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Characteristics of ozone and its precursors in Northern China: A comparative study of three sites

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ABSTRACT

Regional composite pollution and variation of atmospheric oxidizing ability are significant problems in Beijing and its surrounding areas. In particular, a southwest–northeast prevailing wind makes nonlinear variation of ozone and its precursors complex. In this study, simultaneous measurements of surface ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen oxide (NO_x) and carbon monoxide (CO) were carried out from August 2009 to June 2010 to investigate ozone level and precursor concentrations in Northern China. Gucheng (GC), Longtanhu (LTH) and Xinglong (XL) were selected to represent rural area, urban area and background area in North China Plain, respectively. The results showed that there were two peaks for primary pollutants (NO_x and CO) at urban and rural areas, and the highest values appeared nearly on rush hours. There was a single peak for O_3 and O_x with peak values appearing at afternoon. The primary pollutants at urban and rural areas were higher than those in background region. However, the concentration of secondary pollutant O_3 at downwind background areas was much higher than other sites due to transportation. Diurnal variations of pollutants indicated that O_3 and O_x had peak values at afternoon, while other primary pollutants showed two peak values nearly on rush hours. Furthermore, high concentrations of O_3 and O_x at background site XL also implied a robust atmospheric oxidizing ability. A positive correlation was observed between CO and O_3 at XL site, which implied that air masses to the site had a large loading of anthropogenic emission experiencing strong photochemical processing. The correlation between CO and O_3 was negative at GC and LTH, which indicated that local emission of precursors had significant influence on the formation of ozone. There was a positive correlation between NO_x and O_x at GC and XL, which implied that NO_x contributed to the formation of ozone, while a negative correlation meant titration in urban site LTH neutralized the formation of ozone due to high level of NO.

1. Introduction

Surface ozone plays a crucial role in both stratosphere and troposphere as a secondary pollutant, which is produced by the photochemical oxidation of carbon monoxide (CO) and non-methane volatile organic compounds (NMVOCs) in the presence of nitrogen oxides. In the stratosphere, it can absorb ultraviolet radiation (Mckenzie et al., 1999), which does harm to human beings and other creatures, also in the troposphere a suitable amount of ozone is beneficial for air purification because of its high reactivity. However, with the rapid growth of industrialization and urbanization, the pollution of surface ozone and NO_x has been an intractable problem in the mega

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cities and population centers (Jacob et al., 1993; Wang et al., 2006; Shan et al., 2008, 2009, 2010; Chelani, 2009; Xin et al., 2010; Tang et al., 2012). Generally, the levels of photochemical oxidants can be reduced by controlling their precursors (i.e. NO_x and VOC_S) (Seinfeld and Pandis, 2006). However, it should be noted that the levels of O_3 and NO_x are inextricable linked resulting from the chemical coupling of ozone and nitrogen oxides (Minoura, 1999). Thus, the response to the reduction of nitrogen oxide emissions is nonlinear and any resultant reduction of nitrogen dioxide is accompanied by an increase concentration of ozone (Mazzeo et al., 2005; Singla et al., 2011).

The North China Plain (NCP) region, one of the areas with the highest population density all over the world, has suffered from severe air pollution for decades. Many studies (Wang et al., 2006, 2010; Streets et al., 2007; Xu et al., 2011a, 2011b, 2011c; Lin et al., 2011; Tang et al., 2012) have been conducted on surface ozone in Beijing and its surrounding cities. Lin et al. (2008) found that ground ozone level and atmospheric oxidant O_x ($O_x = O_3 + NO_2$) in a rural site of NCP were 28.5 + 13.8 ppb and 47.1 + 8.5 ppb, respectively. Researches on Beijing area (Wang et al., 2006; Xu et al., 2011a, 2011b, 2011c; Tang et al., 2009, 2012) showed that surface ozone mixing rate varied significantly from place to place, exceeded the standard of National Environmental Quality in many observation periods.

Previous studies mainly focus on the variation of a single station, which can give us limited knowledge of the characteristics of surface ozone and atmospheric oxidation ability. In particular, air pollution in North China Plain has been a severe regional composite pollution (Xu et al., 2011a, 2011b, 2011c; Streets et al., 2007; Chan and Yao, 2008; Duan et al., 2008) of fine particle matters and gaseous pollutants due to the massive consumption of fossil fuel. Different kinds of topographical sites should be put together to investigate air pollution problems on a regional scale. However, there is only a few researches on regional scale pollution of surface ozone (Lin et al., 2008; Tang et al., 2012) compared with that in other places of China (Tu et al., 2007; Sun et al., 2010; Tang et al., 2012) and other population delta in European and American (Li et al., 2002; Chu et al., 2003; Grewe et al., 2012).

To achieve the promising goal of "Green Olympic Game" in the 29th Summer Olympic Games, Beijing government took many effective measures to reduce anthropogenic emissions cooperating with other local governments in the NCP. For instance, local governments in the NCP have managed to relocate old industrial facilities. Some 300 000 heavily polluting vehicles (the so called yellow-label vehicles) were banned from driving in the Beijing Municipality, and other vehicles have been restricted rigorously based on the odd and even number rule. The road-traveling automobiles reduced about 1.95 million a day during the Olympic Games (Mao, 2008). As a result, the mean concentration of $O_{3\text{-}8\ h\ max}$, O_x, NO_2 and $PM_{2.5}$ was 114 ± 29 μg m^{-3}, 95 ± 17 μg m^{-3}, 23 ± 4 μg m^{-3} and 56 ± 28 μg m^{-3} in the region during the Olympic Games, respectively, and fell by 20.2%, 18.9%, 13% and 43.7%, respectively (Xin et al., 2010).

In this study, surface ozone level and atmospheric oxidation ability in urban area, rural area and background area of NCP were investigated via data sets from three selected sites. Comparative study of surface ozone was conducted through annual variation, daily variation, atmospheric oxidation ability and precursor concentration correlation with ozone formation, along with meteorological parameters in the observation period. We hope the study will benefit air pollution control in NCP.

2. Methods and data

2.1. Site location and weather conditions

Gucheng (GC) site (39°15N.115°73E, 15.2 m asl), positioned in countryside of Baoding city, is in the central zone of Beijing–Tianjin–Baoding area as Fig. 1 shows. Taihang Mountains (south-west-to-northeast trend) is about 30 km away from the west of the site. The highway connecting Beijing and Shijiazhuang is about 7 km away from east of the site. In addition, the surrounding of the site is farms and village. The main crops are wheat in winter and spring whereas corn in summer and fall (Lin et al., 2009). Longtanhu (LTH) site (39°87N.116°43E, 44 m asl) is located in Longtanhu park within the second Ring Road. The highway from Beijing to Tianjin and Beijing to Shenyang is in the south of the site. The surrounding of the site is covered with grasses and trees. Thus, the site in the central of Beijing can stand for pollution level in urban background area of NCP region. Xinglong (XL) site (40°39N.117°57E, 960 m asl) is in the south of Yanshan Mountains, located in the National Astronomical Observation Base of Hebei province. Fig. 2 showed air mass backward trajectories at XL site during observation periods using HYSPLIT. The air mass from south contributes 45% (air mass 3), and the air masses from northwest contribute to 37% (air mass 2 and air mass 4). Beijing is about 115 km from southwest in a straight line and industrial city Tangshan is about 100 km from southeast. The surrounding is covered with trees and bushes, and villagers in this arcadia live on fruit trees and are farmers. Thus, it is appropriate to carry out background observation of the atmospheric composition in NCP region.

The weather in NCP is typically influenced by monsoon circulation, which means that the meteorological factors have significant transition from season to season. The meteorological data is obtained from China Meteorological Data Sharing Service System (http://cdc.cma.gov.cn/home.do). The four seasons are established according to astronomy, which means that spring includes March, April and May; Summer includes June, July and August; fall includes September, October and November; and winter includes December, January and February. Fig. 3 showed a general weather condition of Beijing during the observation period, the precipitation mainly occurs in summer with lower pressure, while the humidity and temperature are lower in winter and higher in other seasons. The wind speed and wind direction of four seasons are presented in Fig. 4. The extreme high-wind speed corresponding with wind direction is mostly less than 4 m s^{-1}, and the prevailing wind directions are NNE and SE, especially in summer and winter. The three sites, located on the route of southwest to northeast prevailing wind, are suitable places of studying surface ozone chemistry in NCP.

2.2. Instruments and data sets

Commercial trace gas instruments (Thermo Environmental Instruments Inc., USA i-Series) were utilized to continuously