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Ground-level ozone in urban Beijing over a 1-year period: Temporal variations and relationship to atmospheric oxidation

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ABSTRACT

Regional ozone pollution has become a major environmental concern in China, especially in densely populated and economically vibrant regions such as North China, including Beijing. To address this issue, surface ozone and its precursors (CO, NO, and NO_2) from December 2012 to November 2013 at 12 sites in urban Beijing and 2 sites in suburban Beijing were analyzed. The annual average concentrations of O_3, CO, NO, and NO_2 in urban Beijing were 45.5 ± 50.2 μg m^{-3}, 1.5 ± 1.3 mg m^{-3}, 27.3 ± 42.7 μg m^{-3}, and 58.3 + 32.0 μg m^{-3}, respectively. The concentration of ozone was highest during summer, whereas concentrations of its precursors were highest during winter. Diurnal variations in ozone presented as a single-peak curve, with the peak appearing at about 15:00–16:00. Diurnal variations in most ozone precursors showed bimodal curves; the first peak appeared at about 08:00–09:00, and the second peak appeared at night. Hourly concentrations of ozone on the weekend were higher than those on weekdays between 11:00 and 24:00 in urban Beijing, which was suggestive of a significant *weekend effect*. This may be because NO inhibition on the weekend is weaker than that on weekdays during the ozone formation phase. Diurnal variations in O_X (NO_2 + O_3) showed a single peak, which appeared at 15:00 or 16:00. The results of correlation analysis among O_X, O_3, and NO_2 suggested that O_X was mainly controlled by O_3 during the day and by NO_2 during the night throughout the year. O_X was controlled by NO_2 during both the day and night during winter due to the low concentration of O_3. The regional transport of ozone along the upwind direction was found in a typical ozone pollution event in summer in Beijing.

1. Introduction

China has experienced rapid economic growth over the past two decades, accompanied by the development of large-scale industries and services. However, the economic boom has led to a general decline in environmental quality, especially in urban cities and city cluster regions (Hao and Wang, 2005; Shao et al., 2006; Chan and Yao, 2008). Beijing has a population of 16 million within an area of 16,800 km^2, making it one of the largest and most densely populated cities in China. Beijing is located on the northwestern border of the North China Plain and is surrounded by mountains on the north, east, and west. Many heavily populated industrialized cities are close to Beijing on the southwest and southeast (Xu et al., 2011). Unfavorable geographical conditions and the rapid growth in traffic emission and regional pollutant emission make Beijing one of the most polluted cities in China (Lin et al., 2008; Rose et al., 2010; Yang et al., 2009; Zhang et al., 2012).

As one of the most important oxidants and the dominant precursor of radicals (OH and NO_3) in the atmospheric troposphere (Wang et al., 2015; Masclin et al., 2013), ozone plays an important role in the atmospheric energy budget and chemistry. Ozone pollution may contribute to climate change and cause adverse effects in humans as well as ecosystems (Mills et al., 2011; Tang et al., 2013; Tilmes et al., 2012). Both the increase in tropospheric ozone and the depletion of stratospheric ozone influence climate change (Staehelin et al., 1994; Guicherit and Roemer, 2000; Vingarzan, 2004; Pudasainee et al., 2010). In the troposphere, photolysis of ozone by solar UV radiation to electronically excited O (^1D) and the subsequent reaction with water vapor are major sources of OH radicals (Lin et al., 2008). At a high pH (pH > 5), ozone in the aqueous phase reacts rapidly with S (IV) to form sulfate and hence contributes to acid deposition (Tanner and Schorran, 1995). In the troposphere, ozone originates from both *in situ* photochemical production through reactions of its precursors and

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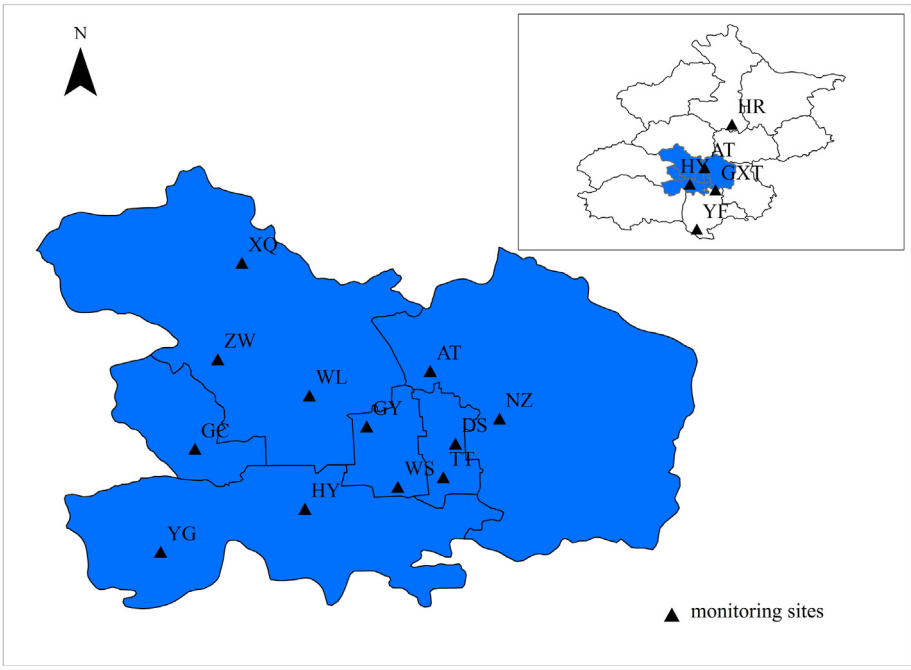

Fig. 1. Location of the 12 sites in urban Beijing and the two sites in suburban Beijing and the GXT Observatory.

vertical and horizontal transport (Singla et al., 2011; Ploeger et al., 2011; Im et al., 2011). In megacities, elevated concentrations of surface ozone are mainly caused by the increased concentration of its precursors (Wang et al., 2000; Molina and Molina, 2004; Ran et al., 2009), which originate from anthropogenic sources (Chameides et al., 1992; Bowman and Seinfeld, 1994; Finlayson-Pitts and Pitts, 1997; Tang et al., 2010). Additionally, frequent high-O_3 events occur not only in cities but also in rural areas, where local emission of anthropogenic pollutants is not important. This phenomenon is usually caused by the transport of polluted air masses and photochemical formation of ozone (Chan et al., 2003; Xu et al., 2008; Ge et al., 2012).

Studies on ozone have been performed in some large city agglomerations in China, such as the Pearl River Delta (Huang et al., 2011; Wei et al., 2012; Zhang et al., 2013; Li et al., 2011), the Yangtze River Delta (Ran et al., 2009; Luo et al., 2000; Ding et al., 2013; Li et al., 2012), and the Beijing–Tianjin–Hebei region. In Beijing, some studies have examined concentration trends and spatio-temporal variations in surface ozone and its precursors (Shao et al., 2009; Wang et al., 2010a; Ma et al., 2011; Wang et al., 2012). For example, Tang et al. (2009) found that ozone concentrations increased at a rate of 1.1 ± 0.5 ppbv/yr during 2001–2006 in Beijing. Some studies have focused on the ozone production processes and formation regimes, which are known to be complicated and non-uniformly distributed (An, 2006; Chou et al., 2009; Yuan et al., 2009). Lu et al. (2010) concluded that both NO_x- and VOC-sensitive chemistry exist at urban and suburban sites during ozone production, suggesting that it is important to investigate ozone-related processes individually in different regions because there is no geographically uniform response to NO_x and VOCs owing to the intricate emission conditions in the Beijing area. Some studies have highlighted the importance of regional transport from the urban to rural area of Beijing (Wang et al., 2006; Meng et al., 2009; Wang et al., 2008). For instance, Wang et al. (2010b) conducted field studies at three sites that lie roughly on a south–north axis in and outside Beijing before and during the 2008 Olympics. Based on the difference between the maximum 1-h ozone concentration at the urban site and the ozone value at the same time at the upwind site, they concluded that regional sources contributed 34–88% of the peak ozone level at the urban site during the selected episodes. Additionally, the ozone production efficiency, sensitivity of ozone to precursor emissions, and effectiveness of emission restrictions for ozone air quality have been discussed (Yang et al., 2011; Chou et al., 2009; Xie et al., 2008; Duan et al., 2008; Xing et al., 2011; Gao and Zhang, 2012; Wang et al., 2013; Shi et al., 2015; Lu et al., 2006).

In this study, concentrations of ozone and its precursors (CO, NO, NO_2) were monitored continuously at 12 sites in urban Beijing and 2 sites in suburban Beijing for over four seasons. The main objectives of this report were to (1) characterize the concentration and temporal variations of ozone and its precursors in urban Beijing; (2) discuss the relationship between ozone and atmospheric oxidation; and (3) investigate the regional transport of ozone during a high-ozone event.

2. Measurements

2.1. Monitoring sites and monitoring time

Twelve sites in urban Beijing and two sites in suburban Beijing were selected in this study (Fig. 1). Monitoring data, including concentrations of O_3, CO, NO, NO_2, and meteorological elements from December 2012

Table 1
Monthly average concentrations of ozone and its precursors at the 12 sites in urban Beijing.

	CO/mg m^{-3}	NO/μg m^{-3}	NO_2/μg m^{-3}	O_3/μg m^{-3}
January	3.6 ± 2.2	73.9 ± 58.4	93.3 ± 40.1	13.9 ± 17.3
February	2.0 ± 1.4	23.3 ± 30.3	60.9 ± 31.2	29.7 ± 24.4
March	1.6 ± 1.1	25.2 ± 37.9	68.6 ± 37.1	33.6 ± 29.7
April	0.9 ± 0.6	13.0 ± 28.0	47.5 ± 24.6	57.4 ± 36.6
May	1.0 ± 0.5	9.0 ± 15.5	53.6 ± 24.8	78.6 ± 58.9
June	1.4 ± 0.8	7.9 ± 11.1	51.7 ± 19.3	70.0 ± 66.1
July	1.0 ± 0.5	5.5 ± 10.4	42.2 ± 17.7	74.0 ± 64.1
August	0.9 ± 0.4	4.5 ± 9.7	41.8 ± 19.4	76.9 ± 63.7
September	1.2 ± 0.6	16.9 ± 22.9	54.6 ± 22.3	45.2 ± 49.8
October	1.2 ± 0.8	34.7 ± 39.9	64.1 ± 32.1	26.0 ± 28.6
November	1.5 ± 1.1	55.8 ± 62.2	56.0 ± 36.1	21.0 ± 21.4
December	2.2 ± 1.4	57.1 ± 52.4	64.8 ± 31.7	18.2 ± 21.1
Annual average	1.5 ± 1.3	27.3 ± 42.7	58.3 + 32.0	45.5 ± 50.2