precipitation can scavenge or reduce air pollutants, and differences in $PM_{2.5}$ concentrations increased with precipitation amount at both the rural and urban stations. The differences in $PM_{2.5}$ concentration at SDZ were significant for moderate and heavy precipitation and rainstorms ($p < 0.01$), whereas the differences in $PM_{2.5}$ concentrations at BL station were significant for light and moderate precipitation ($p < 0.05$) and heavy precipitation and rainstorms ($p < 0.01$). Only the differences in O_3 concentrations at the BL station were significant ($p < 0.05$) for trace and light precipitation. Moreover, the differences in O_3 concentrations showed a slightly downward trend as precipitation increased, especially at the rural station. Generally, the long-term observations showed that more precipitation can significantly reduce $PM_{2.5}$ concentrations in both urban and rural areas in Beijing, while trace and light precipitation can more effectively decrease O_3 concentration.

3.4. Concentrations of O_3 and $PM_{2.5}$ on haze and non-haze days

Based on the long-term observational data, the concentrations of O_3 and $PM_{2.5}$ on haze days and non-haze days were evaluated. As shown in Fig. 6, both the $PM_{2.5}$ and O_3 concentrations were larger on haze days than on non-haze days at both the urban and rural stations. The concentrations of $PM_{2.5}$ on haze days increased by 114% and 162% compared with that on non-haze days at BL and SDZ, respectively. Moreover, the rates of $PM_{2.5}$ concentration at the rural station increased by a greater amount at the urban station, which may have been caused by lower background concentrations of $PM_{2.5}$ in the rural area compared with that of the city on non-haze days. In addition, air pollutants often showed a fine spatial consistency during heavy pollution (Wang et al., 2013); thus, the increment of $PM_{2.5}$ concentrations in rural areas was larger than that in urban areas. Normally, haze days were associated with calm winds and/or high *RH*, which are favorable for the accumulation and hygroscopic growth of pollutants; thus, the increase in pollutant concentrations on haze days is reasonable. Furthermore, we noted that the number of haze days with daily $PM_{2.5}$ concentrations greater than 75 ug/m^3 (defined as a pollution day) were approximately 51% and 48% of the total pollution days at the urban and rural stations respectively, which indicates that haze days are a major manifestation of air pollution in Beijing.

The concentration of O_3 on haze days increased by 3% and 20% compared with that on non-haze days at the BL and SDZ stations, respectively. Thus, the O_3 concentrations on haze days were not much higher than that on non-haze days, which may have been caused by a suppression of photochemical reactions because of the reduced sunshine on haze days, which could lead to reduced increases of O_3 on haze days, particularly in urban areas.

4. Discussion

Undoubtedly, the variability and long-term trends of air pollutant concentrations are affected by local and regional pollutant emissions. Thus, detailed and accurate pollutant emission data are essential for understanding of the evolution of $PM_{2.5}$ and O_3 concentrations. However, the real and dynamic emission data for Beijing and its adjacent areas were not available, although certain studies have reported that the pollutant emissions over northern China were controlled by the government because of the 2008 Olympic Games in Beijing (An et al., 2007; Zhang et al., 2010; Gao et al., 2011). Because of the lack of the emission data, studies on the quantitative relationship between the evolution of pollutant concentrations and local and regional pollutant emission were limited. However, previous studies demonstrated that air pollution in Beijing was seriously affected by the transport of pollutants from other provinces of northern China (Zheng et al., 2005; Zhang et al., 2013a,b; Wang et al., 2013). Currently, the transmission path and amount of pollutants from external areas and their configuration with different synoptic patterns are not clear. These problems suggest that the statistical relationships between pollutant concentrations and meteorological factors include uncertainties. Thus, further studies based on additional monitoring data will be necessary to unravel these issues.

Another interesting phenomenon found in this study was that the high positive correlation coefficients between wind speed and O_3 concentrations in winter. Intuitively, increases of wind speed resulting in higher concentrations of O_3 may appear strange. We think that increases of O_3 concentrations with heavy winds in winter were caused by horizontal advection and a sinking motion. The horizontal advection draws O_3 from windward regions to leeward areas. Moreover, the intense sinking motion in winter draws O_3 from the middle-upper troposphere to the ground (Sicard et al., 2009). Thus, positive correlations between O_3 concentrations and wind speed are reasonable.

5. Conclusions

Based on the hourly and daily air pollutant concentrations and meteorological datasets since 2005, the long-term evolution of surface O_3 and $PM_{2.5}$ concentrations and their relationships with meteorological conditions at the rural (SDZ) and urban (BL) Beijing stations were statistically analyzed in this study. The main conclusions include the following.

(1) According to the long-term records, the mean $PM_{2.5}$ concentration in urban areas were obviously lower (by 10%–30%) than that reported in previous studies that sampled early or short-time records. Although the concentrations of $PM_{2.5}$ decreased significantly in recent decades, the results suggest that air pollution is still a serious problem in Beijing, and ozone pollution will become more serious in the near future.

(2) The daily variability of air pollutant concentrations was mainly attributed to the daily weather condition. In winter, W_s and *RH* were the most closely correlated with O_3 at both stations, followed by *S*, W_d and *P*, whereas *RH* and *S* were the most closely correlated with $PM_{2.5}$, followed by W_s, *P*, W_d and *T*. The consistent coefficients between the raw and high-frequency correlations suggested that stable corresponding relations occurred between them. Furthermore, the seven meteorological factors (W_s, W_d, *T*, *RH*, *P*, *R* and *S*) can explain 50% (45%) and 59% (52%) variances of the winter daily $PM_{2.5}$ (O_3) concentrations at the BL and SDZ stations, respectively. The correlation coefficients and explained variances in spring and autumn were generally less than those in winter and larger than those in summer.

(3) The concentrations of $PM_{2.5}$ and O_3 at the urban station of BL peaked in the southwest and northeast directions, whereas the concentrations peaked in the southwest direction at the rural station of SDZ, suggesting the influence of pollutant transport from urban areas of Beijing and south-central regions of Hebei Province on the pollutant concentrations in rural areas with southwesterly winds. Moreover, the long-term observations also showed that increased precipitation can significantly reduce $PM_{2.5}$ concentrations in both urban and rural areas in Beijing, whereas trace and light precipitation and can decrease O_3 concentrations more effectively.

(4) Compared with normal days, the concentrations of $PM_{2.5}$ (O_3) on haze days increased by 114% (3%) and 162% (20%) compared with that on non-haze days at the urban and rural stations, respectively. Moreover, the numbers of haze days with air pollution were approximately 51% and 48% of the total pollution days at the urban and rural stations, respectively, which suggested that the presentation of haze is a major manifestation of air pollution in Beijing.

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