Measurement of surface ozone and its precursors in urban and rural sites in Beijing

Jing Xu\textsuperscript{a,b,d,*}, Xiaoling Zhang\textsuperscript{a,c}, Xiaofeng Xu\textsuperscript{a}, Xiujuan Zhao\textsuperscript{a}, Wei Meng\textsuperscript{a}, Weiwei Pu\textsuperscript{a}

\textsuperscript{a} The institute of urban meteorology; Center for Atmosphere Watch and Analysis of Beijing Meteorology Bureau, CMA, Beijing, China
\textsuperscript{b} Chinese Academy of Meteorological Sciences; Key Laboratory for Atmospheric Chemistry; Center for Atmosphere Watch and Services, CMA, Beijing, China
\textsuperscript{c} Shangdianzi National Station for Atmospheric Background Observation, Beijing, China
\textsuperscript{d} Graduate University of Chinese Academy of Sciences, Beijing, China

Abstract

A 4 year time continues measurements of ozone and its precursors including NO, NO\textsubscript{2} and CO at an urban and a rural site in Beijing area from January 2005 to December 2008 were analyzed to investigate the seasonal and diurnal variation characters of ozone and its precursors, and to understand the effects of local meteorological conditions. Pronounced seasonal variations of ozone and its precursors were observed in urban area, with the maximum ozone mixing rations appearing in late spring and early summer, minimum appearing in winter. Precursors NO, NO\textsubscript{2} and CO show opposite seasonal variation patterns to that of ozone. In rural area, O\textsubscript{3}, NO and NO\textsubscript{2} show similar seasonal variation patterns to that of urban area. While affected by the local natural plants emissions, CO reaches maximum in summer in rural area. Typical polluted cities diurnal variation patterns of ozone and precursors NO, NO\textsubscript{2} and CO were observed in urban area, characterized by the peak ozone value appearing at 14:00 and valley during nighttime, precursors showing two peaks related two the morning and evening rushes and reaching valley at ozone peaking time. In rural area, ozone shows similar diurnal pattern, while affected by pollutants transported from upwind urban area, peak value appearing time be delayed by several hours to that of urban area, except in winter. Meteorological conditions, especially boundary layer’s changing do primary contribution to the diurnal variation of ozone precursors CO and NO\textsubscript{2}, with the highest mixing ratios appearing during night time and lowest around noon time in rural area. NO appears single peak in dawn coming from HONO decomposed by the sunlight at rural site.

© 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Ozone, Nitrogen oxides, Carbon monoxide, Seasonal variation, Diurnal variation, Beijing;
1. Introduction

Beijing is one of the world’s largest cities with population over 15 million and covering 16807.8 km$^2$. Intensive urbanization and economic development have occurred during last two decades in China. Which leads to serious air pollution problems characterized by high concentrations of particulate and sulfur dioxide, due to the increasing in coal, traffic and energy consumption(He et al., 2001; Wang et al., 2005; Hao and Wang, 2005; Molina and Molina, 2004). The majority of attention on air pollution has been focused on traditional pollutants like particulate matter and sulfur component; only limited and scattered studies were published regarding photochemical ozone pollution. Nevertheless available data indicate rather serious ozone pollution in Beijing(Tang,2004;Hao and Wang, 2005;Shao et al.,2006;Wang et al.,2006). For example, data reported by Wang Tao show that in June-July 2005 daily maximum ozone concentrations exceeded 120ppbv for 13 days within 39 days with the peak hourly value of 286ppbv(Wang et al.,2006).Thus, it is necessary to gain a good understanding of ozone pollution. Previous researches on ozone chemistry in China have been focused in city cluster regions, such as Yangtze River delta(Cheung and Wang, 2001; Chan et al.,2003; Wang et al.,2005), the Pearl River delta(Ding et al., 2004). The ozone chemistry studies in China were mainly concentrated in Hong Kong(So and Wang, 2003; Wang et al., 2003; Lam et al., 2005; Zhang et al., 2007; Zhang et al.,2008 ). Sparse studies were also reported Shanghai(Geng et al., 2007), Nanjing(Tu et al., 2007) and Tianjin city(Bian et al., 2007). Most studies about surface ozone and its precursors in Beijing were based on the measurements over a short time period and at rural stations (Wang et al.,2006; Wang et al., 2008). Thus, these studies are far from overall understanding of ozone pollution in Beijing.

Since a few years, instruments of ozone and other pollutants have been set up at an urban and a rural station in Beijing to monitor the long-term changes in these pollutants. In this article we report the results on ozone and its precursors including CO, NO and NO$_2$ by analyzing the routine continuous measurements on pollutants over 4 years from January 2005 to December 2008. The objective of the present work is to study the continuous surface concentrations of NO, NO$_2$, NO$\_x$, CO and O$_3$ verifying the seasonal and diurnal variations and their relationship with the meteorological conditions at urban and rural stations in Beijing.

2. Results and discussion

2.1 Seasonal variation

2.1.1 Seasonal variation in urban area

Statistical summary of hourly average concentration of O$_3$ and its precursors for each season is given in Table 1. In urban area, the mean O$_3$ concentration is 24.45±28.53ppbv(n=31816) during the period of January 1, 2005 to December 31,2008. The mean concentrations of CO, NO and NO$_2$ are 1.32±1.35ppmv(n=32975), 26.58±45.17ppbv(n=33441) and 29.64±17.74ppbv(n=33441), respectively. Significant seasonal difference in concentration level exists for each air pollutant, according to the Kruskal-Wallis test ($\alpha=0.001$). Mean concentration of O$_3$ in different seasons follow the order of summer>spring>autumn>winter. Precursors NO, NO$_2$ and CO show almost contrary seasonal variation patterns to that of O$_3$ with higher values appearing in winter and autumn and lower values appearing in summer and spring. Which results from the seasonal variability of sources emissions and different photochemical reaction rate to generate ozone. The seasonal difference is more pronounced for NO. As can be seen in Table 1, mean concentration of NO in winter is almost 7 times higher than in summer. Compare to the other cities in China, the O$_3$ level at this site is within the measured range. For instance, the annual averaged hourly concentrations of O$_3$ ranged from 14.1 to 27ppb in Nanjing, from 13 to 34ppb in Hong Kong and from 13.8 to 29.3ppb in Taipei respectively(Tu et al., 2007; So et al., 2003; Chou et al., 2006).The mean concentration of CO (1.38±1.4ppm) in Beijing is much higher than that in Hong Kong (ranged from 0.49 to 0.86ppm) and close to that in Nanjing (1.13±0.88ppm). For NO$\_x$, the mean concentration measured in Beijing city is within the measured rang in Hong Kong (ranged from 7 to 74ppb) and higher than that in Nanjing.
2.1.2 Seasonal variation in rural area

In rural area, the mean O_3 concentration is 35.90±23.76 ppb (n=34864). The mean concentrations of CO, NO and NO_2 are 0.74±0.58 ppmv (n=33801), 0.82±2.07 ppb (n=29978) and 11.00±11.27 ppb (n=29987), respectively. Mean concentration of O_3, NO, NO_2 in different seasons follow the same order of that observed in the urban area. While the seasonal variation of CO differs from that observed in the urban area characterized by appearing maximum in summer and minimum in winter. In rural area, local natural carbon monoxide sources are more important than anthropogenic. Methane decomposed by organisms and hydrocarbons emitted by plants react with OH producing CO. Which results in the peak value of CO appearing in summer. Previous study also confirms that the contribution of isoprene emitted from vegetable to atmospheric formaldehyde in the ambient air of Beijing (Zhang et al., 2009). Then formaldehyde products CO through photolysis process. The mean daytime mixing ratios of CO are 0.84 ppmv in summertime, equal to the total summer averaged concentration and higher than the result 0.60 ppmv observed at another rural station in Beijing in summer 2006 (Wang et al., 2008).

Table 1 Statistical summary of hourly average concentrations of O_3 and its precursors for each season.

<table>
<thead>
<tr>
<th>Station</th>
<th>Season</th>
<th>O_3 (ppb)</th>
<th>CO (ppm)</th>
<th>NO (ppb)</th>
<th>NO_2 (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean (SD)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL</td>
<td>Spring</td>
<td>28.45±24.10</td>
<td>1.05±1.03</td>
<td>17.22±31.73</td>
<td>27.35±17.23</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8252</td>
<td>8337</td>
<td>8266</td>
<td>8266</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>40.78±36.19</td>
<td>0.94±0.77</td>
<td>7.17±17.19</td>
<td>22.91±11.61</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8544</td>
<td>8664</td>
<td>8608</td>
<td>8608</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>16.53±24.00</td>
<td>1.49±1.33</td>
<td>37.22±52.56</td>
<td>36.06±19.31</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8176</td>
<td>8320</td>
<td>8609</td>
<td>8609</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>9.01±10.29</td>
<td>1.85±1.88</td>
<td>46.77±58.78</td>
<td>32.36±18.91</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>6844</td>
<td>7654</td>
<td>7958</td>
<td>7958</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>Mean (SD)</td>
<td>24.45±28.53</td>
<td>1.32±1.35</td>
<td>26.58±45.17</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>31816</td>
<td>32975</td>
<td>33441</td>
<td>33441</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>43.22±19.59</td>
<td>0.68±0.53</td>
<td>0.45±0.82</td>
<td>10.23±8.42</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8826</td>
<td>8369</td>
<td>7470</td>
<td>7470</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>46.7±29.48</td>
<td>0.86±0.50</td>
<td>0.31±0.48</td>
<td>6.81±4.47</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8819</td>
<td>8331</td>
<td>7741</td>
<td>7741</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>29.8±21.51</td>
<td>0.77±0.59</td>
<td>0.94±2.10</td>
<td>12.50±9.99</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8710</td>
<td>8584</td>
<td>7907</td>
<td>7907</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>23.0±12.46</td>
<td>0.65±0.64</td>
<td>1.67±3.40</td>
<td>14.98±14.08</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>8509</td>
<td>8517</td>
<td>6860</td>
<td>6860</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>Mean (SD)</td>
<td>35.9±23.76</td>
<td>0.74±0.58</td>
<td>0.82±2.07</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>34864</td>
<td>33801</td>
<td>29978</td>
<td>29978</td>
</tr>
</tbody>
</table>

* Seasons are defined as spring is March-May; Summer: June-August; Autumn: September-November; Winter: January-February, December.

* S.D. represents standard deviation.

* N represents number of observations.

2.1.3 Comparison of two stations

Fig. 1 shows the monthly averaged ozone and its precursors mixing ratios measured at two stations from January 2005 to December 2008. Looking at the pollutants separately, the monthly variations of ozone mixing ratios in two area show similar patterns with the character of ozone maximum always occurring around May/June. The late spring/early summer maximum observed at this site is similar to the observations at many other cities in Northern Hemisphere (Pochanart et al., 2001; Satio et al., 2002; Zhang et al., 2002). There are still no certain causes for this maximum for a certain site yet. Some recognized
capable causes published including the anthropogenic and natural contributions (Satio et al., 2002; Zhang et al., 2002), enhanced photochemistry after a wintertime accumulation of precursors, intrusion of O\textsubscript{3} rich air mass from stratospheric to troposphere, and large-scale transport (Salisbury et al., 2002; Zhang and Oanh, 2002; Ribas and Peñuelas, 2004). The highest O\textsubscript{3} is in May/June, which has good meteorological conditions for photochemical reactions to generate O\textsubscript{3}, with higher temperature, higher ultraviolet radiation and lower wind speed. The highest concentrations of troposphere ozone always occur in the warmer seasons and times of greater sunlight in which the incident solar radiation is greater (Teixeira et al., 2009; Laakso et al., 2008). The early summer maximum of surface O\textsubscript{3} observed in Beijing is similar to the Nanjing city (Tu et al., 2007), but (except in 2006) not same as a common seasonal characteristic of summer minimum in some coastal East Asia cities, Shanghai, Hongkong, Nagoya in Japan, and Bangkok in Thailand (Xu et al., 1997; Chan et al., 1998; Satio et al., 2002; Zhang et al., 2002). Previous studies of the summer minimum in these cities were concluded to the contribution of the inflow of the clean maritime tropic air mass associated with Asian monsoon. Though the climate in Beijing is also influenced by the Asian monsoon. Southern and southeastern monsoon prevailing in summer. Before reaching Beijing, the monsoon passes through the Shangdong peninsula, Hebei and Tianjin province. All these regions are rapid economic and industrial development areas of China. O\textsubscript{3} and its precursors such as NO\textsubscript{x}, CO and VOCs emitted from these regions have been transported to the downwind area, which may attribute to the O\textsubscript{3} accumulation and production in Beijing in summer.

Monthly variations of NO\textsubscript{x} mixing ratios in two area also show similar patters with the character of NO\textsubscript{x} maximum occuring around November to January, which is almost opposite to that of O\textsubscript{3}. The higher values appear in late autumn and winter, while the lower values appear in summer. There are about two reasons for this pattern. The first one may partly be greater photochemical reaction involving the precursors due to the higher solar radiation in summer than in other seasons, lead to the lower concentrations of these pollutants. Another causes is the increase in air pollution in winter due to heating fuels consumed. In urban area, monthly variation of CO mixing ratios are similar to that of NO\textsubscript{x}. Monthly variation of CO mixing ratios in rural area are more complex than that in urban station with almost no uniform yearly patter. Besides, from Fig.1 we can find that CO shows a significant higher values in June than in other summer months in both stations. The most probable reason for the elevated CO concentration in this certain period is the combustion of the straw crop (Li et al., 2008a; Li et al., 2008b). Some previous studies in other areas also find this phenomena (Tu et al., 2007; Laakso et al., 2008).

Statistical summary of hourly O\textsubscript{3} air quality for each season is given in Table 1. As we can see, in both stations, the highest hours/days of high ozone (defined as the hourly concentration of ozone above NAAQS, 102ppb) appear in summer. Then follows the autumn and spring. While there is no high ozone
hour/day in winter. In urban and rural area, the highest hourly O$_3$ concentrations are recorded both in
summer with the value of 271.56ppbv and 189.27ppbv respectively in this study. Which is comparable to
the previous record 286ppb at an rural site in Beijing (Wang et al., 2006).

2.2 Diurnal variation

2.2.1 Diurnal variation of O$_3$

In urban area, diurnal variations of O$_3$ shows typical patterns for large polluted cities around the
world(Lal et al., 2000; Dueñas et al., 2002; Zhang and Oanh, 2002; Mazzeo et al., 2005), with
minimum values in the early morning, a strong rise during the morning with the increasing solar radiation,
peak mixing ratios at about 14:00, and a decline due to ozone destruction by NO during night time(Fig.2).
This feature can be explained by the activating role of solar radiation in photochemical ozone generation
in the mixing layer and ozone transport from upper layers(Klumpp et al., 2006). Once the nocturnal
inversion layer has been established, no major changes in ozone concentration occur until rupture of
inversion layers and photochemical reactions start again with beginning of the daylight period(Coyle et al.,
2002; Dueñas et al., 2002;). In rural area, diurnal variations of O$_3$ shows almost similar patter with that of
urban area. The most distinctive differences of O$_3$ diurnal variation pattern between two stations is that
the peak O$_3$ mixing ratios observed at rural station is delayed by several hours of the peak observed at
urban station except in winter. In urban area, the peak values observed at the peak solar radiation time
about 14:00 for all seasons. In rural area, the peak values observed at 14:00 in winter, at 16:00 in autumn
and at 17:00 in summer and spring. which reveals that the photochemical reaction are the primary source
of O$_3$ regeneration in urban area, while the transportation from upwind urban area to rural area contributes
to the accumulation of O$_3$ in SDZ station, especially in spring and summer. As be given before, the
prevailing direction is south from afternoon to early night making for pollutants transported from urban
area to the downwind rural area. The strong influence of air quality in rural area by urban plume of
Beijing has been also observed by Wang et al., (2006) and Lin et al.(2008). Lin et al.(2008) calculated the
difference of ozone mixing rations observed at SDZ station for south and north wind directions. Results
show 25~31ppbv for each hour from 13:00 to 19:00 in afternoon. Compare to the night time ozone
mixing ratios observed urban station, that observed at rural station is much higher. Which results in the
lower “titration reaction” rate between O$_3$ and NO. As can be seen in Fig.2, the concentration of NO$_x$
in urban area is much higher than that of rural area.

2.2.2 Diurnal variation of CO , NO and NO$_2$

In urban area, precursors NO, NO$_2$ and CO show an almost opposite diurnal variation patterns to
that of ozone, characterized by high concentrations during night and early morning and low
concentrations during daytime, especially noon and afternoon. All the diurnal variations of CO ,NO and
NO$_2$ have two peaks related to the morning and evening rush hours. The early morning peak appear at
07:00/08:00. Then, according with sunlight starting a series of photochemical reactions, the
concentrations of the precursors decrease in good agreement with the increasing in that of O$_3$. The
precursors reach their minimum values at around 14:00 when O$_3$ reaches its maximum. The similar
diurnal variation patterns in O$_3$ precursors were also observed in many urban areas around the world (Lal
et al., 2000; Dueñas et al., 2002; Zhang and Oanh, 2002; Mazzeo et al., 2005). This typical diurnal
variation is not only affected by the emissions, but also by the local meteorological conditions. For all the
meteorological conditions, boundary layer’s height plays the most important role in the diurnal variation
of the pollutants directly by diluted process. The daily behavior pattern of boundary layer is characterized
by lower height values during the night and before the sunrise. During nighttime the earth surface
becomes colder promoting the stratification of the lower layers near the surface as well the formation of a
‘nocturnal stable boundary layer’(Stull, 1997). After the first morning hours, the incidence of solar
radiation warms the surface, destroys the ‘nocturnal stable boundary layer’, and makes the ‘convective
mixing layer’, with turbulent vortexes responsible for the vertical movements in the lower atmosphere,
thus increasing the height of the mixing layer. In the beginning of afternoon, this layer reaches its maximum value, the convection is responsible for the maximum dispersion within this layer. With sunset, decreases incidence of solar radiation and convection, the surface’s cooling again favors the formation of a ‘stable nocturnal boundary layer’, which develops during the night.

In rural area, diurnal variations of precursors NO, NO$_2$ and CO are different to that of urban area. At rural site, meteorological conditions does significantly contribute to the diurnal variation of ozone precursors because of the extremely low emission levels of CO and NO. CO and NO$_2$ show almost similar diurnal variation with the character of maximum during nighttime and minimum around noontime, which related to the mixing layer variation closely. NO mixing ratios appear peak in dawn and valley around 17:00. Besides, the appearing time of peak for each season coincides with the sunrise time characterized by 06:00 in summer, 07:00 in spring, 08:00 in autumn and 09:00 in winter. NO is one of a primary reactive pollutant. HONO accumulated during the night time and decomposed by the sunlight is the only source of the early morning peak at the clean rural area.
3. Conclusion

Continuous measurements of surface ozone and its precursors CO, NO and NO₂ for four years were carried out at urban and rural stations. Long-term measurement results of ozone and precursors were not yet published in Beijing area. The aim of the present study was to give the basic character of ozone and its precursors including seasonal and diurnal variations, and to study the impact of local meteorological conditions on surface ozone pollution.

Pronounced seasonal variation of ozone was observed in both urban and rural area, with the maximum ozone mixing ratios appearing in late spring and early summer, minimum appearing in winter. The highest percentage of high ozone hours/days also appearing in summer, with the peak ozone hourly mixing ratios 271.56ppbv and 189.27ppbv recorded during this study period at urban and rural station respectively. In urban area, precursors NO, NO₂ and CO show opposite seasonal variation patterns to that of ozone driven by corresponding seasonal variability in source emissions and meteorological conditions in urban area. In rural area, O₃, NO and NO₂ show similar seasonal variation patterns to that of urban area. While affected by the local natural plants emissions, CO reaches maximum in summer in rural area.

Typical polluted cities diurnal variation patterns of ozone and precursors NO, NO₂ and CO were observed in urban area, characterized by the peak ozone value appearing at 14:00 and valley during nighttime. Precursors show two peaks related to the morning and evening rushes, reaching valley at ozone peaking time destructed by photochemical reaction and diluted by the meteorological condition. In rural area, ozone shows similar diurnal pattern to that of urban area. While affected by pollutants transported from upwind urban area, peak diurnal value appearing time in rural area was delayed by 2 hours in autumn, 3 hours in summer and spring to 14:00 in urban area. Meteorological conditions, especially boundary layer’s changing do primary contribution to the diurnal variation of ozone precursors CO and NO₂, with the highest mixing ratios appearing during night time and lowest around noon time in rural area. NO appears single peak in dawn coming from HONO decomposed by the sunlight at rural site.

Acknowledgements:

We thank the staff of the Atmospheric Watch and Analysis Center of Institute of Urban Meteorology, Beijing, for carrying out the measurements. This work was supported by NSFC41075111 and GYHY200806027.

References: