



## Analysis of the Relationship between O<sub>3</sub>, NO and NO<sub>2</sub> in Tianjin, China

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### ABSTRACT

The continuous measurement of nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>) and ozone (O<sub>3</sub>) was conducted in Tianjin from September 8 to October 15, 2006. The data were used to investigate the relationship between the O<sub>3</sub> distribution and its association with ambient concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> (NO and NO<sub>2</sub>). The measured concentrations of the pollutants in the study area varied as a function of time, while peaks in NO, NO<sub>2</sub> and O<sub>3</sub> all occurred in succession in the daytime. The diurnal cycle of ground-level ozone concentration showed a mid-day peak and lower nighttime concentrations. Furthermore, an inverse relationship was found between O<sub>3</sub>, NO, NO<sub>2</sub> and NO<sub>x</sub>. In addition, a linear relationship between NO<sub>2</sub> and NO<sub>x</sub>, as well as NO and NO<sub>x</sub>, and a polynomial relationship between O<sub>3</sub> and NO<sub>2</sub>/NO was found.

The variation in the level of oxidant (O<sub>3</sub> and NO<sub>2</sub>) with NO<sub>2</sub> was also obtained. It can be seen that OX concentration at a given location is made up of two parts: one independent and the other dependent on NO<sub>2</sub> concentration. The independent part can be considered as a regional contribution and is about 20 ppb in Tianjin.

An obvious difference in NO, NO<sub>x</sub> and O<sub>3</sub> concentrations between weekdays and weekends was also found, but this difference did not appear in NO<sub>2</sub>.

Lastly, the diurnal variation of O<sub>3</sub> concentration under different meteorological conditions was demonstrated and analyzed.

**Keywords:** Nitrogen oxides; Ozone; Oxidant; Regional contribution; Weekend effect.

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### INTRODUCTION

One of the main problems caused by air pollution in urban areas is photochemical oxidants. Among these, ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>) are particularly important because they are capable of causing adverse effects on human health (WHO, 2000). The formation of ground level ozone depends on the intensity of solar radiation, the absolute concentrations of NO<sub>x</sub> and VOC<sub>s</sub> (Volatile Organic Compounds) and the ratio of NO<sub>x</sub> to VOC<sub>s</sub> (Nevers, 2000). A large number of observations have shown that on clear days the concentration of ozone rises with increasing intensity of solar radiation and temperature. The weekend effect has been reported in some areas, both have tried to analyze the causes of weekend effect and find effective ozone control strategies (Qin, 2004; Atkinson-Palombo, 2006). However, this phenomenon is not well understood because relatively low concentrations of ozone precursors

(NO<sub>x</sub> and VOC) at weekends has been reported in some areas of America (Qin *et al.*, 2004) and Japan (Sakamoto *et al.*, 2005).

The concentration of photochemical oxidants can be decreased by controlling their precursors: nitrogen oxides NO<sub>x</sub> (NO and NO<sub>2</sub>) and VOCs (Peng *et al.*, 2006; Geng *et al.*, 2007). However, the efficiency of emission control also depends on the relationship between primary and secondary pollutants, as well as ambient meteorological conditions. Owing to the chemical coupling of O<sub>3</sub> and NO<sub>x</sub>, the levels of O<sub>3</sub> and NO<sub>2</sub> are inextricably linked. Therefore, the response to reduction in the emission of NO<sub>x</sub> is remarkably non-linear (Porg, 1997) and any resultant reduction in the level of NO<sub>2</sub> is invariably accompanied by an increase in the level of O<sub>3</sub>. In addition, changes in the local level of O<sub>3</sub> and NO<sub>2</sub> will lead to an increasing background level. It is therefore necessary to obtain a thorough understanding of the relationships among O<sub>3</sub>, NO and NO<sub>2</sub> under various atmospheric conditions. As a result, different authors (Clapp *et al.*, 2001; Mazzeo *et al.*, 2005; Chou *et al.*, 2006) have studied the relationships among ambient levels of O<sub>3</sub>, NO and NO<sub>2</sub> to improve the understanding of the chemical coupling among them.

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Tianjin, located in east-central China, with latitude of 39°N and longitude of 117°E, is one of the most developed cities in China. It has one of the largest population densities in the world, with more than 3.73 million residents living in an area of 330km<sup>2</sup>. The rate of economic development in the region is very rapid, with an annual growth in GDP of 14.5%. The total length of roads has been doubled since 1990 and built-up area has increased by 45%. Traffic has also rapidly increased and the number of cars has dramatically risen. In 2004, there were nearly 1.05 million registered cars, which is approximately 3 times to that of 1999. As a result, energy consumption has also rapidly increased, which may have led to an increase in photochemical pollution.

There have only been a few studies examining the atmospheric chemistry of this city. For example, Hai Bian (Bian *et al.*, 2007; Han *et al.*, 2009; Li *et al.*, 2009; Gu *et al.*, 2010) presented evidence that aerosol particles have a strong effect on the surface ozone concentration in Tianjin. However, O<sub>3</sub> concentration and its precursors were not systemically measured and the relationship between O<sub>3</sub> and its precursors was not analyzed. Such measurements are urgently needed in the Tianjin region.

In our work, the ambient concentrations of O<sub>3</sub>, NO, NO<sub>2</sub> and NO<sub>x</sub> were measured continuously in Tianjin from September 8 to October 15, 2006. For the first time in this city, data was used for the investigation of the variation of NO, NO<sub>2</sub>, NO<sub>x</sub>, and O<sub>3</sub>. The variation of oxidant OX (O<sub>3</sub> and NO<sub>2</sub>) concentration with NO<sub>2</sub> is also investigated, contributing to a better understanding of the atmospheric sources of OX in this area.

The relationships among the O<sub>3</sub>, NO and NO<sub>2</sub> concentrations were used to forecast the O<sub>3</sub> concentration. Furthermore, the difference in concentrations between the weekdays and weekends, and O<sub>3</sub> concentrations under different meteorological conditions were also discussed.

## METHOROLOGY

### *Site Description*

The monitoring site was located in an open area with an elevation of about 3 m above sea level, and was located at 39°06'N, 117°10'E. Within a radius of about 1 km of the measured area, the land was flat with some low residential buildings as well as many commercial buildings that steadily increased in density to the west and south. Heiniucheng road runs E-W at a mean distance of approximately 100 m from the monitoring site. Youyinan road extends S-N about 100 m east of the site. The measuring instrument was installed on top of a building. Air samples were drawn through the pipes fixed on the wall that was about 2 m above the ground. The concentrations of O<sub>3</sub>, NO<sub>x</sub>, NO, NO<sub>2</sub>, ultraviolet irradiance (UV) and other meteorological factors (ambient air temperature, relative humidity, wind speed and wind direction) were continuously measured for 38 days (from September 8 to October 15, 2006).

### *Measurements and Instrumentation*

Ozone was measured using an EC9810B ozone analyzer

through UV-absorption method, while NO<sub>x</sub>, NO<sub>2</sub> were measured with an EC9841B NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer combines microprocessor control with gas phase chemiluminescence technology to provide accurate measurements of NO/NO<sub>2</sub>/NO<sub>x</sub> in the range of 0–20 ppm with a detection limit of < 0.4 ppb (Ran *et al.*, 2009). NO was calculated with NO<sub>x</sub> and NO<sub>2</sub> (NO = NO<sub>x</sub> – NO<sub>2</sub>). Quality control checks were performed every 3 days including inspection of the shelter and instruments as well as zero, precision and span checks. The filter was replaced once every 2 weeks and a calibration was made every month. The Standard samples of O<sub>3</sub> and NO<sub>x</sub> were purchased from National Standard Substance Institute of China. The ozone concentration was recorded every minute, NO<sub>x</sub> and NO<sub>2</sub> were recorded every 3 minutes.

## RESULTS AND DISCUSSION

### *Hourly Variation of O<sub>3</sub>, NO, NO<sub>2</sub> and NO<sub>x</sub> Concentrations*

The observed average diurnal variation of NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> concentrations during this period are shown in Fig. 1. In general, the diurnal cycle of ozone concentration reaches a peak during the middle of the day and has lower nighttime concentrations. The ozone concentration slowly increases after the sun rises, reaching its maximum during the daytime, and then slowly decreases until the next morning.

The diurnal cycle of NO, NO<sub>2</sub> and NO<sub>x</sub> are shaped like double waves. The morning peak is higher in magnitude than the evening peak. The morning peak of NO<sub>2</sub> appears 1–2 hours after the NO peak, and the O<sub>3</sub> peak appears about 6 hours after the NO peak and 5 hours after NO<sub>2</sub> peak. After the morning peak (7:00), NO diminishes until it reaches its lowest value at 13:00. Both the NO and NO<sub>2</sub> decrease correlate with an increase in O<sub>3</sub>. During night time, surface emission of NO were limited inside the nocturnal planetary boundary layer (NPBL), NO reach its second highest value between 21:00 and 23:00. This pattern in the temporal variability of air pollutants can be found in cities worldwide (Sanchez *et al.*, 2007). Sometimes the variations are affected by local air circulations or short-term meteorological effects (Pudasinee *et al.*, 2006; Costabile *et al.*, 2007), but the basic pattern always remains. Concentrations vary in different cities depending on background air pollution, specific emission conditions and general meteorological conditions.

This variation is mainly due to photochemical formation and meteorological conditions. From 08:00 to 14:00–15:00, an increase in global solar radiation and the height of the mixing layer results in a decrease in NO<sub>x</sub> concentration and an increase in O<sub>3</sub> (Ulke and Mazzeo, 1998). Simultaneous measurement of O<sub>3</sub> and UV during the daytime (from 7:00 to 19:00, see Fig. 2) shows that the O<sub>3</sub> concentration is highly correlated to UV irradiance (W/m<sup>2</sup>). The diurnal cycles of O<sub>3</sub> and UV flux are similar, with the O<sub>3</sub> maximum occurring at 14:00, which is about 1–2 hours after the UV flux maximum. Statistical analysis reveals that the correlation between O<sub>3</sub> and UV is significant with a correlation coefficient (R) of 0.75.

NO is a primary contaminant, whereas O<sub>3</sub> and a large

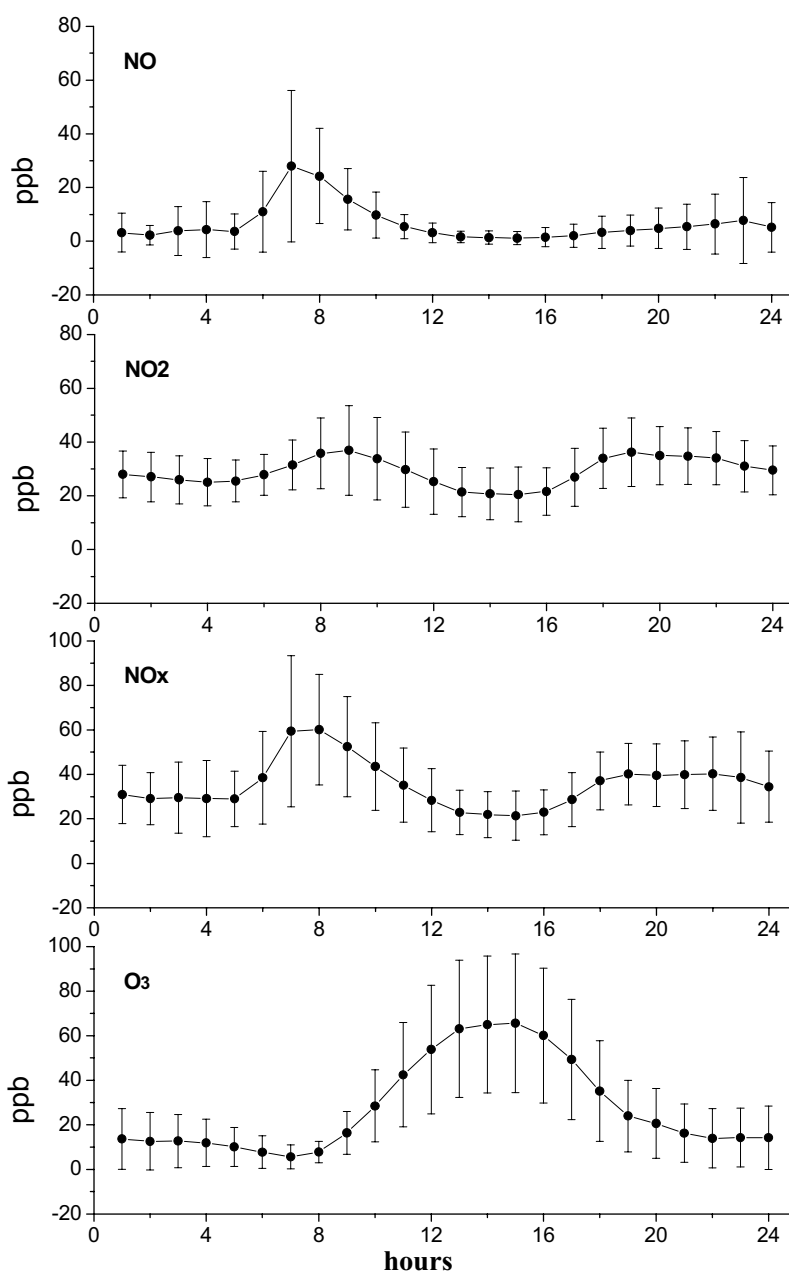


Fig. 1. Daily variation of mean values of NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> concentration (averaging time: 60 min).

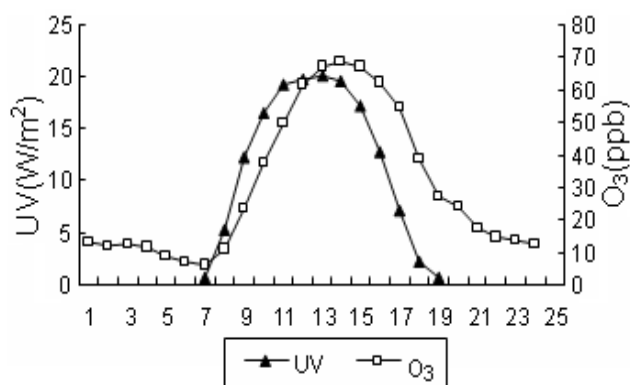


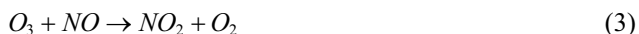
Fig. 2. The average O<sub>3</sub> concentrations and UV irradiance during the observation period.

percentage of NO<sub>2</sub> are secondary contaminants, formed through a set of complex reactions. At 7:00, sunlight begins to induce a series of photochemical reactions. NO is converted to NO<sub>2</sub> via a reaction with O<sub>3</sub>, and during daytime hours NO<sub>2</sub> is converted back to NO as a result of photolysis, which leads to the regeneration of O<sub>3</sub>. Another factor that influences air-pollutant concentrations is the height of the mixing layer over the city. On a clear day, pollutants would be diluted when mixing layer rises during the daytime and be limited to inside the NPBL during the nighttime. The average NPBL height during this period in Tianjin was 132 m (Han *et al.*, 2009), which is similar to that in Beijing (130 km from Tianjin) (Liu *et al.*, 2002). Emitted pollutants such as NO are kept beneath this inversion, which may cause the hourly NO<sub>x</sub> concentration

to increase during the night.

**Chemical Coupling of O<sub>3</sub>, NO and NO<sub>2</sub>**

It is well established that the inter-conversion of O<sub>3</sub>, NO and NO<sub>2</sub> under atmospheric conditions is generally dominated by the following reactions (Kenty et al., 2007):



M (usually N<sub>2</sub> or O<sub>2</sub>) represents a molecule that absorbs the excess vibrational energy and thereby stabilizes the O<sub>3</sub> molecule formed. *hν* represents the energy of a photon (with a wavelength of < 424 nm) and O is an active monoatomic oxygen molecule. These equations form a cycle with no net chemistry i.e. the overall effect of reaction (2) is the reverse of reaction (1). These reactions therefore represent a closed system in which the NO<sub>x</sub> (NO and NO<sub>2</sub>) components and the OX (O<sub>3</sub> and NO<sub>2</sub>) components relate separately. During daytime hours, NO, NO<sub>2</sub> and O<sub>3</sub> are typically equilibrated on a timescale of a few minutes. This is known as a photostationary state.

NO, NO<sub>2</sub> and O<sub>3</sub> concentrations are related by the following equation:  $[NO] \cdot [O_3] / [NO_2] = J_2 / k_1$ , where *J*<sub>2</sub> is

the rate of NO<sub>2</sub> photolysis, and *k*<sub>1</sub> is the rate coefficient for the reaction of NO with O<sub>3</sub>. The variation of the mean value of *J*<sub>2</sub>/*k*<sub>1</sub> over time, obtained using observed measurements of NO, NO<sub>2</sub> and O<sub>3</sub> is shown in Fig. 3. The mean values of *J*<sub>2</sub>/*k*<sub>1</sub> vary between 0.176 and 5.513 ppb and the maximum value occurred at 10:00.

Coefficient *k*<sub>1</sub> varies as a function of temperature (*T*). Seinfeld and Pandis (1998) proposed the following equation for *k*<sub>1</sub>. As expected, the variation of *k*<sub>1</sub> is similar to the variation of the mean air temperature.

$$k_1(1/ppm/min) = 3.23 \times 10^3 \exp[-1430/T] \tag{4}$$

Fig. 4 presents the variation in daytime O<sub>3</sub> concentration as a function of the NO<sub>2</sub>/NO ratio (sample interval: 30 min). The level of O<sub>3</sub> increases with an increase in [NO<sub>2</sub>]/[NO]. According to Fig. 4, O<sub>3</sub> concentration increases rapidly at small values of [NO<sub>2</sub>]/[NO], this maybe implicated that when O<sub>3</sub> was at low levels, the reactions of production of O<sub>3</sub> was dominated reaction. When O<sub>3</sub> concentration reached about 90 ppb, it tended to remain relatively stable. This shows that at higher levels, O<sub>3</sub> concentration is close to reaching a photostationary state. We fit these data to the polynomial function of *Ln*[NO<sub>2</sub>]/[NO], which can be used to forecast the O<sub>3</sub> concentration during the daytime:

$$[O_3] = 19.678 \times \ln[NO_2]/[NO] + 1.378 \tag{5}$$

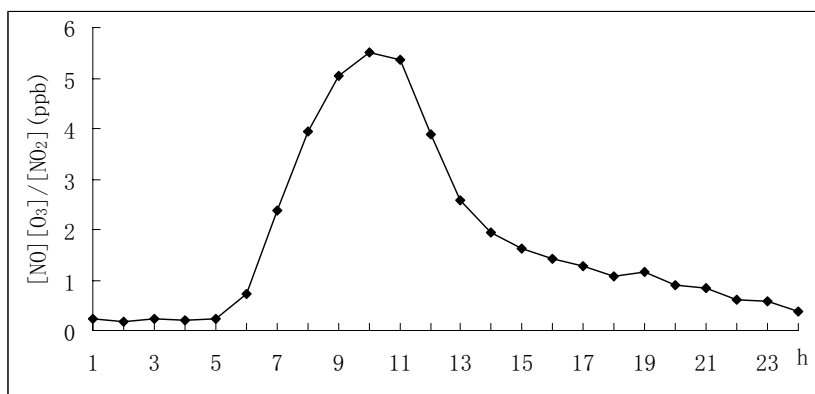


Fig. 3. Daily variation of mean values of *J*<sub>2</sub>/*k*<sub>1</sub> (ppb).

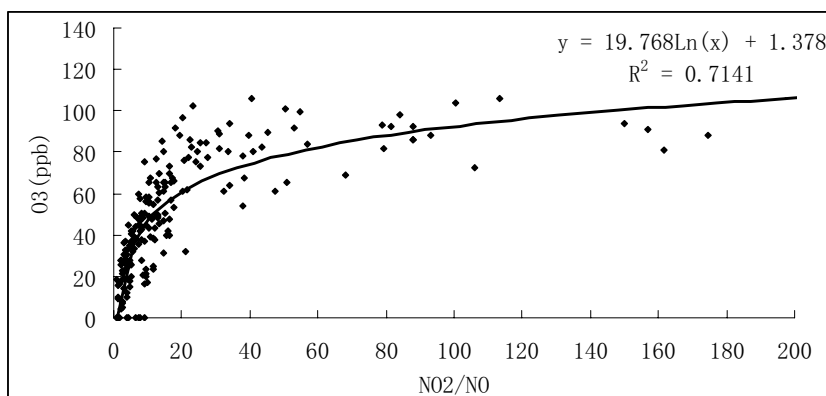


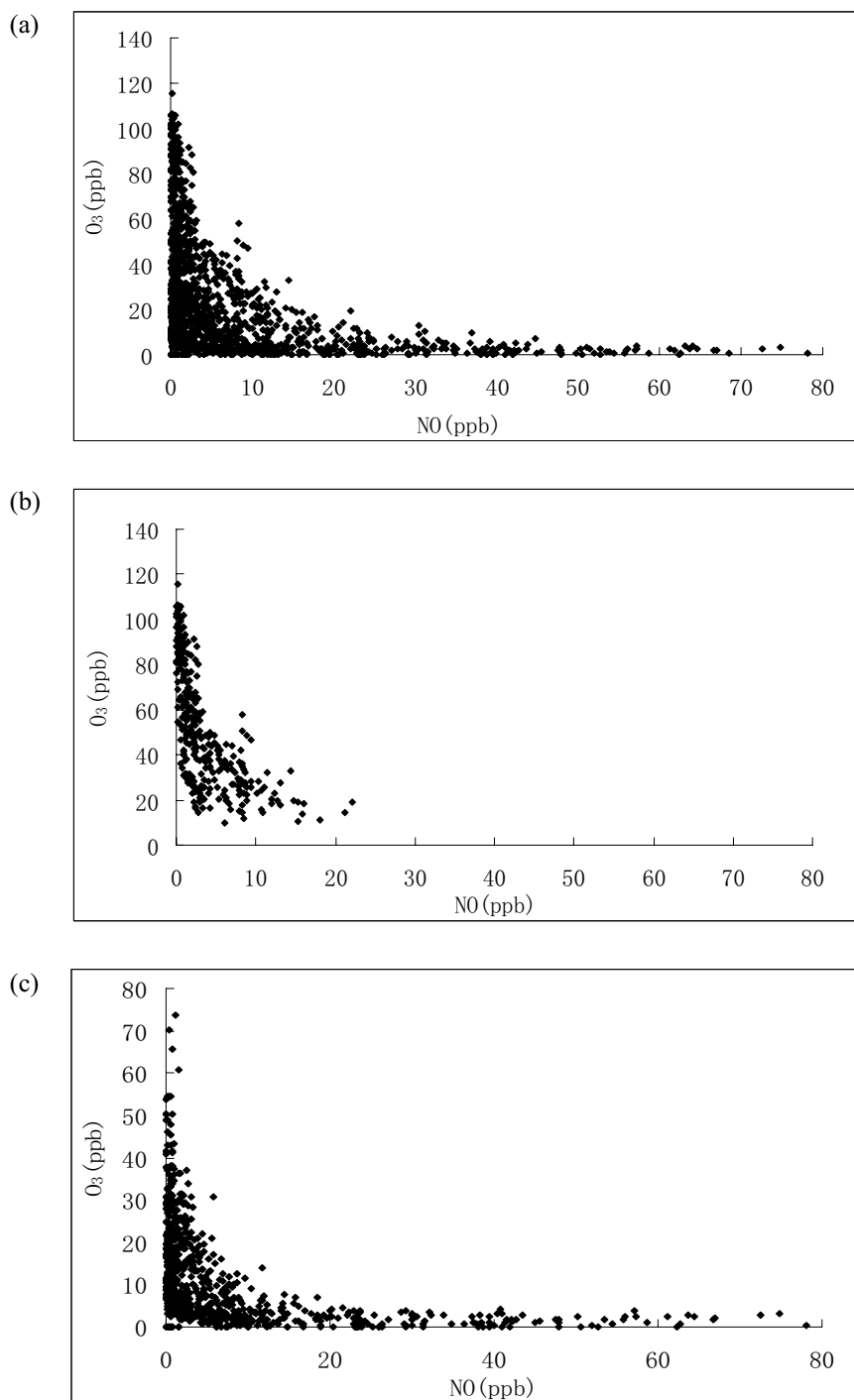
Fig. 4. O<sub>3</sub> concentration varies with the [NO<sub>2</sub>]/[NO] ration.

Fig. 5 shows the comparison between the average concentration of NO and O<sub>3</sub>, measured every 30 minutes. Three different time periods were used for comparison: the whole day, daytime-period (from 10:00am to 16:00pm) and nighttime period (from 18:00pm to 8:00am). The mean concentration of O<sub>3</sub> diminishes with the rise of NO. The largest observed concentrations of NO and O<sub>3</sub> are 22 and 117 ppb during daytime, and 79 and 74 ppb during nighttime, respectively. These values indicate that the highest mean concentration of O<sub>3</sub> during daytime is greater

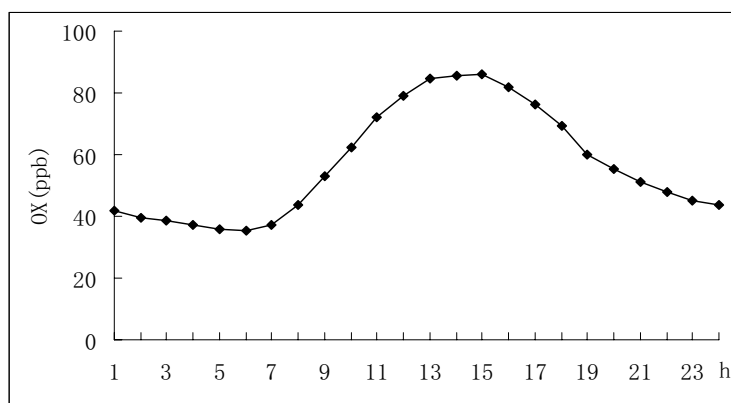
than at night. While a higher mean concentration of NO at night than during daytime period.

#### *Diurnal Variation of [OX]*

If photochemical processes have an influence on OX levels in polluted areas, then a difference between the behavior of OX during daytime and nighttime would be expected. Fig. 6 shows the daily variation in the mean value of OX concentration (average sample interval: 30 min). Similar to the variation of O<sub>3</sub>, OX concentration



**Fig. 5.** Variation of mean values of O<sub>3</sub> with NO: (a) whole day; (b) daytime; (c) nighttime.



**Fig. 6.** Daily variation of mean values of OX.

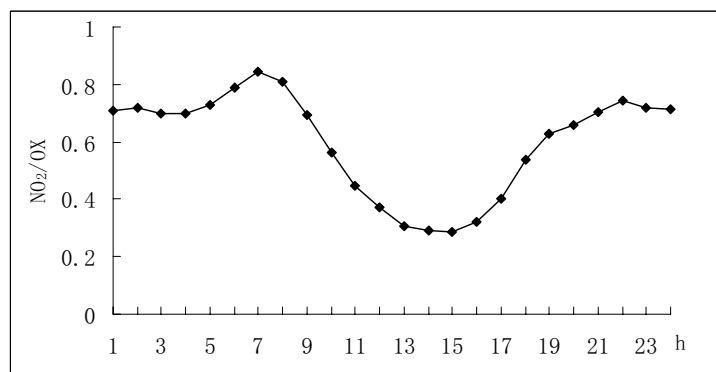
shows a mid-day peak and lower nighttime concentrations. The OX concentration slowly raises after sunrise, reaches a maximum during the day, and then decreases until the next morning. This is due to photochemical O<sub>3</sub> formation. Fig. 7 shows the daily variation of [NO<sub>2</sub>]/[OX]. Differences in the partitioning of NO<sub>2</sub> and O<sub>3</sub> may be related to the rate of chemical processes, or the time available for them to occur. For example, a smaller ratio of [NO<sub>2</sub>]/[OX] due to the higher concentration of O<sub>3</sub> during the day.

#### **Variation of Daily Values of [NO<sub>2</sub>]/[OX] with [NO<sub>x</sub>]**

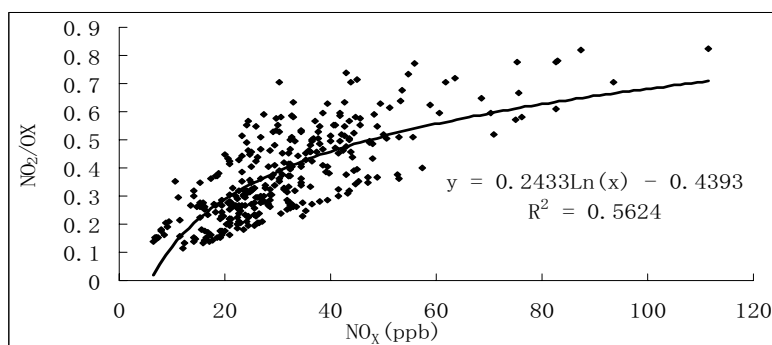
Based on the photostationary state relationship presented in section 3.2, it is possible to infer an expected variation in daytime average [NO<sub>2</sub>]/[OX] values with [NO<sub>x</sub>]. This

variation is shown in Fig. 8 along with the fitted empirical expression. The data shows that a progressively greater proportion of OX is in the form of NO<sub>2</sub> as the level of NO<sub>x</sub> increases. The high values of [NO<sub>2</sub>]/[OX] can be explained by an additional oxidation process changing NO to NO<sub>2</sub>.

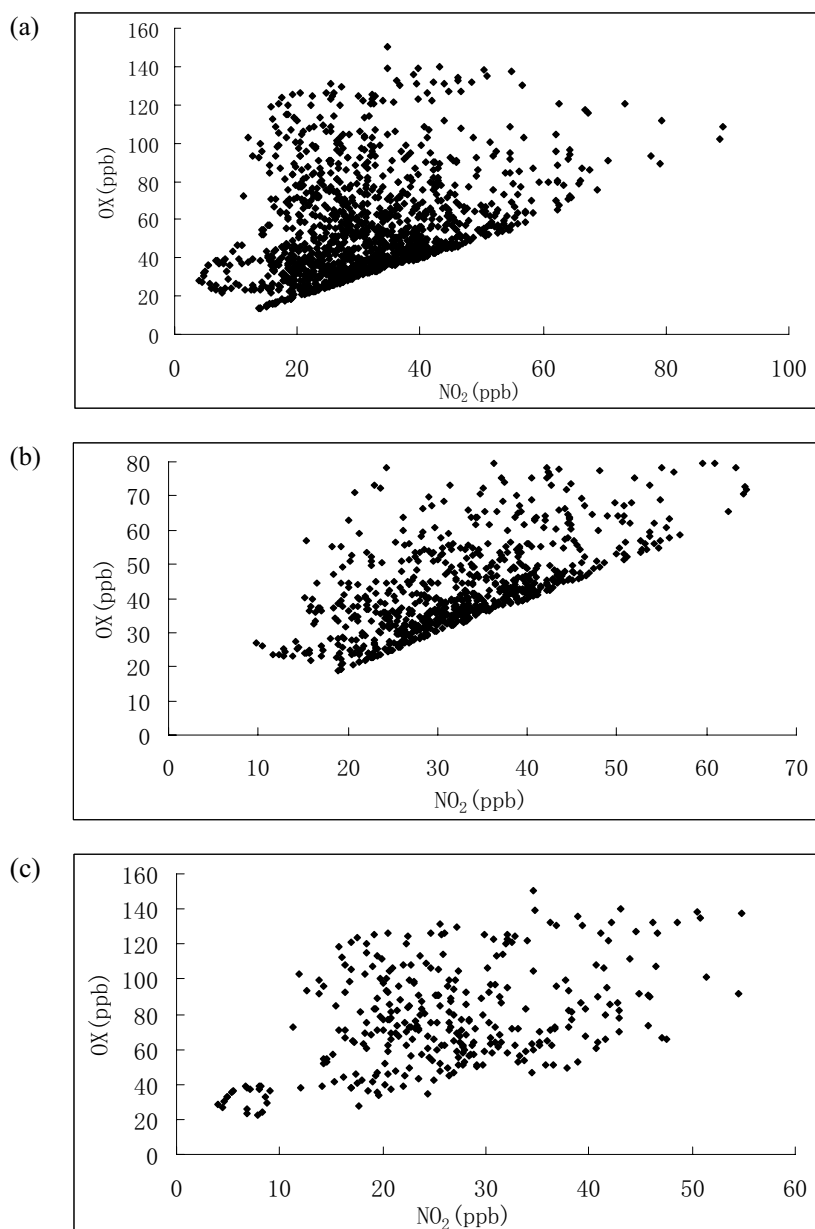
If the photochemical processes have an influence on OX levels at polluted areas, then a difference between the behavior of OX during daytime and nighttime hours might be expected (Mazzeo *et al.*, 2005). The variation in the mean value of OX concentration (recorded every 30 min) against the level of NO<sub>2</sub> is shown in Fig. 9. The OX increase with NO<sub>2</sub> appears to have a linear relationship as shown in the figure. Furthermore, it can be seen that the OX at a given location has an NO<sub>2</sub>-dependent contribution



**Fig. 7.** Daily variation of mean values of NO<sub>2</sub>/OX.



**Fig. 8.** Variation of daytime mean values of NO<sub>2</sub>/OX with the level of NO<sub>x</sub>.



**Fig. 9.** Variation of mean OX with NO<sub>2</sub>: (a) whole day; (b) nighttime; (c) daytime.

and an NO<sub>2</sub>-dependent contribution. The independent contribution can be considered as a regional contribution. The NO<sub>2</sub>-dependent contribution can be considered as a local contribution and is correlated with the level of primary pollution. We can infer that the [NO<sub>2</sub>]-dependent local contribution to [OX] at night is about 50% lower than during the daytime. The regional contributions to [O<sub>3</sub>] during daytime and nighttime are similar, both at about 20 ppb according to the intercept of the relationship between [OX] and [NO<sub>2</sub>].

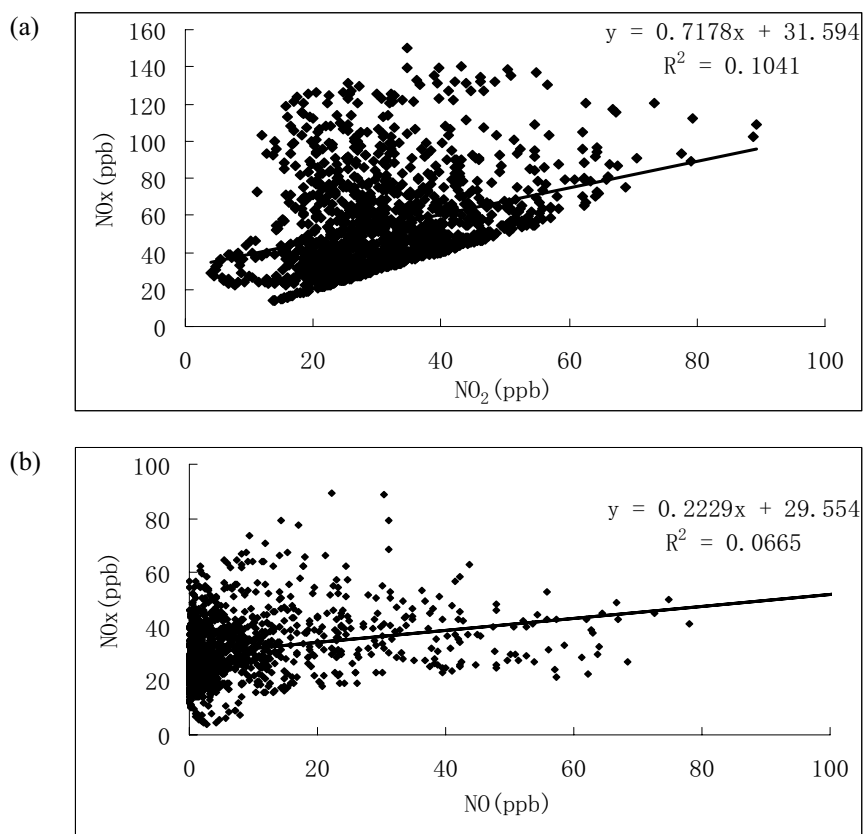
#### **The Relationship among NO, NO<sub>2</sub> and NO<sub>x</sub>**

Fig. 10 presents the variation of [NO<sub>x</sub>] with [NO] and [NO<sub>2</sub>] using the mean observed data (sample interval: 30 min). We fitted the data to a linear function, but the correlation was weak. However, different results were

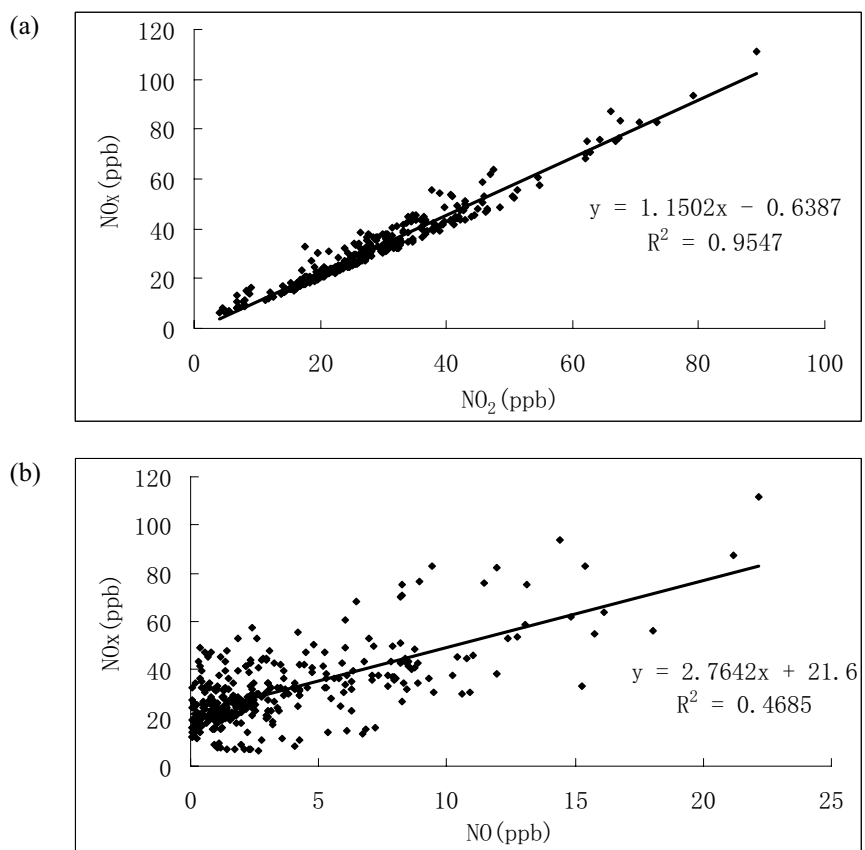
obtained when the observed data were divided into daytime and nighttime periods (Fig. 11 and Fig. 12). During the daytime, there was a good linear correlation between NO<sub>x</sub> and NO<sub>2</sub>, while at night there was a strong correlation between NO<sub>x</sub> and NO.

#### **The Difference between Weekdays and Weekends**

We divided the observation period into two parts: weekdays and weekends. The diurnal cycles of NO and NO<sub>2</sub> during weekdays (NO-W and NO<sub>2</sub>-W) and weekends (NO-R and NO<sub>2</sub>-R) are shown in Fig. 13. Due to traffic intensity, the NO level was comparatively higher on weekdays than on weekends. In addition, the average diurnal variation on weekdays was greater for NO than for NO<sub>2</sub>. This is because NO<sub>2</sub> has a longer lifetime than the more reactive NO.

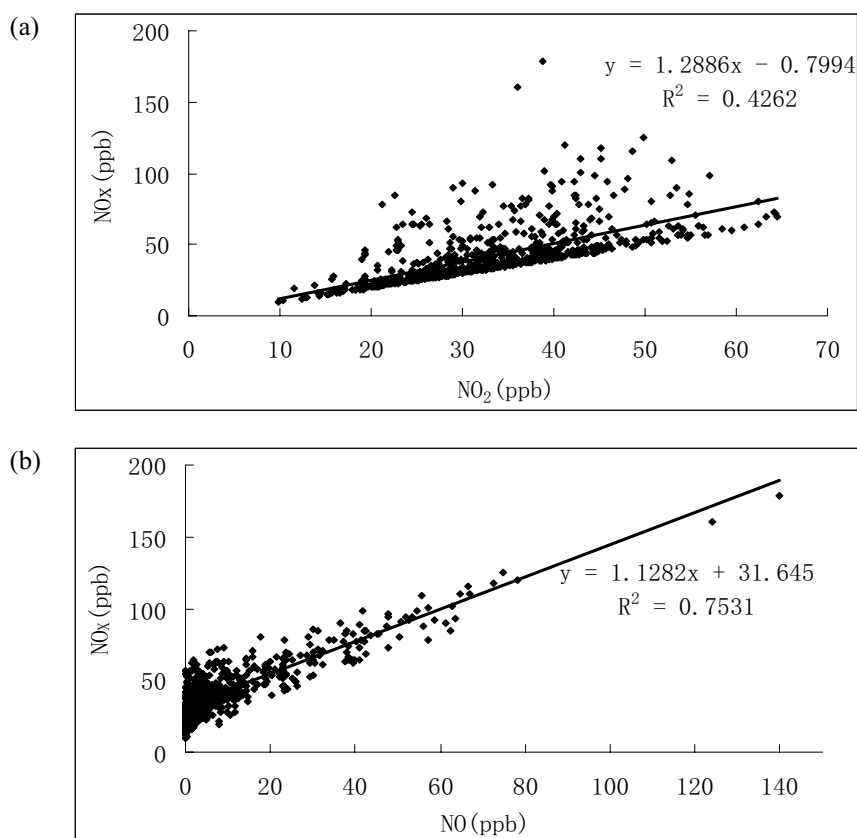


**Fig. 10.** Mean values of NO<sub>x</sub> varies with (a) NO<sub>2</sub> and (b) NO.

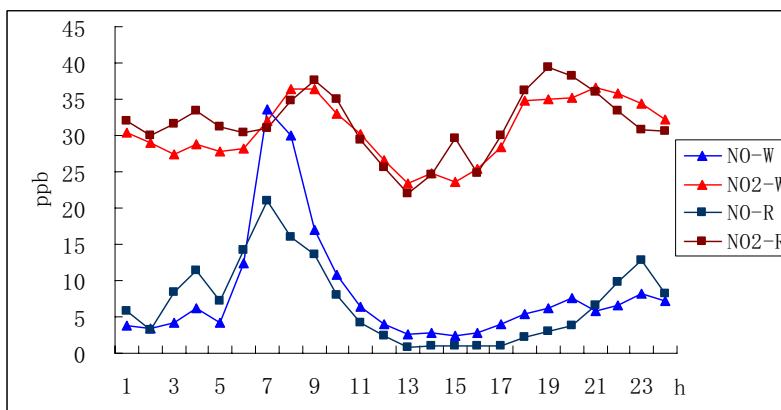


**Fig. 11.** Mean values of NO<sub>x</sub> varies with (a) NO<sub>2</sub> and (b) NO during daytime.





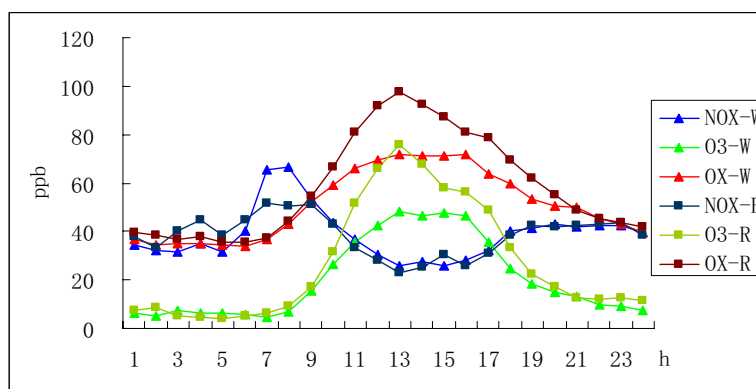
**Fig. 12.** Mean values of NO<sub>x</sub> varies with (a) NO<sub>2</sub> and (b) NO during nighttime.



**Fig. 13.** Daily variation of mean values of NO, NO<sub>2</sub> for weekdays and weekends.

Fig. 14 presents the daily variation of the mean values of NO<sub>x</sub>, O<sub>3</sub> and OX during weekdays and weekends. The average maximum value of O<sub>3</sub> at weekends was higher than on weekdays, which was also true for OX. The pattern of temporal variability presented here can also be found in other cities (Mayer, 1999). The mechanism for the weekend effect is still not well understood. However, the California Air Resource Board has proposed some hypotheses to explain the weekend effect in California (Carb, 2003). These include (i) The sensitivity of ozone formation to VOC concentration, combined with a decrease in weekend NO<sub>x</sub> emissions, (ii) difference in timing of NO<sub>x</sub> emissions, (iii) carryover of ozone and precursor concentrations on Friday

and Saturday nights, and (iv) increased weekend emissions. Moreover, Marr and Harley (Marr and Harley, 2002a, b) proposed a decrease in absorption of sunlight due to lower fine particle concentration during weekends, resulting in enhanced ozone formation. In our case, there was not apparent difference in meteorological conditions between weekdays and weekend, such as the average wind speeds were 1.1 and 1.3 m/s, the solar radiation were 8.0 and 7.9 w/m<sup>2</sup> respectively. So the weekend effect can be explained to some extent using the following mechanism: low NO emissions during weekend mornings consume less O<sub>3</sub>, then, in the daytime, it can not be depleted further. Therefore, there is an accumulation of ozone.



**Fig. 14.** Daily variation of mean values of NO<sub>x</sub>, O<sub>3</sub> and OX for weekdays and weekends.

**O<sub>3</sub> Concentration and Meteorological Conditions**

The O<sub>3</sub> concentration in relation to wind direction is shown in Fig. 15. It can be observed that when wind blows from NE-N-NW sector the O<sub>3</sub> concentration is lower than in the cases in which wind blows from SW-S-SE sector, the sea breeze have little influence on the O<sub>3</sub> concentration.

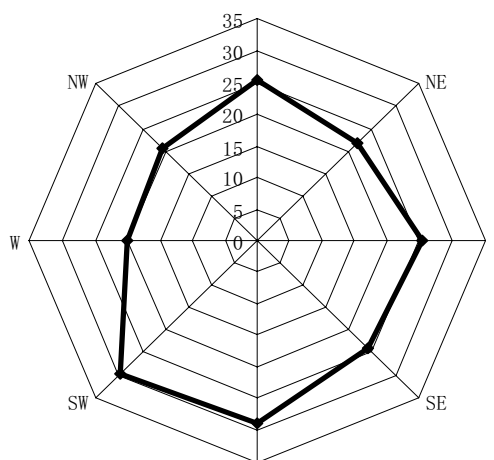
Despite the fact that the data are collected in autumn, we tried to investigate the influence of the intensity of solar radiation on variation of O<sub>3</sub>. We divided the O<sub>3</sub> data into three groups. Fig. 16 shows the variation in daily concentration of O<sub>3</sub> during sunny days (clear sky days), foggy days (fog usually disappears between 9:00 and 11:00) and cloudy days (accompanying light showers). On foggy days, the O<sub>3</sub> concentration increased slowly in the morning and on rainy days the maximum value was about half that of clear days.

**CONCLUSIONS**

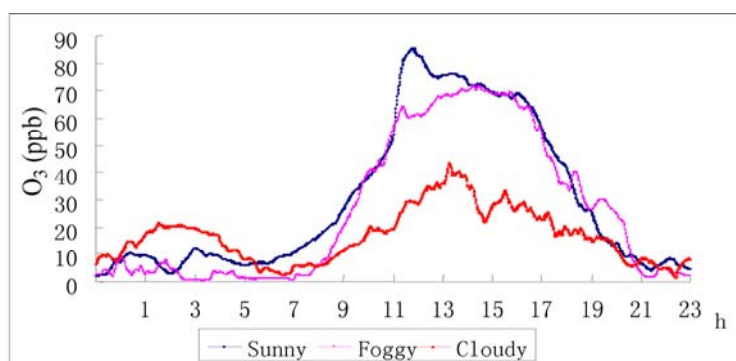
This article analyses the concentrations of NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> measured in Tianjin over 38 complete days in autumn. The results indicate that the diurnal cycle of ozone concentration has a mid-day peak and lower nighttime concentrations. The ozone concentration slowly rises after the sun rises, reaching a maximum during the daytime and then decreases until the next morning. This is due to photochemical O<sub>3</sub> formation. The shape and amplitude of ozone cycles is strongly influenced by meteorological conditions and prevailing levels of precursors (NO<sub>x</sub>). In the study area, the daily cycle of NO concentration arises from

vehicular emissions, and its conversion to NO<sub>2</sub> had a major impact on the daily cycle of ozone levels. We also found a linear relationship between NO<sub>2</sub> and NO<sub>x</sub>, as well as NO and NO<sub>x</sub>, and a polynomial relationship between O<sub>3</sub> and NO<sub>2</sub>/NO, which could be useful in O<sub>3</sub> forecasting and air pollution control strategies.

The level of [OX] is influenced by NO<sub>2</sub>-independent and NO<sub>2</sub>-dependent contributions. The former is due to regional background O<sub>3</sub> concentration, and the latter correlates to the local level of primary pollution. The regional background O<sub>3</sub> concentration in Tianjin is about 20 ppb.



**Fig. 15.** Rose of O<sub>3</sub> concentration.



**Fig. 16.** Daily variation of mean values of O<sub>3</sub> under different meteorological condition.

Our observations also reveal that production of O<sub>3</sub> is significantly higher during weekends than weekdays (the weekend effect). The mechanisms for the weekend effect are still not well understood and needs further study.

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