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Impacts of a strong cold front on concentrations of HONO, HCHO, O_3, and NO_2 in the heavy traffic urban area of Beijing

Junling An*, Wei Zhang, Yu Qu

State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT

Much rain and strong winds caused by a cold front occurred in Beijing during the period of Sep. 27 to Oct. 4, 2004 and led to sharp drops in maximum and mean concentrations of HONO, HCHO, O_3, and NO_2, i.e., the maximum concentrations were reduced by 5.9, 21.3, 45.6, and 44.4 ppb, respectively, and the mean concentrations were decreased by 4.0, 5.5, 30.3, and 32.3 ppb, respectively. For daily HO_x production rates HONO photolysis was the largest contributor and over 90% contributions were from photolysis of HONO and HCHO. Large number and area percentages of soot aggregate from PM10, and high correlations between concentrations of PM10 and chemical formation of HONO suggested that heterogeneous reactions of NO_2 on surfaces of soot aggregate could be a key source of HONO in the heavy traffic areas of Beijing during the night and should be considered in air quality simulations for such areas.

1. Introduction

Hydroxyl radical (OH) is the primary oxidant in the atmosphere, responsible for the oxidation and removal of most natural and anthropogenic trace gases (Levy, 1971; Logan et al., 1981). The OH radical and hydroperoxyl radical (HO_2) (collectively called HO_x) interconvert to each other rapidly and play a key role in tropospheric chemistry. Ozone (O_3), nitrous acid (HONO), and formaldehyde (HCHO) are three dominant photolytic HO_x precursors in the troposphere, other HO_x sources include the photolysis of peroxides and other carbonyl compounds, and reactions of O_3 and alkenes.

The chemistry of HONO has been extensively studied in the urban atmosphere in Europe (e.g., Perner and Platt, 1979; Andrés-Hernández et al., 1996; Reisinger, 2000; Stutz et al., 2002; Acker et al., 2006) and in North America (e.g., Harris et al., 1982; Lammel and Cape, 1996). Related studies are very limited in China (Zhou et al., 2002; Su et al., 2008). It is generally believed that HONO is produced mainly through the heterogeneous reaction between NO_2 and water vapor in high NO_x ($= NO + NO_2$) environments (Lammel and Perner, 1988; Harrison et al., 1996; Andrés-Hernández et al., 1996) but the detailed mechanism is still under discussion. Recent studies (Stemmler et al., 2006) have showed that the conversion of NO_2 to HONO is significantly enhanced in the presence of organic materials. HONO can reach parts per billion by volume (ppb) at night and its photolysis the following morning can be a dominant source of OH in the urban atmosphere.

HCHO is an abundant carbonyl compound in the atmospheric boundary layer. HCHO is largely produced in situ as an intermediate in the oxidation of volatile organic compounds (VOCs), both anthropogenic and biogenic, especially alkenes (Dodge, 1990). Photolysis of one HCHO molecule leads to production of two HO_2 radicals and could be a significant source for HO_x in the lower troposphere in urban areas with high levels of anthropogenic VOCs (Kleinman et al., 1997).

This paper focuses on the effects of rain and winds caused by a strong cold front that occurred in Beijing during the period of Sep. 27 to Oct. 4, 2004 on the major HO_x precursors, i.e., HONO, HCHO, and O_3, changes in the contributions of photolysis of the three precursors to HO_x production rates, and possible sources of high HONO concentrations in the heavy traffic urban area of Beijing during the night.

2. Experimental setup

Measurements at the Institute of Atmospheric Physics (IAP) of the Chinese Academy of Sciences (CAS), Beijing were conducted from Sep. 27 to Oct. 4, 2004. IAP is surrounded by heavy traffic

* Corresponding author. Tel.: +86 10 82080598; fax: +86 10 62024951.
E-mail address: anjl@mail.iap.ac.cn (J. An).

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routes, approximately 1.8 km north to the fourth Ring heavy traffic route, about 20 m south to Beitucheng West Road and nearly 1 km south to the third Ring heavy traffic route, approximately 500 m west to Badaling expressway, and 50 m east to Beichen West Road and nearly 1.5 km east to Beichen Road (Fig. 1). The traffic flow rates are very high in the Badaling expressway and the third and fourth Rings, with the highest value of 229 vehicles per minute (Fig. 1). Home-made differential optical absorption spectroscopy (DOAS), consisting of a xenon arc lamp, a Cassegrain sending and receiving telescope and a spectrograph-detector system, was sited on the roof of the graduate apartment of IAP of CAS, at a height of 20 m above the ground. The retroreflector array was placed on the roof of the office building of the Institute of Geology and Geophysics (IGG), CAS. The fixed light path was 375 m (one way) west to the DOAS system (Fig. 1). The slotted disk detector (Perner and Platt, 1979) is modified by a 1024-pixel photodiode array (PDA) detector due to the PDA advantages in the built-in multiplexing capability and long light integration. Details of the DOAS system can be seen in Qin et al. (2006). The detection limit is 0.36 ppb for HONO, 1.6 ppb for HCHO, 2.0 ppb for O_3, and 0.88 ppb for NO_2, respectively (Qin et al., 2006; Alicke et al., 2002). O_3 was also measured with a Thermo Environmental Instruments (TEI) model 49 analyzer, with a detection limit of 1 ppb, and NO_2 and NO were also measured by conventional chemiluminescent gas analyzer (TEI Model 42C), with a detection limit of 0.05 ppb (Liu et al., 2000) in order to compare with DOAS measurements. The mass concentration of particulate matter (PM10) was measured with an RP1400 (Rupprecht & Patashnik, U.S.A.), with a detection limit of 0.05×10^{-6} g m^{-3} (Zhang et al., 2006). O_3 and NO_x analyzers were placed on the 8-m-high above-ground platform of the 325 m meteorological tower, about 200 m east to the Badaling expressway. For PM_{10} the sampling site was located on the roof of the office building of LAPC, 40 m east away from the meteorological tower. Eight-meter-high above-ground wind direction and speed, air temperature and relative humidity were automatically recorded by the meteorological tower (Liu et al., 2000).

3. Results and discussion

Sep. 27 was cloudless. The relative humidity reached a maximum of 94% at night and a minimum of 44% at noon. The wind speed was low and its maximum was less than 2 m s^{-1} (Fig. 2). The dominant wind was northeasterly. Sep. 28 was cloudy. Wind speeds and directions showed minor variations (Fig. 2). From 18:00 on Sep. 29 to 12:00 on Sep. 30 dominant winds changed into southeasterly and wind speeds increased, with a maximum of 4 m s^{-1} (Fig. 2). The relative humidity generally increased over 80% (Fig. 2). The rain began at 9:30 on Sep. 30 and ceased at 18:00. The northwesterly became strong and lasted approximately 1 day, with a maximum of 6.5 m s^{-1} on Oct. 1 (Fig. 2). The relative humidity showed a sharp drop and then kept at low values within this period (Fig. 2). From Oct. 2 to 4 the dominant winds were northeasterly or southeasterly and wind speeds were low (Fig. 2). All the 3 days were cloudless. Diurnal variations of air temperature and relative humidity from Oct. 2 to 4 were similar to those on Sep. 27 (Fig. 2).

The correlations between measurements of DOAS, and the O_3 and NO_x analyzers were good, with correlation coefficients being larger than or equal to 0.85 (Figs. 3 and 4). NO_2 (12 ppb) concentration bias measured by the two methods (Fig. 3) may be related to the heavy traffic emissions from the Badaling expressway, where it is located between the DOAS system and the O_3 and NO_x analyzers, and the distance between the two measurement sites is about 700m (Fig. 1). Surface O_3 concentrations were usually less than 20 ppb at night (Fig. 5). Sharp rises occurred from 9:00 to 14:00 of Sep. 27 due to photochemical reactions. The peak O_3 concentrations lasted only 1 h and then the O_3 concentrations decreased significantly within 3 h (from 15:00 to 18:00). NO_2 concentrations were very high, with the range of 5–75.8 ppb (Fig. 5). The highest NO_2 concentrations occurred at 21:00 and low NO_2 concentrations occurred from 10:00 to 17:00 due to NO_2 photolysis (Fig. 5). Elevated HONO concentrations usually occurred at night or in the early morning, with a maximum of 7.2 ppb (Fig. 6), corresponding to 6.8 ppb hourly mean levels. This is higher than the maximum of 5.3 ppb measured in Beijing by Qin et al. (2006) and much higher than that of 2.7 ppb measured at the Peking University campus, Beijing by Zhou et al. (2002) and 2 ppb measured in Rome by Acker et al. (2006). The lowest HONO concentrations generally occurred from 9:00 to 16:00 in the cloudless daytime (Fig. 6). HCHO concentrations peaked at 21:35, with a maximum of 29.3 ppb on Sep. 27 (Fig. 6). This is similar to the maximum of 25.3 ppb measured in Beijing by Pang and Mu (2006). On Sep. 28, daily variations in the concentrations of HONO, HCHO, O_3, and NO_2 were not obvious due to large fractions of clouds (Fig. 6). O_3

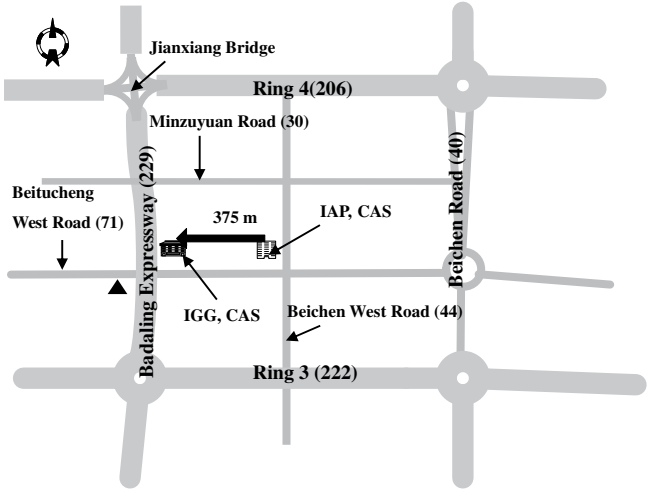

Fig. 1. Schematic map of the measurement site in Beijing. IAP, IGG, and CAS denotes Institute of Atmospheric Physics, Institute of Geology and Geophysics, and Chinese Academy of Sciences, respectively. Solid triangle stands for the place where the 325 m meteorological tower is located. Numbers marked in brackets are average traffic flow rates (vehicles/minute) during the day.

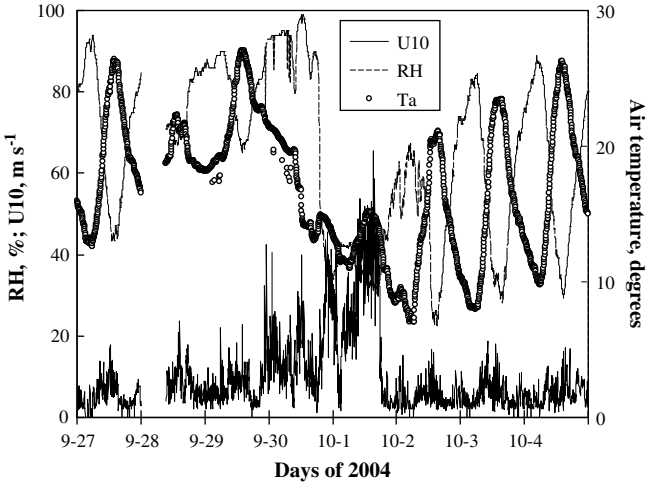

Fig. 2. Time series of air temperature (°C), relative humidity (%), and wind speed (m s^{-1}) at 8 m above the ground from September 27 to October 4, 2004. U10 denotes wind speed is multiplied by 10.