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Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011

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Abstract

Increased levels of ground-level ozone (O_3), reflecting the oxidative capacity of the atmosphere, are of increasing concern. High levels of total oxidants ($O_x = O_3 + NO_2$) have been persistently observed as a feature of Beijing's air pollution. Beijing is a typical global 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_3 with simultaneous changes in NO_x and volatile organic compounds (VOCs) between 2005 and 2011 were analyzed. Both NO_x and anthropogenic VOCs in Beijing decreased over the study period, 1.4 ppbv yr^{-1} and 1.6 ppbv yr^{-1} respectively, the VOCs reactivity, in term of OH loss rate showed an indistinct statistical trend due to the large contribution from naturally emitted isoprene. Meanwhile, the daytime average O_3 concentrations increased significantly at an annual rate 2.6 ppbv yr^{-1}, around 5 % yr^{-1} between 2005 and 2011. Considering the influence of NO titration effect and the increasing in regional background in the North China Plain (NCP), the main reason for such an increase in oxidants was 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, $P(O_x)$ increased rapidly due to increased VOC levels and decreasing of NO_2, while from 2006 to2011, $P(O_x)$ remained high though, decreased slightly as a consequence of the decrease in both VOC reactivity (5 % yr^{-1}) and NO_x (4 % yr^{-1}). Measurements have shown that the air pollution control efforts of Beijing city were effective in cutting ozone precursors, but even led to higher ground-level ozone. Therefore, putting ozone as the target for air quality, a faster reduction of VOCs, especially the reactive VOCs, will be needed to go together with NO_x emission control programs.

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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 ozone concentration > 93.3 ppbv) between 2001 and 2005 (Duan et al., 2008). The highest daily maximum 1 h (DMA-1 h) ozone concentration in 1997 was 162 ppbv (Duan et al., 2008), but reached 186 ppbv in 2008, the year of Olympic Games (T. Wang et al., 2010). Given that ground-level ozone levels were already high, the trend of ozone in Beijing has been of increasing concern. Unlike urban areas in the US where ozone concentrations have been declining (Lefohn et al., 2010), limited studies conducted in China have shown that ozone levels in both regional background and urban areas were increasing (Meng et al., 2009; T. Wang et al., 2009; Xu et al., 2008). 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 O_3 concentrations increased by 1.1 ppbv yr^{-1} in summer months (July–September) between 2001 and 2006 (Tang et al., 2009). Recently ozonesonde measurements proved that ozone in the lower troposphere (0–3 km) over Beijing during summer months increased at the rate of 3 % yr^{-1} between 2002 and 2010 (Y. Wang et al., 2012b).

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 $O_3 + NO_2$ increased by 0.69 ppbv yr^{-1} from 1994 to 2007 (T. Wang et al., 2009). The total oxidant levels in Taipei remained constant, but the maximum ozone levels increased by 0.90 ppbv yr^{-1} from 1994 to 2003 (Chou et al., 2006). The previous studies on urban/regional ozone pollution in China mainly focused on pollution episodes (Duan et al., 2008), while the understanding of factors driving long-term ozone trends remain undetermined due to the lack of simultaneous measurements of ozone and its precursors (NO_x, and VOCs)

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(Tang et al., 2009; T. Wang et al., 2009), especially lacking is speciated VOCs data (Chou et al., 2006; J. Zhang et al., 2011).

To minimize potential increasing levels of ground-level ozone, great efforts have been made to reduce emissions of ozone precursors: NO_x and volatile organic compounds (VOCs). Emissions of NO_x and VOCs in Beijing have fluctuated due to both rapid economic development and stringent air quality control measures. The total number of the vehicles in Beijing reached almost 5.2 million at the end of 2012 with an annual growth rate of 12 % yr^{-1} in the last decade (http://www.bjjtgl.gov.cn). Vehicle emissions are one of the most important sources of ozone precursors in Beijing (Song et al., 2007). Furthermore, energy consumption increased on average by 6.8 % yr^{-1} from 1995 to 2010 (http://www.bjstats.gov.cn), which is a strong driving force for larger NO_x and VOCs emissions. Beijing municipal government has been implementing a series of the Municipal Clean Air Action Plan since 1998 (http://www.bjepb.gov.cn). Together with the abatement of stationary combustion sources, vehicular emission controls were also conducted, including upgrading the quality of gasoline and diesel, putting limits on on-road vehicle fleet and eliminating heavy-polluting yellow-labeled vehicles (S. X. Wang et al., 2010). 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.

Aiming at identifying major factors for the trends of ground-level ozone, this study investigated the variations of ground-level O_3 in summer in Beijing and its relationship with changes of its precursors for 7 yr. Using ground-based measurements in August (between 2005 and 2011) at one urban site in Beijing, we obtained a dataset of O_3 levels in August with simultaneous measurements of NO_x and speciated VOCs. The temporal and chemical characteristics of O_3, NO_x 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.

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2 Data and methodology

2.1 Ozone and NO_x 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 a.g.l.) on campus of Peking University (PKU). The site is near the 4th Ring Road with high density of traffic. At this site, ozone and NO_x ($NO_x = NO + NO_2$) were measured simultaneously. Ozone was measured by ultraviolet spectrophotometry using an EC9810 ozone analyzer (ECOTECH, Inc., Knoxfield, Australia). Ambient NO and NO_2 was measured by gas-phase chemiluminescence using an ECOTECH EC9841 NO_x analyzer with molybdenum oxide catalysts. This prevalent type of NO_x measurement technique is known (Dunlea et al., 2007) to have interferences from non-NO_x reactive nitrogen species (e.g. NO_3, N_2O_5, HNO_3, $RONO_2$, PAN). Therefore the total oxidant O_x (the sum of the observed O_3 and NO_2) determined in this study would mean $O_x = O_3 + NO_2 + NO_3 + 2N_2O_5 + HNO_3 + RONO_2 + PAN$, which in fact can be better way to describe the photochemical ozone production potentials. For all the gas pollutant measurements, automatic zero and span checks were conducted daily, and multi-point calibrations were performed weekly.

For the changing of NO_x in Beijing, we use the satellite vertical column density (VCD) data of tropospheric NO_2 (integrated from ground to 150 mbar) over Beijing from OMI instrument to make an inter-comparison with ground-based NO_x measurements. 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). 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, Beijing urban area (about 3000 km^2) is very small, the standard product of Level 2 (Version 1.1.0.2, and Collection 3) was chosen for reprocessing. The data were excluded when cloud amount that day was above 30 %. The spatial resolution of Level 2 products is 13 km × 24 km at nadir. Daily averages come

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from the mean of VCDs in all effective pixels within the domain. Other VCD data of tropospheric NO_2 over the North China Plain or Beijing were collected from literature, all these data were monthly averages in August.

2.2 VOCs datasets

Measurements of VOCs between 2005 and 2011 were performed by on-line techniques 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 USA, 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 system developed by Earth System Research Lab (ESRL), NOAA (Goldan et al., 2004). C2–C5 alkanes, C2–C4 alkenes, and acetylene are separated on an Al_2O_3/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 PLOT column was used for separating C3–C6 compounds, with a DB-1 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. A PLOT column connected to an FID is used for analyzing C2–C4 compounds, and the DB-1 column connected to a MS detector 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 the on-line GC-FID/PID system of PKU (Syntech Spectra GC955 series 600/800 VOC analyzer). One for C3–C5 VOCs equips duel detectors (Photo Ionization Detector (PID) and FID) with a PLOT column and a pre-concentrator at 5 °C. The other one targets C6–C10 VOCs with 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

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and RSD of most species are 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 pre-concentrator by using adsorbent-free electrical cryogenic technology, this is a modification of previously commercial system which used adsorbent under liquid nitrogen.

Stringent inter-comparison experiments were conducted between the PKU laboratory and RCEC laboratory. The systematic bias in most species between different analysis systems was less than 20 % (Shao et al., 2009). An inter-comparison using gas chromatography-flame ionization detector/mass spectrometry (GC-FID/MS) was conducted for several samples at PKU laboratory. These different measurements indicated a strong linear relationship with a bias for most hourly measurements of less than 30 %.

The VOC species quantified differed among the different analytical systems and only the species that were commonly measured in all years were used in this work. The 18 typical abundant VOCs species (except for C2 compounds) were: alkanes (propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, and hexane), alkenes (propene, trans-2-butene, 1-butene, cis-2-butene, 1-pentene, trans-2-pentene, and isoprene), and 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, these species were selected to represent the measured hydrocarbons and used for discussion in this paper.

2.3 Meteorology and trend analysis method

We used a simple linear regression (the least-squares method) to investigate temporal trends. Daytime (07:00–19:00 LT) average, daily maximum 8 h average, and daily maximum 1 h averages were calculated from measurements and used for the evaluation of ozone trends. Daytime averages of NO_x and VOCs were also analyzed. The null hypothesis was 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

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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. Meteorological parameters, including wind speed (WS), wind direction (WD), atmospheric pressure (P), air temperature (T), and relative humidity (RH), during the August monitoring periods 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

The atmospheric O_3 concentration can be influenced by ozone production, ozone photolysis, chemical loss, dry deposition, and transportation. Field observations and modeling work have demonstrated that ozone episodes in Beijing were mainly due to local ozone production (Liu et al., 2012; Parrish et al., 2012). To investigate the role of variations in levels of ozone precursors in 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 concentrations. The represented photochemistry in the formula simulates the urban situation at noon, and total oxidant production $P(O_x)$ is computed according to following Eq. (1). The rate of HO_x production $P(HO_x)$ is mainly dependent on HONO, VOCs, 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:

$$P(O_x) = 2k_1[VOC]\cdot[OH]$$
$$= \frac{2k_1[VOC]\cdot 2P(HO_x)}{\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{(1-\alpha)}\right) + \sqrt{\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{1-\alpha}\right)^2 + \frac{8P(HO_x)(k_4+k_5+k_6)(k_1[VOC])^2}{((1-\alpha)k_{2a}[NO])^2}}}$$

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$$= \frac{4P(HO_x)}{\left(\frac{k_3[NO_2]}{k_1[VOC]} + \frac{\alpha}{1-\alpha}\right) + \sqrt{\left(\frac{k_3[NO_2]}{k_1[VOC]} + \frac{\alpha}{1-\alpha}\right)^2 + \frac{8P(HO_x)(k_4+k_5+k_6)}{((1-\alpha)k_{2a}[NO])^2}}} \quad (1)$$

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 ($\sum k_{1,i}[VOC_i]$). α 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 reaction constants of peroxy radicals collision 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 °C, and temperature in 2005 was lowest and that in 2007 was the highest. The average of wind speeds was less than 2 m s^{-1}, suggesting atmosphere was generally stable in August in Beijing. The 90th percentile relative humidity at PKU decreased significantly by around 1 % yr^{-1}. But precipitation in Beijing did not show decreasing trend over the same time period. Therefore, the meteorological parameters might play only a minor role in the ozone trends in Beijing. We 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 (07:00–19:00 LT, 12 h) averages and daily maximum 1 h averages (DMA-1 h) of ozone and O_x, respectively (Figs. 1 and 2). Daytime ozone in August between 2005 and 2011 ranged from 42 to 63 ppbv and the DMA-1 h ozone ranged from 71 to 103 ppbv. In August 2011, ozone

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concentrations 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 and the DMA-1 h O_x ranged from 91 to 123 ppbv. Ozone and O_x shared similar variations in these years, for ozone accounted for 70 % of O_x concentrations in 2006, increasing to more than 80 % in 2011. Recently modeling results revealed that ozone concentrations in the North China Plain including Beijing was the hot-spot in Northeast Asia areas (Nawahda et al., 2013).

Figure 3 shows the diurnal variations of ozone from 2005 to 2011. It was apparent that the averages of ozone concentrations between 2009 and 2011 were higher than that between 2005 and 2007. Also noteworthy was that the peak time for ozone levels delayed. The nocturnal ozone concentrations in 2008 which were much higher than other years, might be due to stringent control on NO_x.

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. The trend of daytime ozone in Beijing in summertime, derived from the monthly averages, was an increase of 2.6 ± 0.9 ppbv yr^{-1}, increasing at a rate of 5.3 % yr^{-1} ($n = 7$, $r^2 = 0.61$). The trend of the DMA-1 h ozone in Beijing in summertime, derived from the monthly averages, was an increase of 3.2 ± 2.0 ppbv yr^{-1}, increasing at a rate of 4.0 % yr^{-1} ($n = 7$, $r^2 = 0.34$). The regression of averages was more stable because inter-annual variability was usually sensitive to higher numbers. As to the trend of total oxidants (the daytime O_x), the data in five years were taken into account because NO_x data in 2005 were not available and the short-term controls on NO_x in 2008 distorting the O_x 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^{-1} ($n = 5$, $r^2 = 0.30$), increasing at a rate of 2.4 % yr^{-1}. The trend of DMA-1 h O_x in Beijing in summertime, derived from the monthly averages, was an increase of 2.2 ± 2.5 ppbv yr^{-1}, increasing at a rate of 2.0 % yr^{-1} ($n = 5$, $r^2 = 0.20$).

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3.2 Variations of NO_x

Daytime concentrations of NO_2 and NO_x at the PKU site decreased significantly from 2005 to 2011, but it had a slight increase since 2009 in the post-Olympics period. Owing to the special short-term control measures in August 2008 for the Olympics, the 2008 data were excluded from the linear regression to derive the NO_x trend. The descending slope of NO_x concentrations was $1.4 \pm 0.4\,\mathrm{ppbv\,yr^{-1}}$ ($-4\,\%\,\mathrm{yr^{-1}}$, $n = 5$, $r^2 = 0.76^*$), whereas NO_2 decreased by $1.1 \pm 0.3\,\mathrm{ppbv\,yr^{-1}}$ ($-4\,\%\,\mathrm{yr^{-1}}$, $n = 5$, $r^2 = 0.79^*$) and NO contributed the rest of the decrease (Fig. 4). The decreasing rate of 24 h NO_2 concentrations was estimated to be 2–3 $\%\,\mathrm{yr^{-1}}$ referring to all available data (from 1997 to 2011) of Annals of the Beijing Municipal Environmental Protection Bureau (Fig. 5). A study on long-term variations in NO_x in Beijing indicated that the turning point of NO_x variations occurred around 1999 (J. Zhang et al., 2011). However, NO_x concentrations have rebounded since 2008 and hence decreasing rate is not as large as it was between 2002 and 2006 (approximately $-8\,\%\,\mathrm{yr^{-1}}$) (Tang et al., 2009).

We used satellite data to verify the trends of NO_x obtained from ground based measurements. The collected VCD data came from different instruments: GOME, SCIAMACHY or OMI. The defined domains of North China Plain (NCP) were also not the same. However, the VCD of tropospheric NO_2 in this large region around Beijing in different literature references showed a comparable growth during 1996–2009 at 0.2–$0.3 \times 10^{15}\,\mathrm{molecules\,cm^{-2}\,yr^{-1}}$ (Lin and McElroy, 2011; Richter et al., 2005; T. Wang et al., 2009; X. Zhang et al., 2007). This suggested that NO_x emissions in North China increased steadily for a long time. But recent NO_x emissions in Beijing changed as a U-shaped curve: effective reduction during 2005–2008 and rebound since 2009 (Fig. 6). Previous studies have shown that emission control measures for the 2008 Olympic Games were quite effective in Beijing city (H. Wang et al., 2010; S. X. Wang et al., 2010). However, increasing power plant activity has increased NO_x emissions in surrounding provinces (S. Wang et al., 2012c). Increasing NO_x around Beijing may enhance the regional ozone backgrounds in the NCP, because the ozone chemistry in

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suburban and rural areas were generally under NO_x-limited regime and increasing NO_x led to elevated ozone production. Reduction of NO_x in Beijing without controlling the increase of NO_x around Beijing will aggravate ozone pollution in Beijing.

3.3 Variations of VOCs

The variations in VOC concentrations were summarized in Fig. 7. Daytime VOC concentrations decreased by 1.8 ± 0.8 ppbv yr^{-1} (-7 % yr^{-1}, $n = 6$, $r^2 = 0.59$). However, the concentrations 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 concentrations were found to decrease by 1.6 ± 0.6 ppbv yr^{-1} (-6 % yr^{-1}, $n = 5$, $r^2 = 0.70^*$). Alkane compounds were the largest contributor to the decreasing trend with a rate of decrease of 1.0 ± 0.4 ppbv yr^{-1} (-7 % yr^{-1}, $n = 6$, $r^2 = 0.72^*$, excluding the data in 2008). Aromatics decreased at a rate of 0.5 ± 0.2 ppbv yr^{-1} (-6 % yr^{-1}, $n = 5$, $r^2 = 0.60$, 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^{-1} (-7 % yr^{-1}, $n = 6$, $r^2 = 0.50$). Isopentane, as well as butenes, tracers for gasoline evaporation, decreased significantly (Fig. 8), benzene and toluene, originate from both combustion and solvent usage, also decreased (Fig. 9). 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), which should influence the levels of ambient VOCs and NO_x. However, isoprene, as a very reactive species from biogenic emissions, had no evident trend, its ambient concentration varied largely with temperature and light intensity (Fig. 10). Because the k_{OH} of isoprene is very large (Atkinson and Arey, 2003), variations in its concentration 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 ± 0.34 s^{-1} yr^{-1} (-5 % yr^{-1}, $n = 5$, $r^2 = 0.41$, excluding the data in 2007 and 2008), which was lower than the rate

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of decrease in VOC concentrations. This estimation of VOC reactivity was comparable with a modeling study in Beijing (Lu et al., 2010).

Previous research on VOC concentrations in Beijing showed that the peak value of the total VOC (ppbC) concentration occurred in 2003 (Wang et al., 2012a). Comparing with 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

Regarding the evident increase in ground-level ozone, around 2.6 ppbv yr^{-1} for daily average, the NO titration effect could have had only a minor contribution, as the NO levels decreased by 0.2 ppbv yr^{-1}. The increasing in regional background might have larger contribution, we did not have long term measurements for the trend of regional ozone background in China. 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, we derived from their work that the ozone increased at rate of 1.0 ppbv yr^{-1}, and the measurements at a remote site in Southern China showed an increase of ozone at 0.58 ppbv yr^{-1} from 1994–2007 (T. Wang et al., 2009). Using these numbers, we estimated that the change of regional background might contribute 22 % to 38 % to our measured increase of ozone. We surmised that such an increase was mainly due to local photochemistry.

A simplified method to calculate $P(O_x)$ was used to better understand the variations in ozone concentrations and its precursors in cities in Canada, US, and Mexico (Farmer et al., 2011; Geddes et al., 2009; LaFranchi et al., 2011). We adopted this model to explore the variations in O_x with NO_x and VOC reactivity. The inputs of the model were localized by using direct measurement data and parameters based on previous modeling results for Beijing city: observed NO_2, NO, and VOCs were used in Eq. (1). From Eq. (1), $P(HO_x)$, $[NO_2]/k_1[VOC]$, [NO], and the branch reaction yield of alkyl nitrates, α, are the key factors for computing $P(O_x)$. $P(HO_x)$ is mainly dependent on HONO, OVOCs, and ozone photolysis, which was assumed to be 6.6 ppbv h^{-1}

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under average conditions and 14.6 ppbv h^{-1} as a peak value at noon based on CAREBeijing-2007 data (Liu et al., 2012). The value of α was set as 0.04, which is close to our estimation for Beijing. Other parameters in Eq. (1) are the kinetic constants obtained from the literature (Atkinson and Arey, 2003; Farmer et al., 2011; Geddes et al., 2009): $k_1 = 0.29\,\text{ppbv}^{-1}\,\text{s}^{-1}$, $k_2 = 8\times10^{-12}\,\text{cm}^3\,\text{s}^{-1}$, $k_3 = 1.1\times10^{-11}\,\text{cm}^3\,\text{s}^{-1}$, $k_4 = 6.8\times10^{-14}\,\text{cm}^3\,\text{s}^{-1}$, $k_5 = 2.74\times10^{-12}\,\text{cm}^3\,\text{s}^{-1}$, and $k_6 = 8\times10^{-12}\,\text{cm}^3\,\text{s}^{-1}$.

We plotted $P(O_x)$ with NO_x concentrations and VOC reactivity; like many other urban sites, the PKU site fell within a VOC-limited regime (red box in Fig. 11) in which decreasing NO_x concentrations 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 h^{-1}, 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] concentrations in 2007 was estimated to be 5.3×10^6 molecules cm^{-3}, also close to daytime average value of [OH] at 4.8×10^6 molecules cm^{-3} given by the box model (Liu et al., 2012).

We used summertime NO_x and VOC data to calculate $P(O_x)$ from 2001 to 2011. The total oxidant production variations between 2001 and 2006 (red line) and 2006 and 2011 (blue line) were presented in Fig. 11. Modeling results indicated that $P(O_x)$ was increasing rapidly between 2001 and 2006 while a very slight decrease in $P(O_x)$ was observed in most recent five years. According to this calculation, the major driving force for the $P(O_x)$ was the change in $[NO_2]/k_1[\text{VOC}]$. Between 2001 and 2006, VOC levels increased while NO_2 levels dropped; therefore the ratio of $[NO_2]/k_1[\text{VOC}]$ dropped significantly and the consequently the $P(O_x)$ increased rapidly. VOCs and NO_x both decreased between 2006 and 2011 and the decrease in VOC reactivity (5 % yr^{-1}) was slightly larger than the decrease in NO_x (4 % yr^{-1}), leading to tiny increase in the ratio of $[NO_2]/k_1[\text{VOC}]$, and, hence, a slight decrease in $P(O_x)$. This modeling result agrees with previous measurements but disagrees with recent observations. We admit that

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this quantitative trend of $P(O_x)$ has large uncertainty due to inter-annual variability, especially in 2003 and 2007 when higher VOC values were obtained.

CO and OVOCs can both react with the OH radical so that the calculated $P(O_x)$ 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 (Fig. 5), close to the rate of decrease for VOC concentrations, whereas satellite observations show 4 % yr^{-1} (even higher in summer) increase in formaldehyde in Beijing since 1997 (De Smedt et al., 2010; Q. Zhang et al., 2012). The increase in formaldehyde may suggest similar increase of other carbonyls like acetaldehyde. Increasing OVOCs will promote the $P(HO_x)$ directly and then enhance $P(O_x)$. Hence, variations of OVOCs need to be further investigated for a better understanding of O_x trends.

4 Summary

We conducted a 7 yr observation on ozone concentrations 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^{-1}, about 5 % yr^{-1}. The daily maximum 1 h averages of ozone increased at rate of 4 % yr^{-1}. However, the major precursors of ozone formation, NO_x and VOCs, showed decreasing trends over the same period. NO_x concentrations decrease at the rate of 4 % yr^{-1} significantly and the reactivity of VOCs decreases at the rate of 5 % yr^{-1} with larger uncertainties.

It is important for the ground-level ozone control measures to know that the ambient concentrations of both ozone precursors, NO_x and VOCs, showed a declining trend in Beijing, while ozone levels as well as total oxidants ($O_3 + NO_2$) 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/NO_x, the faster reduction of VOCs reactivity would be very effective for decreasing total oxidants (Fig. 11). However, the central government of China has planned to perform enforced mandatory abatement of NO_x during the 12th 5 yr-plan period (2011–2015). Due to the complexity of VOCs

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sources, especially the difficulty to cut specifically the VOC reactivities, 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.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/1019/2014/acpd-14-1019-2014-supplement.pdf.

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

Year	Percentile	Temperature, °C	Pressure, hPa	RH, %	WS, $m s^{-1}$	WD, °
2005	10 %	21.1	996.1	52.0	0.8	33.0
	90 %	30.4	1010.0	91.0	3.1	254.0
2006	10 %	22.7	996.4	45.3	0.2	81.5
	90 %	32.8	1004.4	92.4	2.6	325.5
2007	10 %	22.9	992.6	–	0.0	110.0
	90 %	34.5	1004.9	–	2.8	360.0
2008	10 %	21.8	995.1	44.2	0.0	88.0
	90 %	33.1	1001.6	90.4	2.2	328.0
2009	10 %	22.4	995.3	37.7	0.0	49.1
	90 %	33.9	1005.9	90.0	2.7	355.0
2010	10 %	22.7	994.8	34.4	0.7	86.7
	90 %	32.3	1006.8	83.4	3.2	283.0
2011	10 %	22.8	994.9	48.1	0.3	113.9
	90 %	32.1	1005.7	82.8	2.4	318.8

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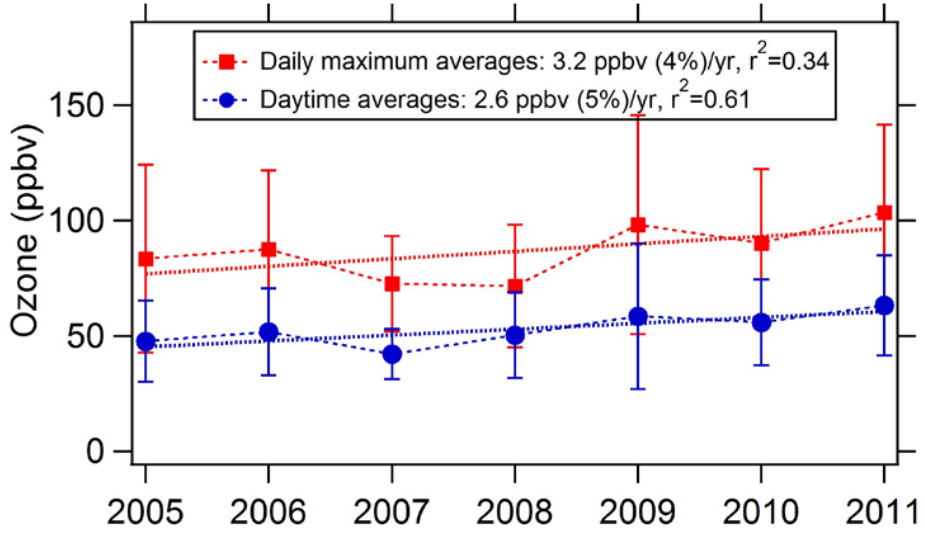

Fig. 1. Variations in daytime averages (blue dots) and daily maximum averages (red squares) of ozone in Beijing, August between 2005 and 2011.

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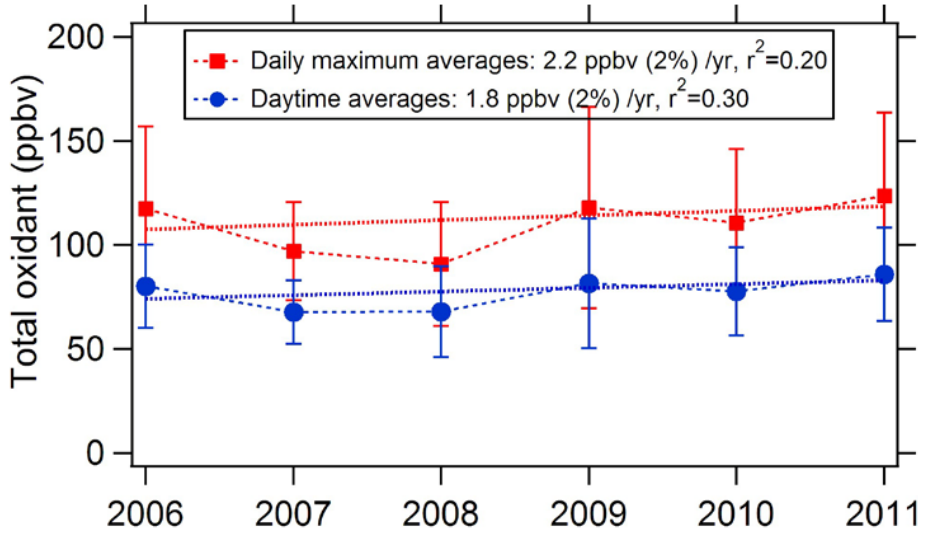

Fig. 2. Variations in daytime averages (blue dots) and daily maximum averages (red squares) of O_x in Beijing, August between 2006 and 2011.

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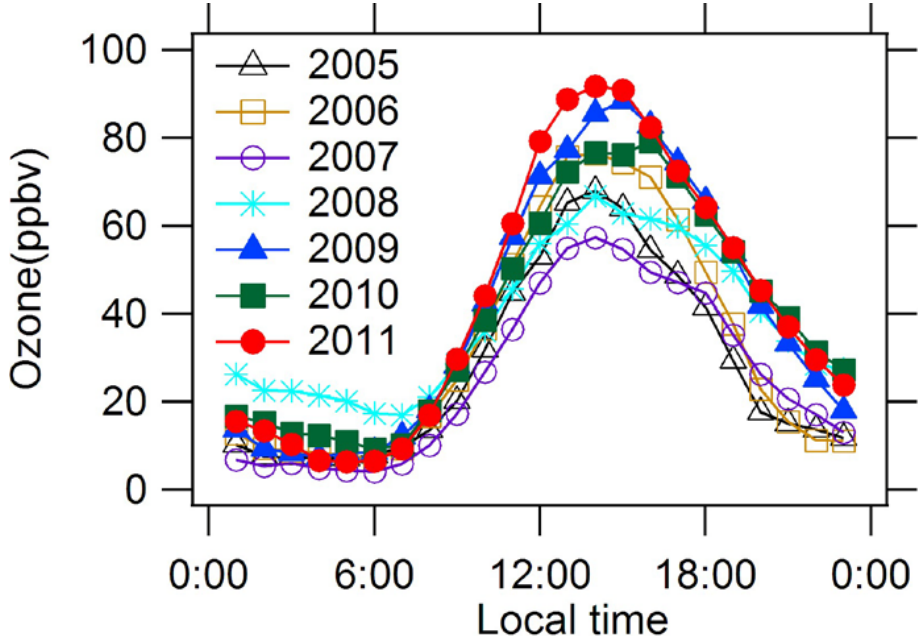

Fig. 3. Diurnal variations of O_3 in Beijing, August between 2005 and 2011.

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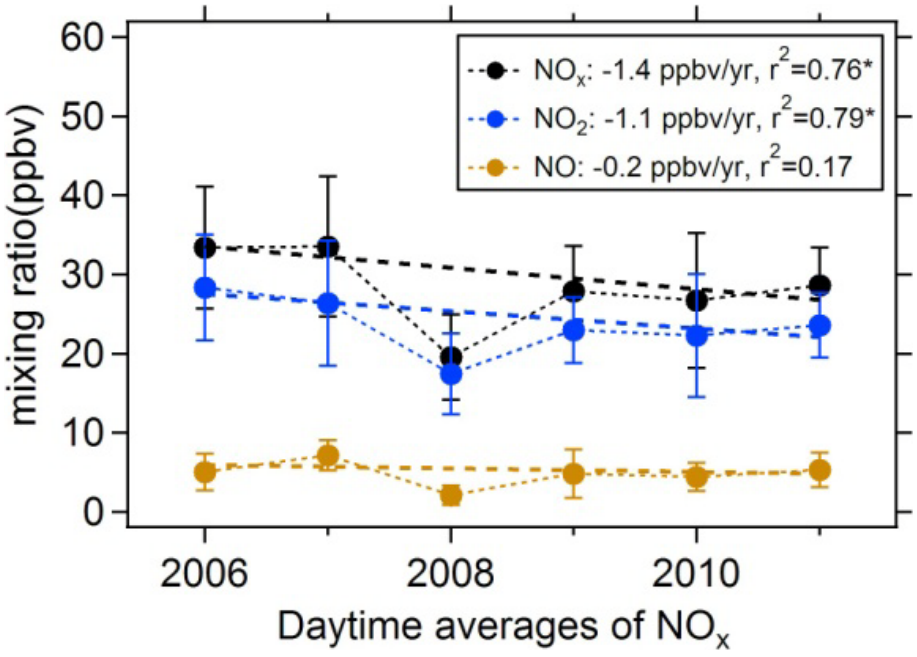

Fig. 4. Variations in the daytime averages of NO_x (black dots), NO_2 (blue dots), and NO (brown dots) in Beijing, August between 2006 and 2011.

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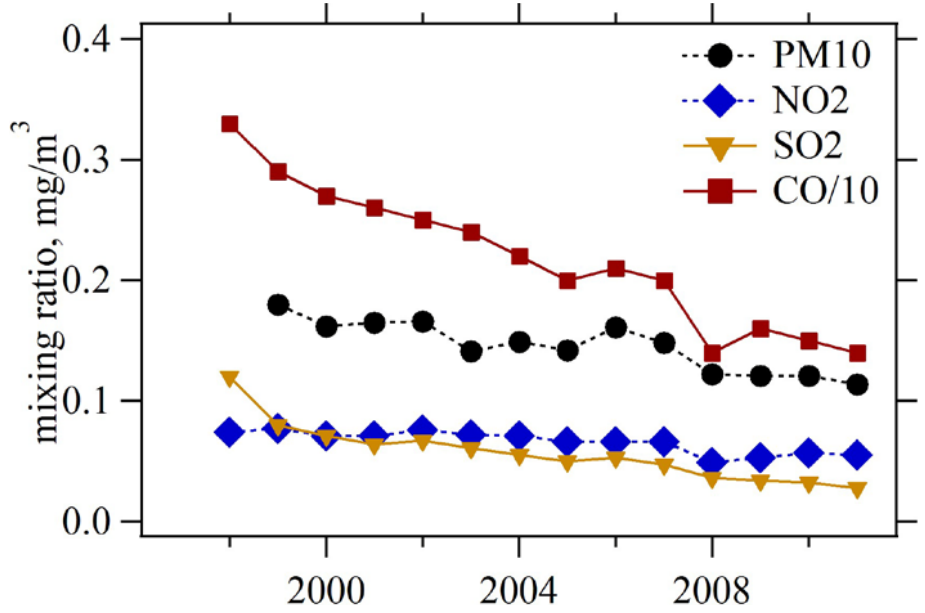

Fig. 5. Variations of 24 h averages of some primary pollutants (PM_{10}, NO_2, SO_2, and CO) reported by the Beijing Municipal Bureau of Environment Protection between 1998 and 2011.

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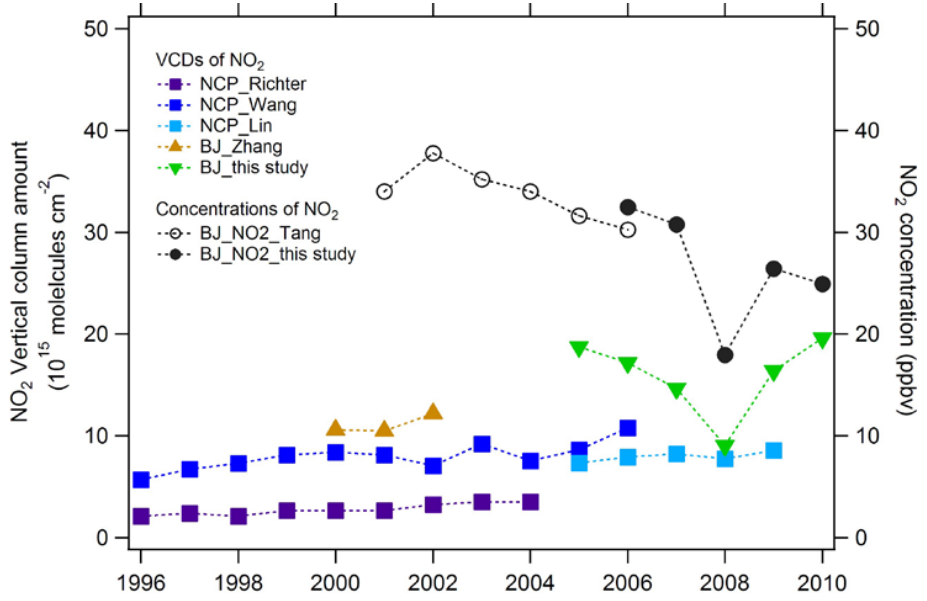

Fig. 6. Variations of VCDs of tropospheric NO_2 in the North China Plain (NCP) including Beijing.

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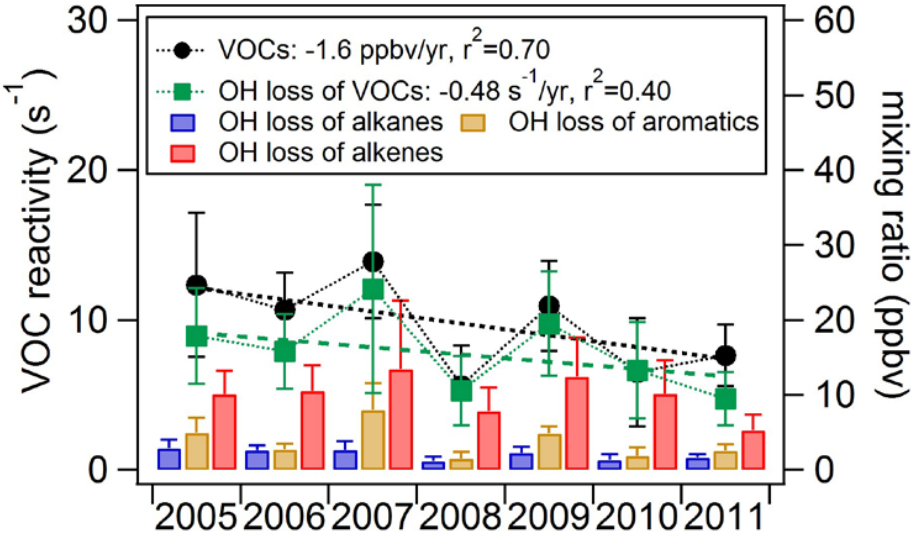

Fig. 7. Variations in the daytime averages of VOC concentrations (black dots) and the corresponding OH loss rates (green squares) in Beijing, August between 2005 and 2011, showing the calculated contribution to OH loss rates from alkanes (blue bars), aromatics (brown bars), and alkenes (red bars).

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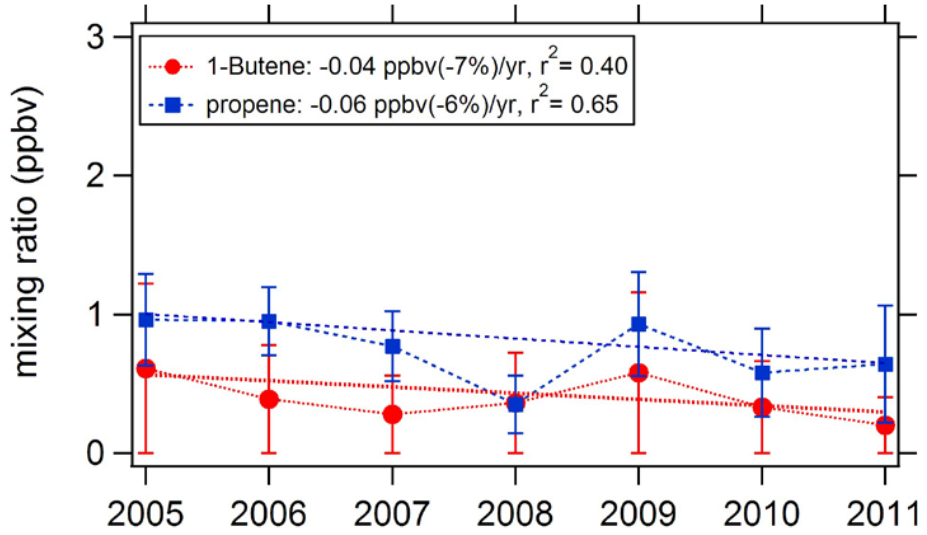

Fig. 8. Variations in the daytime averages of 1-butene (red dots) and propene (blue squares) concentrations in Beijing, August between 2005 and 2011.

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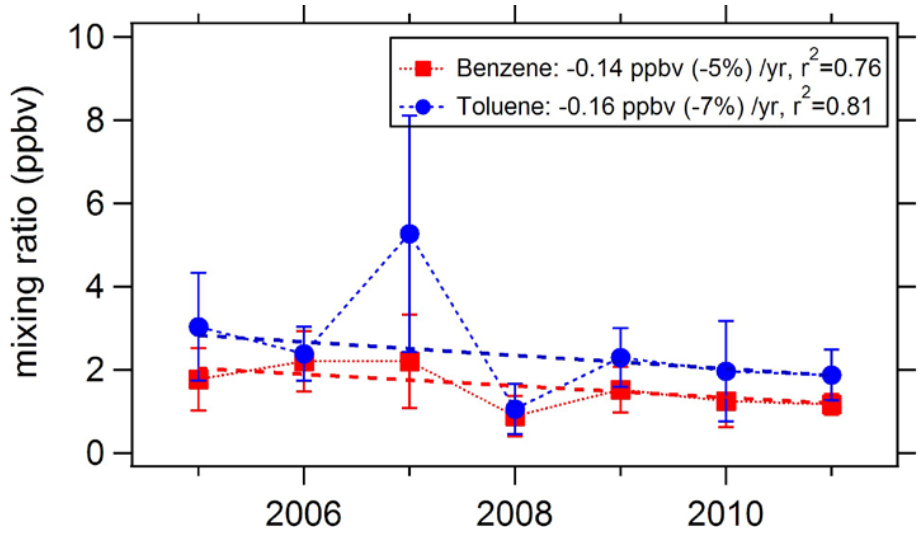

Fig. 9. Variations in the daytime averages of benzene (red squares) and toluene (blue dots) concentrations in Beijing, August between 2005 and 2011.

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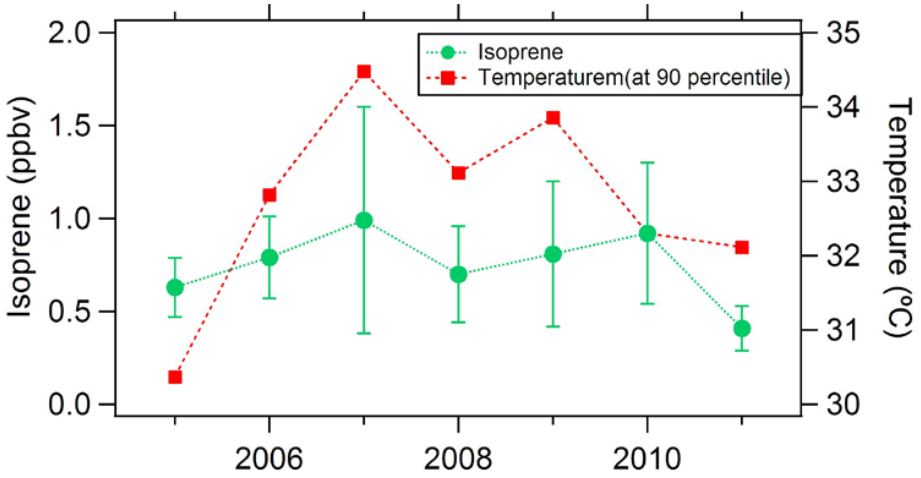

Fig. 10. Variations in the daytime averages of isoprene concentrations (green dots) and 90 percentile temperature (red squares) in Beijing, August between 2005 and 2011.

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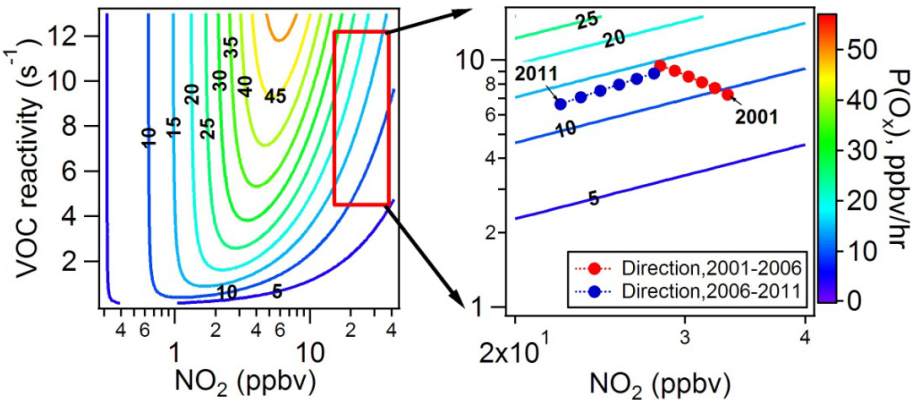

Fig. 11. (Left) contour plot of instantaneous total oxidant production as a function of VOC reactivity and NO_x concentrations. Contour lines represent changes in ozone production of 5 ppbv h^{-1}. The red box represents recent conditions in Beijing; (right) modeling the evolution of total oxidant production 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.

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