Variations of ground-level O₃ and its precursors in Beijing in summertime between 2005 and 2011

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Abstract: Elevated ground-level ozone (O\textsubscript{3}), reflecting atmospheric oxidative capacity, are of increasing concern. High levels of total oxidants (O\textsubscript{x}=O\textsubscript{3}+NO\textsubscript{2}) have been persistently observed as a feature of Beijing’s air pollution. Beijing is a well-known mega-city requiring the enforcement of stringent air quality controls as rapid economic growth continues. To evaluate the effect of air quality controls in recent years, ground-based on-line measurements at an urban site were conducted in summer and the variations in O\textsubscript{3} with simultaneous changes in NO\textsubscript{x} and volatile organic compounds (VOCs) between 2005 and 2011 were analyzed. Both NO\textsubscript{x} and total VOCs in Beijing decreased over the study period, 1.4 ppbv/yr and 1.6 ppbv/yr, respectively. However VOCs reactivity, in term of OH loss rate showed an indistinct statistical trend due to unsteady variations from naturally emitted isoprene, though some anthropogenic species showed decreasing trends, such as pentanes, benzene and toluene. Meanwhile, daytime average O\textsubscript{3} increased rapidly at an annual rate of 2.6 ppbv/yr, around 5%/yr between 2005 and 2011. Considering the influence of NO titration effect and elevated regional ozone background in the North China Plain (NCP), the main reason for such an increase in oxidants was subject to ‘local’ photochemistry. A simplified model was used to evaluate the effect of changes in the levels of ozone precursors on ozone production. We found that between 2001 and 2006, the production rate of total oxidants, P(O\textsubscript{x}) increased rapidly due to increased VOC levels and decreasing NO\textsubscript{2}, while from 2006 to 2011, P(O\textsubscript{x}) remained high though, decreased slightly as a consequence of the decrease in both VOC reactivity.
(-5%/yr) and NOx (-4%/yr). Some observation evidences have shown that Beijing’s
efforts to control air pollution were somehow effective in cutting ozone precursors,
but still left higher ground-level ozone. We surmised that it resulted from potential
contributions from OVOCs and regional transport near Beijing. Therefore, Beijing
needs deeper cooperation with adjacent provinces to control ozone pollution together.

To impel this kind of joint prevention and control program, ground-level ozone should
become a mandatory index for air quality management, and a faster reduction of
VOCs, especially reactive VOCs, in urban areas, should coordinate with national NOx
gas emission control programs.

Keywords: ground-level ozone, trend, VOCs, NOx, ozone production efficiency
1. Introduction

High concentrations of ground-level ozone are harmful to human health, ecosystems, and the global climate (Fiore et al., 2009). Beijing, the second biggest mega-city in China, has been experiencing severe ozone pollution, with around 60 non-attainment days every year for ozone (the day with maximum 1-h mixing ratio of ozone >93.3 ppbv) between 2001 and 2005 (Duan et al., 2008). The highest daily maximum 1-h (DMA-1h) ozone level in 1997 was 162 ppbv (Duan et al., 2008), but reached 186 ppbv in 2008, during the Olympic Games (Wang et al., 2010d). Given that ozone levels were already high, the trend of ground-level ozone in Beijing has been of increasing concern. In contrast to declining ozone levels in urban areas in the U.S. (Lefohn et al., 2010; Pollack et al., 2013), limited studies conducted in China have shown that ozone levels in both regional background and urban areas were increasing (Li et al., 2014; Meng et al., 2009; Xu et al., 2008; Wang et al., 2009b; Wang et al., 2011a). Ozone levels in the lower atmosphere over Beijing increased by 2% annually between 1995 and 2005 according to measurements from onboard aircraft (Ding et al., 2008), and ground-based measurements showed that 24-h average O₃ increased by 1.1 ppbv/yr in summer months (Jul.-Sept.) between 2001 and 2006 (Tang et al., 2009). Recently ozonesonde measurements also proved that ozone in the lower troposphere (0–3 km) over Beijing during summer months increased at the rate of 3%/yr between 2002 and 2010 (Wang et al., 2012b). Moreover, ozone pollution is typically a piece of regional environmental issue. Modelling results demonstrated that
high ozone pollution suffered in a large scale in the North China Plain (NCP) under adverse meteorological condition (Zhao et al., 2009; Nawahda et al., 2013).

The total oxidants (usually estimated by $O_x = O_3 + NO_2$) were used to indicate ambient oxidation capacity (Shiu et al., 2007). In Hong Kong, mean $O_3 + NO_2$ levels increased by 0.69 ppbv/yr from 1994 to 2007 (Wang et al., 2009b). In the PRD area (cluster cities in the Pearl River Delta close to Hong Kong), $O_x$ in urban sites increased by 0.72 ppbv/yr and $O_3$ in urban sites increased by 2.0 ppbv/yr during 10:00-17:00 (local time) from 2006 to 2011 (Li et al., 2014). The total oxidant levels in Taipei remained stable, but the maximum ozone levels increased by 0.90 ppbv/yr from 1994 to 2003 (Chou et al., 2006). Many previous studies on urban/regional ozone pollution in China mainly focused on pollution episodes (Duan et al., 2008), while the understanding of long-term ozone trends remain scarce due to the lack of simultaneous measurements of ozone and its precursors, nitrogen oxidants ($NO_x$) and volatile organic compounds (VOCs) (Tang et al., 2009; Wang et al., 2009b), especially lack of speciated VOCs data (Chou et al., 2006; Zhang et al., 2011).

To minimize increasing levels of ground-level ozone, great efforts have been made to reduce emissions of ozone precursors: $NO_x$ and VOCs in Beijing. Emissions of $NO_x$ and VOCs in Beijing fluctuated with both rapid economic development and stringent air quality control measures. Vehicle emissions are one of the most important sources of ozone precursors in Beijing (Song et al., 2007). The total number of the vehicles in Beijing reached almost 5.2 million at the end of 2012 with average
annual growth rate (AAGR) of 12%/yr in the last decade (http://www.bjjtgl.gov.cn).
Furthermore, energy consumption increased at AAGR of 6.8%/yr from 1995 to 2010
(http://www bjstats.gov.cn), which is a strong driving force for larger NOx and VOCs
emissions. However, Beijing municipal government has been implementing a series
Together with the abatement of stationary combustion sources, vehicular emission
were also controlled, including upgrading the quality of gasoline and diesel, putting
limits on on-road vehicle fleet and eliminating heavy-polluting yellow-labeled
vehicles (Wang et al., 2010c). Some of these control measures were short-term
specially for the 2008 Olympic Games, but others have been kept as long-term
measures. The effectiveness of these control measures needs quantitative evaluation
for follow-on clean air programs.

At regional or global reception sites, the impact from long-range transportation
and long-term emission changes are extraordinarily important to understand ozone
pollution and its temporal trends (Dentener et al., 2011; Wang et al., 2011b). However,
variations in urban site are more complicated in different areas. Aiming at identifying
major factors for Beijing’s trend of ground-level ozone, this study investigated the
variations of ground-level O3 in summer in Beijing and its relationship with changes
of its precursors for 7 years. Using ground-based measurements in August (between
2005 and 2011) at one urban site in Beijing, we obtained a dataset of O3 levels in
August with simultaneous measurements of NOx and speciated VOCs. The temporal
and chemical characteristics of O₃, NOₓ and VOCs variations were evaluated. A simplified model was used to interpret the role of ozone production rate in the variation of ground-level ozone concentrations. Potential impacts from regional variations were also featured in discussion.

2. Data and methodology

2.1 Ozone and NOₓ datasets

Ambient ozone and its precursors were measured at an urban site in Beijing in August between 2005 and 2011. The site (39.99°N, 116.31°E) was located on the roof of a six-story building (~20 m above the ground level) on campus of Peking University (PKU), where is about 20 km northwest of the Tiananmen Square (the core of Beijing). The site is near the 4th Ring Road with high density of traffic without obvious industrial or agriculture sources (Wehner et al., 2008). Temporal variation trends of air pollutants and composition of VOCs were thought to be similar to the downtown so as to be representative for the whole Beijing (Wang et al., 2010a; Xu et al., 2011a; Zhang et al., 2012a; Xu et al., 2011b).

At this site, ozone and NOₓ (NOₓ=NO+NO₂) were measured simultaneously. Ozone was measured by ultraviolet spectrophotometry using an EC9810 ozone analyzer (ECOTECH, Inc., Knoxfield, Australia). Ambient NO and NO₂ were measured by gas-phase chemiluminescence using an ECOTECH EC9841 NOₓ analyzer with molybdenum oxide catalysts. This prevalent type of NOₓ measurement technique is known (Dunlea et al., 2007) to have interferences from non-NOₓ reactive
nitrogen species (referred to as NO\textsubscript{z}, e.g. NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, HNO\textsubscript{3}, RONO\textsubscript{2}, PAN). We had a new NO\textsubscript{2} instrument based on principle of photolysis in 2013. The inter-comparison between these two gave about 10-20\% differences depending on the photochemical status. Considering simultaneous measured PAN (peroxy acetyl nitrates) recently by GC-ECD (gas chromatograph with electron capture detector) and gas-phase HNO\textsubscript{3} by GAC-IC (gas/aerosol collector with ion-exchange chromatography system), we found that PAN and gas-phase HNO\textsubscript{3} were the main contributors to the differences of NO\textsubscript{2} between Mo converter and photolysis instrument. Therefore the total oxidant O\textsubscript{x} (observed O\textsubscript{3} + NO\textsubscript{2}) determined in this study included O\textsubscript{3}, NO\textsubscript{2}, and part of NO\textsubscript{z}, which in fact can be better way to describe total photochemical ozone production potentials. Although there is systematic bias in NO\textsubscript{x} measurements, its impact on trends of NO\textsubscript{x} is limited and acceptable. For all these gas pollutant measurements, automatic zero and span checks were conducted daily, and multi-point calibrations were performed weekly.

To investigate the changing of NO\textsubscript{x} in Beijing, we also use vertical column density (VCD) data of tropospheric NO\textsubscript{2} (integrated from ground to 150 mbar) over Beijing from OMI instrument to make an inter-comparison with ground-based NO\textsubscript{x} measurements. VCD of tropospheric NO\textsubscript{2} is derived from slant column density (SCD) of NO\textsubscript{2} divided by an air mass factor (AMF), where SCD is retrieved from reduced reflectance of ultraviolet-visible spectrophotometry (UV/VIS) radiance measured by satellite instruments and AMF is calculated based on series of other measurements.
NO$_2$ VCDs from OMI data are available from the NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC) ([http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omno2_v003.shtml](http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omno2_v003.shtml)). OMI is a nadir-viewing near-UV/Visible CCD spectrometer aboard NASA’s Earth Observing System’s (EOS) Aura satellite. Since the domain we selected (39.7°N-40.2°N, 116°E-116.75°E), represented as Beijing urban area (about 3000km$^2$), is very small, the standard product of Level 2 (Version 1.1.0.2, and Collection 3) was chosen for re-processing. The spatial resolution of Level 2 products is 13×24 km$^2$ at nadir. Furthermore, data were excluded when cloud amount that day was above 30%. Daily averages come from the mean of VCDs in all effective pixels within the domain. Other VCD data of tropospheric NO$_2$ over the North China Plain (NCP) or Beijing were collected from literatures (Lin and McElroy, 2011; Richter et al., 2005; Wang et al., 2009b; Zhang et al., 2007). Note that all these data were monthly averages in August.

### 2.2 VOCs datasets

Measurements of VOCs between 2005 and 2011 were performed by on-line instruments in three labs: Peking University (PKU) in China, the Aeronomy Laboratory (now the Earth System Research Laboratory, ESRL) of the National Oceanic and Atmospheric Administration (NOAA) in the U.S., and the Research Center for Environmental Changes (RCEC) of Academia Sinica in Taiwan.

The data in 2005 were measured by an on-line GC-FID/MSD (gas chromatograph...
with flame ionization detector and mass spectrometric detector) system developed by
Earth System Research Lab (ESRL), NOAA (Goldan et al., 2004). C2-C5 alkanes
(referred to as alkanes with carbon number between 2 and 5), C2-C4 alkenes, and
acetylene are separated on an Al₂O₃/KCl column and quantified with a flame
ionization detector (FID). C5-C10 alkanes, C5-C9 alkenes, C6-C9 aromatics, and
isoprene are separated on a DB624 column and quantified with quadrupole mass
spectrometer. The data in 2006 were measured by an on-line GC-FID system of
Research Center for Environmental Changes (RCEC), Taiwan. A Porous Layer Open
Tubular (PLOT) column was used for separating C3–C6 compounds, with Agilent
DB-1 (non-polar and low bleed) column for separating C6–C12 compounds (Wang et
al., 2004). The data in 2008 were measured by an on-line GC-FID/MSD system
developed by RCEC. The PLOT column connected to an FID is used for analyzing
C2–C4 compounds, and the DB-1 column connected to a MSD is used for C4-C10
compounds. Method detection limits (MDL) range from 0.05 to 0.14 ppbv, and
relative standard deviations (RSD) of most species are less than 10% (Chang et al.,
2005). The data in 2007, 2009 and 2010 were measured by an on-line GC-FID/PID
system of PKU (Syntech Spectra GC955 series 611/811 ozone precursor analyzer).
GC955-811 ozone precursor analyzer for C3-C5 VOCs equips dual detectors (Photo
Ionization Detector (PID) and FID) with a PLOT column and a pre-concentrator at
5°C. GC955-611 ozone precursor analyzer targets C6-C10 VOCs using a system of a
pre-concentrator at normal atmosphere temperature, an AT-1 column (similar to DB-1),
and a PID (Xie et al., 2008). MDL range from 0.05 to 0.2 ppbv and RSD of species are regularly less than 10%. The data in 2011 were measured by an on-line GC-FID/MSD system developed by PKU; in this system we deployed a custom made preconcentrator by using adsorbent-free electrical cryogenic technology. This is a substitution of previously used system (Entech 7100A preconcentrator) which used liquid nitrogen as an adsorbent.

Stringent inter-comparison experiments were conducted between three laboratories. During each campaign we conducted calibration of instruments and inter-comparisons when two labs involved. Two ways of inter-comparisons were preformed: first is check of VOC standards used by different labs, second is measurement of the same blind samples by different labs. The standard deviations for VOC standard check were less than 10% for all species except for isoprene (which was around 15%), ratios of PKU results and RCEC results varied between 0.87 and 1.11 for all measured species, the inter-comparison between PKU lab and NOAA lab agreed between 0.85-1 (Liu et al., 2008b; Shao et al., 2009). An inter-comparison between online GC-FID/MSD and GC-FID/PID both in PKU laboratory was conducted lasting for one week in 2010. Different measurements show good consistency in time-series data; regression and bias analysis also demonstrate acceptable ratios between them (supplementary information). We were confident that the VOC data in this work were obtained under reliable QA/QC procedures.

However, the quantified VOC species differed among different analytical systems
and only 18 species that were commonly measured in all years were used in this work.

These 18 typical abundant VOCs species (except for C2 compounds) were: 6 alkanes (propane, i-butane, n-butane, i-pentane, n-pentane, and hexane), 7 alkenes (propene, trans-2-butene, 1-butene, cis-2-butene, 1-pentene, trans-2-pentene, and isoprene), and 5 aromatics (benzene, toluene, m,p-xylene, o-xylene, and ethylbenzene). The sum of the OH loss rate of these species accounts for 70–77% of the total VOC reactivity of all quantified species each year. Therefore, those species were selected to represent measured hydrocarbons and used for discussion in this paper.

2.3 Meteorology and trend analysis method

A simple linear regression (the least-squares method) was implemented to investigate temporal trends of ozone and its precursors. Daytime (7:00–19:00) averages, daily maximum 8-h averages, and daily maximum 1-h averages were calculated from measurements and used for the evaluation of ozone trends. Daytime averages of NOx and VOCs were also analyzed. The null hypothesis is that air pollutants and time have no linear relationship and this was tested using the standard F-statistic test (ratio of the mean-square regression to the mean-square residual). The p-value associated with the F-statistic is the probability of mistakenly rejecting the null hypothesis (** p<0.01; * p<0.05).

Meteorological conditions may also contribute to the inter-annual variability. Thus, we also collected some meteorological parameters, including wind speed (WS), wind direction (WD), atmospheric pressure (P), air temperature (T), and relative humidity
(RH), during the monitoring periods. They were continuously recorded by a weather station (LASTEM M7115: LSI-LASTEM, Milan, Italy) at the same site.

2.4 Calculation of total oxidant production rate

Atmospheric $O_3$ concentrations can be influenced by ozone production, ozone photolysis, chemical loss, dry deposition, and transportation. Both regional transport and local ozone production play key roles in ozone accumulation in the episodes (Liu et al., 2010a). Although during the Olympic Game period, contributions from outside Beijing sometimes dominated ozone peak (Wang et al., 2010d), generally speaking, local photochemistry is the most responsible to ozone peak (Streets et al., 2007; Wang et al., 2009c). To investigate the role of variations of ozone precursors on ozone formation, we adopted a simplified approach (Farmer et al., 2011; Geddes et al., 2009) that calculated the instantaneous ozone production rate via VOC reactivity and NO$_x$ mixing ratios. Total oxidant production $P(O_x)$ could be estimated by solving steady state equations for OH, HO$_2$, and RO$_2$ species (LaFranchi et al., 2011), and detailed assumption and derivation could be found in supplementary information. The represented photochemistry in the following formula simulates urban situation at noon, and $P(O_x)$ is computed according to following equation (1). The rate of HO$_x$ production $P(HO_x)$ is mainly dependent on HONO, OVOCs, and ozone photolysis, the value of which was taken from a specific study in Beijing (Liu et al., 2012). Then the corresponding $P(O_x)$ can be solved through a quadratic equation:
\[
(1) \quad P(O_x) = 2k_1[VOC] \cdot [OH] \\
= \frac{2k_1[VOC] \cdot 2P(HO_x)}{(k_3[NO_2] + \frac{ak_1[VOC]}{1-\alpha}) + \sqrt{(k_3[NO_2] + \frac{ak_1[VOC]}{1-\alpha})^2 + \frac{8P(HO_x)(k_4+k_5+k_6)(k_1[VOC])^2}{((1-\alpha)k_{2a}[NO])^2}}} \\
= \frac{4P(HO_x)}{(k_3[NO_2] + \frac{\alpha}{k_1[VOC]} + 1-\alpha) + \sqrt{(k_3[NO_2] + \frac{\alpha}{k_1[VOC]} + 1-\alpha)^2 + \frac{8P(HO_x)(k_4+k_5+k_6)}{((1-\alpha)k_{2a}[NO])^2}}}
\]

Where \(k_{1,i}\) represents the reaction constant between OH radical and individual VOC\(_i\) species, \(k_1[VOC]\) represents the sum of VOC reactivity (\(\sum k_{1,i}[VOC_i]\)). \(\alpha\) is the yield of alkyl nitrates from VOCs, \(k_{2a}\) is the apparent reaction constant between NO and peroxy radicals (RO\(_2\)), \(k_3\) is the reaction constant between NO\(_2\) and OH radical, and \(k_4, k_5, k_6\) are the constants of peroxy radicals reaction between RO\(_2\) and RO\(_2\), RO\(_2\) and HO\(_2\), HO\(_2\) and HO\(_2\) respectively.

### 3. Results and discussion

Temperature and wind speed, which can influence ozone levels directly, showed no significant changes during the study periods (Table 1). The 90th percentile high temperatures in summer were between 30-34 ºC. Temperature in 2005 was lowest and that in 2007 was the highest. The average of wind speeds was less than 2 m/s, suggesting the atmosphere was generally stable in August in Beijing. The 90th percentile relative humidity at PKU decreased significantly by around 1%/yr. But precipitation in Beijing did not show decreasing trend over the same time period. It is found that both sunshine hours and visibility in the NCP area have been decreasing in the past decades (Yang et al., 2009; Zhao et al., 2011). But we couldn’t detect
significant decrease of sunshine hours according to Beijing’s meteorological records in recent decade. Briefly, we think that the meteorological parameters might play only a minor role in the ozone trends in Beijing, and then focus our discussion on chemical processes.

3.1 Variations of $O_3$ and $O_x$

Based on the measurements at the PKU site, we calculated daytime (7:00–19:00, 12-h) averages and daily maximum 1-h averages (DMA-1h) of ozone and $O_x$, respectively (Figure 1). Daytime ozone in August between 2005 and 2011 ranged from 42 to 63 ppbv and the DMA-1h ozone ranged from 71 to 103 ppbv. In August of 2011, recorded ozone levels on approximately two-thirds of days exceeded the national ambient air quality standard for ozone. Daytime $O_x$ in August between 2005 and 2011 ranged from 68 to 86 ppbv with DMA-1h $O_x$ from 91 to 123 ppbv. Ozone and $O_x$ shared similar variations in these years, for ozone accounted for 70-80% of $O_x$ between 2006 and 2011. Recent modeling revealed that ozone concentrations in the North China Plain including Beijing was the hot-spot in Northeast Asia areas and ozone pollution aggravated from 2000 to 2005 (Nawahda et al., 2012; Nawahda et al., 2013).

Figure 2 shows the diurnal variations of ozone and $O_x$ from 2005 to 2011. It is apparent that the averages of ozone levels between 2009 and 2011 were higher than that between 2005 and 2007. Also it is noteworthy that the peak time for ozone levels has delayed. Peak value of $O_x$ diurnal variations usually appears at 1-3 pm (local
time). But the pattern of \( O_x \) diurnal variations in 2007 and 2008 is notably different from other years. In these two years, \( O_x \) levels around the noon were not so high, relatively, and appeared a second peak at 5 pm indicating that transported ozone may play a larger role in these years. Additionally, nocturnal ozone levels in 2008, much higher than other years, might be due to stringent control on \( NO_x \).

It is said that ambient abundance of ozone and its precursors is subject to log-normal distribution (Dentener et al., 2011; Pollack et al., 2013). We plotted cumulative probability calculated from log-normal distribution (expected probability) at y axis with logarithmic ozone and \( O_x \) mixing ratios (actual distribution) at x axis in Figure 3. If measured ozone and \( O_x \) herein also obey distribution of log-normal distribution, the plotted curve in Figure 3 should be, actually it is, closed to a straight line similar to the principle of P-P plot (probability-probability plot). Therefore, we mainly use semi-log plots hereafter to clearly show and discuss observed trends.

Trend lines were derived from simple linear regression to introduce the least uncertainties driven by methodology into the regression (Parrish et al., 2012). Our measurements showed both an increase in ground-level ozone and \( O_x \) in August between 2005 and 2011 (Figure 1). The trend of daytime ozone in Beijing in summertime, derived from the monthly averages, was an increase of \( 2.6 \pm 0.9 \) ppbv/yr, meaning average annual growth rate (AAGR) of \( 5.3\%/yr \) \((n=7, r^2=0.61)\). The trend of DMA-1h ozone in Beijing in summertime was an increase of \( 3.2 \pm 2.0 \) ppbv/yr, increasing at a rate of \( 4.0\%/yr \) \((n=7, r^2=0.34)\). The regression of daytime averages was
more stable, for inter-annual variability in 12-h averages was less sensitive than that in 1-h daily maximum numbers.

As to the trend of total oxidants (daytime O₃), the data in five years (2006, 2007, 2009-2011) were taken into account because NOₓ data in 2005 were not available and the short-term controls on NOₓ in 2008 distorting the O₃ level. The trend of total oxidants in Beijing in summertime, derived from the monthly averages, was an increase of 1.8 ± 1.6 ppbv/yr (n=5, r²=0.30), increasing at a rate of 2.4%/yr. The trend of DMA-1h Oₓ in Beijing in summertime was an increase of 2.2 ± 2.5 ppbv/yr, namely AAGR of 2.0%/yr (n=5, r²=0.20). According to this analysis, the reliability of increase of Oₓ is much lower than that of ozone. This could result from two main reasons. First, temporal variations of ozone and NO₂ are not the same, different diurnal patterns and opposite trends, the summation of O₃ and NO₂ to represent Oₓ certainly moderate or even efface significance of its trend. Second, Oₓ should include many other NO₂ species, like PAN, HONO and gas-phase HNO₃ (Liu et al., 2010b).

Long-term variations of NOₓ or NO₂ in Beijing still remain unclear, though it is reported that the mixing ratio of NOₓ in Beijing decreased to 20 ppbv in August of 2008 compared with 45 ppbv in 2006, and ratio of NOₓ/NOₓ also decreased from 1.7 to 1.3 (Chou et al., 2011). It is suggested that NOₓ will change non-linearly as to abatement of NOₓ emissions. Since there is good correlation between NOₓ and ozone in Beijing’s urban plume (Wang et al., 2006), variations of NOₓ could consequentially influence the trend of Oₓ, trends of which we have no idea due to lack of long-term measurements.

3.2 Variations of NOₓ

Daytime mixing ratios of NO₂ and NOₓ at the PKU site decreased significantly from 2006 to 2011, but it appeared a slight increase since 2009 in the post-Olympics period. Owing to the special short-term control measures in August 2008 for the
Olympics (Wang et al., 2010a), the 2008 data were excluded from the linear regression to derive the NO\textsubscript{x} trend. The descending slope of NO\textsubscript{x} levels was 1.4±0.4 ppbv/yr (-4%/yr, n=5, r\textsuperscript{2}=0.76\textsuperscript{*}), whereas NO\textsubscript{2} decreased by 1.1±0.3 ppbv/yr (-4%/yr, n=5, r\textsuperscript{2}=0.79\textsuperscript{*}) and NO contributed the rest of the decrease (Figure 4). The ratios of daytime average NO\textsubscript{2}/NO in Beijing were between 4-5 except that in 2008 (ratio of [NO\textsubscript{2}]/[NO] = 8). NO\textsubscript{2} levels dominated the mixing ratio of NO\textsubscript{x}. Trend in ratios of [NO\textsubscript{2}]/[NO] was calculated by 0-1%/yr, but it is not significant due to indistinct trend of NO. The decreasing rate of 24-h NO\textsubscript{2} concentrations was estimated to be 2-3%/yr referred to all available data (from 1997 to 2011) of Annals of the Beijing Municipal Environmental Protection Bureau (Figure 5). A study on long-term variations in NO\textsubscript{x} in Beijing indicated that the turning point of NO\textsubscript{x} variations occurred around 1999 (Zhang et al., 2011). However, NO\textsubscript{x} concentrations have rebounded since 2008 and hence decreasing rate is not as large as it was between 2002 and 2006 (approximately -8%/yr) (Tang et al., 2009).

We used satellite data to verify the trends of NO\textsubscript{x} obtained from ground-based measurements. The collected vertical column density (VCD) of tropospheric NO\textsubscript{2} data came from different instruments: GOME, SCIAMACHY and OMI, where defined domains of the NCP (North China Plain) were also not exactly the same. However, the VCDs of tropospheric NO\textsubscript{2} over this large region around Beijing in different references showed a comparable growth during 1996-2009 at 0.2-0.3 ×10\textsuperscript{15} molecules cm\textsuperscript{-2} yr\textsuperscript{-1} (Lin and McElroy, 2011;Richter et al., 2005;Wang et al., 2009b;Zhang et al.,...
This suggested that NO\textsubscript{x} emissions in the NCP increased steadily for a long time. But recent NO\textsubscript{x} emissions in Beijing changed as a U-shaped curve: effective reduction during 2005-2008 and rebound since 2009 (Figure 6). Ground-based NO\textsubscript{x} levels also showed similar U-shape variations, though NO\textsubscript{x} mixing ratios in 2010 was lower than that in 2006 while NO\textsubscript{2} VCDs in 2010 has already exceeded the value in 2006. This difference is not easy to conclude, for NO\textsubscript{x} mixing ratios reflected ground-level NO\textsubscript{x} but NO\textsubscript{2} VCDs include NO\textsubscript{2} integrated from ground to 150 mbar in the atmosphere. Air mass higher than the PBL (planetary boundary layer) will be more mixable. Retrievals of VCD from SCD will additionally introduce uncertainty of AMF. Furthermore, resolution of satellite data may be too rough to compare with a single ground-based observation site. But it is interesting and meaningful to reveal the differences of NO\textsubscript{2} VCD variations between Beijing and the larger NCP area, for there were robust industrial growth outside Beijing but within the NCP area. Actually, in the NCP area, there are two mega-cities (Beijing and Tianjin), and several cities with concentrated energy-intensive and high-polluting industries in Hebei province. Hebei province contributed 15\%, 24\%, 7\%, and 21\% of total production in China in terms of coke, steel, cement and glassware, ranking in 2\textsuperscript{nd}, 1\textsuperscript{st}, 3\textsuperscript{rd}, 1\textsuperscript{st}, respectively, among all provinces in 2011; the production of crude oil, steel, and ethene in Tianjin also listed in Top 5 among all provinces (http://www.stats.gov.cn/tjsj/ndsji/2012/indexch.htm).

But these industrial activities in Beijing came in very rearward position (the last three) except ethene production (8\textsuperscript{th} largest). Production of crude oil and steel doubled, while
production of ethene increased fivefold in Tianjin from 2005 to 2011; production in Hebei also doubled from 2005 to 2011 (http://www.stats.gov.cn/tjsj/ndsj/2006/indexch.htm). At the same time, production of cement in Beijing decreased by 20% and steel production almost decreased by 90% from 2005 to 2011. One research that combined bottom-up NO\textsubscript{x} inventory and NO\textsubscript{2} VCD retrievals demonstrated that emissions from increasing power plant has significantly changed NO\textsubscript{x} inventory: NO\textsubscript{x} emissions from power plants in Beijing decreased whereas emissions in Tianjin and Hebei increased between 2005 and 2007 (Wang et al., 2012a). Emission control measures (e.g. enhanced controls of vehicles, halting some chemical and power plants) for the 2008 Olympic Games were estimated to be effective in Beijing city (Wang et al., 2009a;Wang et al., 2010b;Wang et al., 2010c). Some long-term measures (e.g. move out of energy-intensive factories, updating the gasoline standards) before the Olympic Games in Beijing could be the reason for the decreasing of NO\textsubscript{x} even before 2008 in Beijing. However, increasing NO\textsubscript{x} around Beijing may enhance the regional ozone backgrounds in the NCP, because the ozone chemistry in suburban and rural areas are generally under NO\textsubscript{x}-limited regime and increasing NO\textsubscript{x} will lead to elevated ozone production (Zhao et al., 2009). Reduction of NO\textsubscript{x} in Beijing without controlling the increase of NO\textsubscript{x} around Beijing will aggravate ozone pollution in Beijing.

### 3.3 Variations of VOCs

The variations of VOC levels were summarized in Figure 7. Daytime VOC
mixing ratios decreased by 1.8±0.8 ppbv/yr (-7%/yr, n=6, r²=0.59). Speciated VOC trends were listed in the supplementary information. The levels of aromatics in 2007 were significantly higher than other years, which may be due to the mandatory painting of building exteriors in Beijing at that time. After excluding the data in 2007 and 2008 in the regression, daytime VOC levels were found to decrease by 1.6±0.6 ppbv/yr (-6%/yr, n=5, r²=0.70). Alkane compounds were the largest contributor to the decreasing trend with a rate of -1.0±0.4 ppbv/yr (-7%/yr, n=6, r²=0.72*, excluding the data in 2008). Aromatics decreased at a rate of 0.5±0.2 ppbv/yr (-6%/yr, n=5, r²=0.60, excluding the data in 2007 and 2008). Anthropogenic alkenes (C3–C5 alkenes except isoprene) decreased at a rate of 0.2±0.1 ppbv/yr (-7%/yr, n=6, r²=0.50). I-pentane and n-pentane, referred to tracers for gasoline evaporation, decreased significantly at a rate of 8-10%/yr (Figure 8 and SI), benzene and toluene, originated mainly from combustion by stationary and mobile sources and solvent usage (Cai et al., 2010; Liu et al., 2008a; Song et al., 2007), also decreased significantly at a rate of 5-7% (Figure 9 and SI). Average ratio of toluene/benzene in Beijing was around 1.5, which indicated that traffic contribution should be dominant, for ratio of toluene/benzene in tunnel in China is a little less than 2 (Barletta et al., 2005), but this ratio in stationary combustion is usually lower than 1 (Liu et al., 2008a) and this ratio in solvent is much higher than 1 (Yuan et al., 2010). Although the number of vehicles kept increasing in Beijing city, a recent study showed that vehicular emissions has begun to drop down since 2005 (Wu et al., 2011). All these evidences tend to suggest that emissions from
gasoline vehicles have been decreased in the past 7 years in Beijing. However, isoprene, as a very reactive species from biogenic emissions, showed no evident trend, its ambient concentration varied largely with temperature and light intensity (Figure 10). Because the $k_{\text{OH}}$ of isoprene is several or dozens of times higher than other VOCs in this dataset (Atkinson and Arey, 2003) and its abundance in the atmosphere is not negligible (0.4-1 ppb in average) in total mixing ratios, variations of isoprene could introduce considerable variability into the total VOC reactivity. The contribution to VOC reactivity from alkenes ranged between 56 and 76%. The overall trend of the total OH loss rate due to VOCs was $-0.48\pm0.34$ s\(^{-1}\)/yr (-5%/yr, n=5, $r^2=0.41$, excluding the data in 2007 and 2008), which was lower than the rate of decrease in VOC mixing ratios. This estimation of VOC reactivity was comparable with a modeling study in Beijing (Lu et al., 2010).

Previous research on VOC measurements in Beijing showed that the peak value of the total VOC (in term of ppbC) levels occurred in 2003 (Wang et al., 2012c). Considering that, we infer that VOC levels in summer months may have decreased since then, although the driving force for such a change needs further investigation.

3.4 Changes in total oxidant production

The ozone variations due to NO-NO\(_2\)-O\(_3\) reaction cycling (including the effects of NO titration) could be investigated through the perspective of pseudo steady state ozone concentration ($[O_3]_{\text{pss}}$) if we firstly didn’t consider the contribution of VOCs to propagate radical reaction and its impacts on this cycling. It is expressed as:
\[
\left[ O_3 \right]_{\text{pax}} = j(\text{NO}_2)[\text{NO}_2]/(k_1[\text{NO}])
\]

In which, \([\text{NO}]\) and \([\text{NO}_2]\) represent NO and NO\(_2\) mixing ratios, respectively, \(j(\text{NO}_2)\) is the photolysis rate of NO\(_2\), and \(k_1\) is the rate constant of O\(_3\) with NO. The ozone trend due to reaction cycling of NO-NO\(_2\)-O\(_3\) can be affected by two terms:

- \([\text{NO}_2]/[\text{NO}]\) ratio and \(j(\text{NO}_2)\). NO\(_2\) decreased by 4\% per year and NO decreased by 3-4\% per year (NO decreased by 0.2 ppbv/yr and average NO in the daytime is 5-6 ppbv). It results a constant or slightly decrease of \([\text{NO}_2]/[\text{NO}]\) ratio (0-1\%/yr). The changes of \(j(\text{NO}_2)\) are more uncertain. As discussed in the first paragraph of Section 3, previous studies found that both sunshine hours and visibility in the NCP areas have been decreasing in the past decades (Yang et al., 2009; Zhao et al., 2011). Decreasing visibility will reduce light intensity which directly decreased the photolysis rate of NO\(_2\) at the ground (Ammar et al., 2010), but if this decreasing visibility were resulted from increasing hygroscopic aerosols, the photolysis rate coefficient \(j(\text{NO}_2)\) for the upper atmosphere will increase (Madronich, 1987; Tao and Zhao, 2013). Thus, \(j(\text{NO}_2)\) in the lower troposphere supposed to be decreasing or remain stable in the period of this study. Combined the trends of \([\text{NO}_2]/[\text{NO}]\) ratio and \(j(\text{NO}_2)\) together, ground-level O\(_3\) should be slightly decreasing or remain unchanged due to the reaction cycling of NO-NO\(_2\)-O\(_3\). However, net effect on variations of \(j(\text{NO}_2)\) from decreasing visibility remains to check in case of sufficient data available in the future.

The increasing in regional background might have larger contribution, for at least from the background of the North Hemisphere, there is an annual growth of ozone at
0.2-0.3 ppbv/yr (Parrish et al., 2012). We did not have long-term measurements for the trend of regional ozone background in China, but others (Meng et al., 2009) preformed measurements of trace gaseous pollutants at the Shangdianzi site from 2003-2006, a WMO Global Atmosphere Watch (GAW) background station in Northern China, showing that the ozone increased at rate of 1.0 ppbv/yr, and the measurements at a remote site in Southern China showed an increase of ozone at 0.58 ppbv/yr from 1994-2007 (Wang et al., 2009b). Based on these results, we assumed that regional ozone background in the North China Plain increased at a fixed rate between 0.58-1.0 ppbv/yr. Hence, the change of regional background was estimated to contribute 22-38% of our measured increase of ozone (2.6 ppbv/yr) in Beijing.

Besides these two drivers, we surmised that such an increase was mainly due to ‘local’ photochemistry including emissions of ozone precursors from downtown, suburban, and surrounding areas of Beijing.

A simplified method to calculate P(O\textsubscript{x}) was used to better understand the variations in ozone concentrations and its precursors in cities in Canada, U.S., and Mexico (Geddes et al., 2009; Farmer et al., 2011; LaFranchi et al., 2011). We adopted this model to explore the variations in \textit{O\textsubscript{x}} with NO\textsubscript{x} and VOC reactivity. The inputs of the model were localized by using directly measured data and parameters from previous modeling results for Beijing city: observed NO\textsubscript{2}, NO, and VOCs were used in equation (1). From equation (1), P(HO\textsubscript{x}), [NO\textsubscript{2}]/k\textsubscript{1}[VOC], [NO], and the branch reaction yield of alkyl nitrates, \alpha, are the key factors for computing P(O\textsubscript{x}). P(HO\textsubscript{x}) is
mainly dependent on HONO, OVOCs, and ozone photolysis, which was assumed to
be 6.6 ppbv/hr under average conditions and 14.6 ppbv/hr as a peak value at noon
based on CAREBeijing-2007 data (Liu et al., 2012). The value of $\alpha$ was set as 0.04,
which is close to our estimation for Beijing (Wang et al., 2013). Other parameters in

\[
\begin{align*}
\alpha & = 0.04, \\
k_1 & = 0.29 \text{ ppbv}^{-1}\text{s}^{-1}, \\
k_2 & = 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}, \\
k_3 & = 1.1 \times 10^{-11} \text{ cm}^3\text{s}^{-1}, \\
k_4 & = 6.8 \times 10^{-14} \text{ cm}^3\text{s}^{-1}, \\
k_5 & = 2.74 \times 10^{-12} \text{ cm}^3\text{s}^{-1}, \text{ and } \\
k_6 & = 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}.
\end{align*}
\]

We plotted $P(O_x)$ with NOx concentrations and VOC reactivity; like many other
urban sites, the PKU site fell within a VOC-limited regime (red box in Figure 11) in
which decreasing NOx mixing ratios or increasing VOC reactivity can enhance the
production of ambient oxidants. The results of the model were compared with a box
model study (Liu et al., 2012). The average $P(O_x)$ in 2007 from the present calculation
was 18.3 ppbv/hr, about 60% of the estimated $P(O_x)$ obtained by the box model.
Considering that VOC reactivity from speciated hydrocarbons used in our calculation
was around half of VOC reactivity from total VOC estimated by Lu’s study (Lu et al.,
2010), the $P(O_x)$ derived by two approaches agreed well. The Average [OH]
concentration in 2007 was estimated to be $5.3 \times 10^6$ molecules/cm$^3$, also close to
daytime average value of [OH] at $4.8 \times 10^6$ molecules/cm$^3$ given by the box model
(Liu et al., 2012).

We used summertime NOx and VOC data to calculate $P(O_x)$ from 2001 to 2011.
NOx and VOC data between 2006 and 2011 came from this study, and NOx between
2001 and 2006 from a long-term measurement of ozone and NO\textsubscript{x} between 2001 and 2006 (Tang et al., 2009), VOC data between 2001 and 2006 from a long-term measurement of VOCs in term of ppbC between 2000 and 2007 (Wang et al., 2012c). We assumed that composition of VOCs didn’t change significantly between 2001 and 2006, and transformed VOCs in term of ppbC into OH loss rate of VOCs based on our speciated measurements of VOC in 2005-2006. The total oxidant production variations between 2001 and 2006 (red line) and 2006 and 2011 (blue line) were presented in Figure 11. Modeling results indicated that P(O\textsubscript{x}) was increasing rapidly between 2001 and 2006 while a very slight decrease in P(O\textsubscript{x}) was observed in most recent five years. According to this calculation, the major driving force for the P(O\textsubscript{x}) was the change in [NO\textsubscript{2}]/k\textsubscript{1}[VOC]. Between 2001 and 2006, VOC levels increased while NO\textsubscript{2} levels dropped; therefore the ratio of [NO\textsubscript{2}]/k\textsubscript{1}[VOC] dropped significantly and the consequently the P(O\textsubscript{x}) increased rapidly. VOCs and NO\textsubscript{x} both decreased between 2006 and 2011 and the decrease in VOC reactivity (-5%/yr) was slightly larger than the decrease in NO\textsubscript{x} (-4%/yr), leading to tiny increase in the ratio of [NO\textsubscript{2}]/k\textsubscript{1}[VOC], and, hence, a slight decrease in P(O\textsubscript{x}). This modeling result agrees with previous measurements but disagrees with recent observations. We admit that this quantitative trend of P(O\textsubscript{x}) has large uncertainty due to inter-annual variability, especially in 2003 and 2007 when higher VOC values were obtained.

The disagreement of P(O\textsubscript{x}) calculation and observation may be due to the limitation of P(O\textsubscript{x}) calculation. One reason is that regional ozone background values
are obtained from literatures and we assume a constant changing rate for the past
decade. The other reason is the calculations of OH reactivity may omit some
important species, such as CO and OVOCs. CO and OVOCs can both react with the
OH radical so that the calculated P(Ox) will be higher if the OH reactivity of CO and
OVOCs are included. From measurement, the CO concentrations decreased by about
50% between 2001 and 2011 (Figure 5), about 5%/yr, close to the rate of decrease for
VOCs, whereas satellite observations show 4%/yr (even higher in summer) increase
in formaldehyde in Beijing since 1997 (De Smedt et al., 2010; Zhang et al., 2012b).
The increase in formaldehyde may suggest similar increase of other carbonyls like
acetaldehyde. Carbonyls’ contribution to O₃ formation in summer at PKU site was
estimated by 22-38% (Wang et al., 2013). Increasing OVOCs will promote the P(HOₓ)
directly and then enhance P(Ox). Hence, variations of OVOCs need to be further
investigated for a better understanding of O₃ trends.

4. **Summary**

We conducted a 7-year observation on ground-level ozone levels and its
precursors simultaneously in summertime at PKU site in Beijing. Our measurements
showed that daytime ozone in summertime were increasing at rate of 2.6 ± 0.9
ppbv/yr, about 5%/yr. The daily maximum 1-h averages of ozone increased at rate of
4%/yr. However, the major precursors of ozone formation, NOₓ and VOCs, showed
decreasing trends over the same period. NOₓ mixing ratios decreased at the rate of
4%/yr significantly and the reactivity of VOCs decreased at the rate of 5%/yr with
larger uncertainties.

It is important to know for ground-level ozone control measures that ambient levels of both ozone precursors, NOx and VOCs, showed a declining trend in Beijing, while ozone levels as well as total oxidants (O₃+NO₂) kept on increasing. The computation of total oxidant production rate indicated that the trends of ambient oxidants levels largely depended on the ratio of VOCs/NOx (Pollack et al., 2013), the faster reduction of VOC reactivity would be very effective for decreasing total oxidants (Figure 11). However, the central government of China has planned to perform enforced mandatory abatement of NOx during the 12th 5-year-plan period (2011–2015). Due to the complexity of VOCs sources, especially the difficulty to cut specifically the VOC reactivity, China is lacking a rational strategy of VOCs emissions abatement. If this remains the case, it would mean a continuous rise of production of total oxidants, and hence increasing in ozone concentrations. In order to reduce ground-level ozone, we suggest stricter control on VOCs, especially reactive VOC species. Furthermore, regional increase of NO₂ monitored by satellites over the NCP emphasizes that Beijing needs deeper cooperation with adjacent provinces to control ozone pollution together. If there is no significant progress on NOx emission controls on industrial sources in Hebei and Tianjin, the adverse impacts from transportation to Beijing may be enlarged and counteract the efforts made by Beijing.

This study presents trends of ozone and its precursors from 2005 to 2011 in August. However, some important aspects of research topics, such as contribution of
regional transportation to ozone trend and driving forces of this trend, cannot be
explicitly determined. It can be accomplished by using measurement at both
rural/remote and urban sites, which is lack at this moment. Pollack et al. revealed that
ozone production efficiency in Los Angeles area didn’t change significantly during
the past 50 years but oxidation of NOx into PAN or HNO3 enhanced (Pollack et al.,
2013). Hence, the temporal trends of other secondary oxidation products, e.g. OVOCs,
HNO3 and PAN are also helpful to understand the evolution of local photochemistry
in Beijing. We also note that the historical measurements at PKU site are not
completed. There are no direct measurements of HOx radicals and OH reactivity for a
long time. We are extending this routine measurement and adding measurement of
OH reactivity, which will help to constrain total oxidation capacity in the atmosphere.

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Table 1 Meteorological conditions in August at PKU between 2005 and 2011

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<th>Year</th>
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<th>Pressure, hPa</th>
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Figures

Figure 1 (Upper) Variations in daytime averages (blue triangles) and daily maximum averages (red pentagons) of total oxidants ($O_x$); (Lower) Variations in daytime averages (blue dots) and daily maximum averages (red squares) of ozone ($O_3$) in Beijing, August between 2005 and 2011.
Figure 2 Diurnal variations of $O_x$ (upper) and $O_3$ (lower) in Beijing, August between 2005 and 2011

Figure 3 Logarithmic plots of probability vs. measurement values in terms of ambient $O_3$ (left) and $O_x$ (right) in 1-h daily maximum averages (red) and 12-h daytime averages (blue), respectively, in Beijing, August between 2005 and 2011
Figure 4 Variations in the daytime averages of NOx (black dots), NO₂ (blue dots), and NO (brown dots) in Beijing, August between 2006 and 2011.

Figure 5 Variations of 24-h averages of some primary pollutants (PM₁₀, NO₂, SO₂, and CO) reported by the Beijing Municipal Bureau of Environment Protection between 1998 and 2011.
Figure 6 Variations of VCDs of tropospheric NO₂ over the North China Plain (NCP) including Beijing, compared with ground-level NO₂ mixing ratio in Beijing.

Figure 7 Variations in the daytime VOC averages (black dots) and the corresponding OH loss rates (green squares) in Beijing, August between 2005 and 2011, showing the calculated contribution to OH loss rates from alkanes (blue bars), aromatics (brown bars), and alkenes (red bars).
Figure 8 Variations in the daytime averages of n-pentane (red dots) and i-pentane (blue squares) mixing ratios in Beijing, August between 2005 and 2011.

Figure 9 Variations in the daytime averages of benzene (red dots) and toluene (blue squares) mixing ratios in Beijing, August between 2005 and 2011.
Figure 10 Variations in the daytime averages of isoprene concentrations (green dots) and 90 percentile temperature (red squares) in Beijing, August between 2005 and 2011.

Figure 11 (Left) Contour plot of instantaneous total oxidant production as a function of VOC reactivity and NOx concentrations. Contour lines represent changes in ozone production of 5 ppbv/hr. The red box represents recent conditions in Beijing; (Right) Modeling the evolution of total oxidant production in summer between 2001 and 2011. The red line represents temporal direction between 2001 and 2006, and the blue line represents temporal direction between 2006 and 2011.