



# Ground ozone concentrations over Beijing from 2004 to 2015: Variation patterns, indicative precursors and effects of emission-reduction<sup>☆</sup>

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## ABSTRACT

Based on ozone observation data from urban stations and the Dingling (DL) background station, we investigated the trend of ozone concentrations in Beijing during 2004–2015. For urban stations, both  $O_3_{-1\text{ h}}$  and  $O_3_{-8\text{ h}}$  increased stably with a clear and significant linear pattern and the increase rate was notably higher during the period of May to Sep. Meanwhile, the variation of  $O_3_{-1\text{ h}}$  and  $O_3_{-8\text{ h}}$  for the DL station did not demonstrate a regular pattern. During this period, the differences between the diurnal peak of ozone concentrations at the DL background station and urban stations decreased significantly due to the rapid urbanization of Beijing. Furthermore, we examined simultaneous variations of ozone and its precursors during 2015 Grand Military Parade and 2014 APEC meeting and evaluated the performances of different emission-reduction measures during the two specific events. For 2015 Grand Military Parade, emission-reduction measures were implemented 14 days in advance, which led to a notable decrease of ozone concentrations during the Parade period. For 2014 APEC meeting, emission-reduction measures were not implemented in advance, which led to incomplete VOCs reduction and high VOCs/ $NO_x$  values, and thus a significant increase of ozone concentrations during the APEC period. The emission-reduction measures during APEC and PARADE periods both slowed down the accumulation and cut down the concentration peaks of ozone. We also analyzed simultaneous concentration variations of ozone and its precursors in long time-series. The results proved that compared with other precursors,  $NO_2/NO$  was an effective indicator for ozone concentration in Beijing, especially in urban areas. The findings from this research provide useful reference for better monitoring and managing ozone concentrations in Beijing and other cities through properly designed and implemented emission-reduction measures.

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## 1. Introduction

Ground-level ozone, one of the most important secondary air pollutants in the atmosphere, is generated through photochemical reactions between nitrogen oxides ( $NO_x$ ) and volatile organic

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compounds (VOCs) (Trainer et al., 2000; Sillman, 1999). High concentrations of ozone are serious threats to human health, ecosystems, and global climate (Fiore et al., 2009). According to the new “Ambient Air Quality Standard” (MEP, 2012), the level of daily maximum 8 h-averaged ozone concentration ( $O_3_{-8\text{ h}}$ ), and daily maximum 1 h ozone concentration ( $O_3_{-1\text{ h}}$ ) has a direct influence on the comprehensive air quality level. In this case, soaring ozone concentrations in China have attracted increasing attentions (Lin et al., 2008; Zhang et al., 2007, 2014; Ding et al., 2013; Wang et al., 2013).

A large body of studies has been conducted to understand variations of ozone and photochemical reactions between ozone and its precursors (Chan et al., 2003; Wang et al., 2012; Vingarzan, 2004). Most studies concerning Ozone were concentrated city clusters, such as the Pearl River delta (Li et al., 2011; Wei et al., 2012; Zhang et al., 2013), Yangtze River delta (Ding et al., 2013; Ran et al., 2009; Gao et al., 2017), and Beijing–Tianjin–Hebei (BTH) region (Tang et al., 2009; Shao et al., 2009; Lu et al., 2010). Compared with continuously decreasing ozone concentrations in urban sites in the US (Pollack et al., 2013), recent studies (Meng et al., 2009; Wang et al., 2008a,b,c) suggested that long-term ozone concentrations in China, especially in the BTH region, were rising notably due to stratosphere-to-troposphere transport of O<sub>3</sub> (Xu and Lin, 2011; Lin et al., 2008), decadal circulation shifts (Ding et al., 2013), and large amount of VOCs and NO<sub>x</sub> emissions (Ma et al., 2016).

As one of the most influential and heavily polluted cities in China, characteristics of PM<sub>2.5</sub> and its meteorological driving forces in Beijing have been massively studied (Chen et al., 2016, 2017; etc). Meanwhile, although a general upward trend of ozone concentrations in China has been revealed by previous studies (Ding et al., 2013; Wang et al., 2013; Zhang et al., 2014), long-term spatial and temporal variation patterns of ozone concentrations in Beijing were rarely discussed due to the lack of ozone observation data and other limitations (An, 2006; Chou et al., 2009; Yuan et al., 2009; Lu et al., 2010). On the other hand, with frequent pollution episodes in Beijing, the executive meeting of the State Council implemented “Control measures for air pollution in Beijing from 2012 to 2020” (<http://zhengwu.beijing.gov.cn/gzdt/gggs/t1225355.htm>). According to this plan, the total hours with non-attained ozone concentrations in Beijing should be reduced by 30% compared with that in 2010 and less than 200 h annually. To reduce the concentration of airborne pollutants, emergency measures for emission reduction have been implemented for several times during specific events (Cheng et al., 2017). However, previous emission-reduction measures mainly focused on the reduction of PM<sub>2.5</sub> concentrations, yet the effects of emission-reduction measures on the variation of ozone concentrations were limitedly investigated.

Targeting these gaps, this research aims to examine spatial and temporal variations of ozone concentrations in Beijing based on long-term observation data, and extract effective indicators for better monitoring and control ozone concentrations. In addition to the analysis of general ozone concentrations, we attempt to compare and evaluate the effects of emission reduction measures on ozone concentrations during two specific events (2015 Grand Military Parade and 2014 APEC meeting). With a better understanding of characteristics and influencing factors of ozone concentrations, this research may provide useful reference for proposing effective measures to reduce ozone concentrations in Beijing and other cities.

## 2. Materials and methods

### 2.1. Study sites

Beijing is located at 115.7°–117.4° E, 39.4°–41.6° N and the northwest edge of the North China Plain. As the capital and a heavily polluted city in China, Beijing has a more advanced air quality monitoring network than other cities in China (BJEPB, 2014). In 2001, an air quality monitoring network, including 35 stations (Fig. 1), was established by the Beijing Municipal Environmental Monitoring Center (BJMEMC, <http://zx.bjmemc.com.cn/>). These 35 stations are located in different parts of Beijing, so these stations may be further categorized into urban stations, suburban stations and background stations according to their locations. Twelve urban monitoring sites (XS, DS, GY, TT, WSXG, AT, NZG, WL,

GC, SY, CP, HR), located in central Beijing and one background station DL (116.22° E, 40.29° N, about 45 km northwest of Tiananmen square)<sup>1</sup> were selected for this study. The DL station is a background station. Meteorological data at the Guanxiangtai station (GXT, 54511, 116.46° E, 39.80° N) in Beijing were downloaded from the Department of Atmospheric Science, College of Engineering, University of Wyoming (<http://weather.uwyo.edu/upperair/sounding.html>). In this study, we retrieved long time-series NO<sub>2</sub> and HCHO VCDs (Vertical Column Densities) information from the OMI products in the GY site (116.33° E, 39.93° N), Beijing. With these emission data, we attempt to examine the correlation between different pollutants and PO<sub>3</sub> (ozone production rate) annually and during specific periods.

### 2.2. Monitoring instruments

Ozone are monitored using the 49C ozone analyzer instruments (Thermo Fisher Corporation, USA). An ozone calibrator (49IPS) traceable to the Standard Reference Photometer maintained by the WMO World Calibration Center is used to calibrate the ozone analyzers. The ozone monitoring instrument at each station has a zero cross calibration every three days, precision audit every three months, and an accuracy check every six months to ensure the accuracy of ozone monitoring. Thermo Fisher 42C NO–NO<sub>2</sub>–NO<sub>x</sub> analyzer is used to monitor NO and NO<sub>2</sub> concentrations. All operational procedures are conducted strictly following “The Specification of Environmental Air Quality Automatic Monitoring Technology” (HJ/T193–2005, [http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/jcgfffbz/200601/t20060101\\_71675.htm](http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/jcgfffbz/200601/t20060101_71675.htm)), and all equipment are calibrated and maintained regularly by technicians.

## 3. Methods

Based on long-term observation data, we firstly examined long-term variations of O<sub>3</sub> concentrations in Beijing during 2004–2015. Simple linear regression and nonparametric test (Z Test) were implemented to investigate the ozone trend in Beijing. We analyzed simultaneous variations of other airborne pollutants as well and attempted to reveal underlying relationship between other pollutants and O<sub>3</sub> through Spearman correlation coefficient (Rs) and P values. Furthermore, we attempt to analyze the variation of O<sub>3</sub> concentrations during specific events and evaluate the effects of different emission reduction strategies on the variation of O<sub>3</sub>. In the past several years, two major events, Asia-Pacific Economic Cooperation (APEC) meeting (from 1st, November to 12th, November 2014) and the parade on the 70th Victory Memorial Day for the Chinese People's War of Resistance against Japanese Aggression (September 3rd, 2015), were held in Beijing. As different contingent measures were implemented during two events and the influence of these emission reduction measures on O<sub>3</sub> concentrations varied significantly, this research may provide useful reference for better designing and implementing contingent measures to reduce O<sub>3</sub> concentrations.

<sup>1</sup> The DL background station is located in Dingling, a natural attraction far away from central Beijing and limitedly influenced by human-induced emission of airborne pollutants. Therefore, the DL station has been formally set as the background station for monitoring air quality in Beijing since 1984. In 1984, Beijing Municipal Environmental Protection Bureau built the first national automatic monitoring system including 8 air quality monitoring stations and the DL station as a city background station (clean-control station). In 2008, the Ministry of Environmental Protection in China further defined the DL station as a background station for Beijing air quality monitoring and data collected from this station was not used for calculating the mean value of urban airborne pollutants. So DL station has been frequently employed as the background station for understanding air quality variations in Beijing.

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