Atmospheric Environment 45 (2011) 4735–4744

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Impacts of HONO sources on the air quality in Beijing, Tianjin and Hebei Province of China

Ying Li [a,b], Junling An [a,*], Min Min [c], Wei Zhang [d], Feng Wang [a,b,e], Pinhua Xie [f]

[a] *State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, Beijing 100029, China*
[b] *Graduate University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Key Laboratory of Radiometric Calibration and Validation for Environmental Satellites, National Satellite Meteorological Center, China Meteorological Administration, Beijing 100081, China*
[d] *China Aviation Meteorological Center, Beijing 100122, China*
[e] *Anhui Public Meteorological Services Center, Hefei 230061, China*
[f] *Key Laboratory of Environment Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China*

ARTICLE INFO

Article history:
Received 27 September 2010
Received in revised form
29 March 2011
Accepted 10 April 2011

Keywords:
Nitrous acid
Heterogeneous reaction
WRF–Chem
DOAS

ABSTRACT

Incorporated into the WRF–Chem model are the three HONO sources, i.e., the reaction of photo-excited NO_2 with water (NO_2^* chemistry), heterogeneous reactions on aerosol surfaces, and HONO emissions. Four case simulations were performed in Beijing, Tianjin, and Hebei Province (BTH region) in August of 2007. Results indicate that the NO_2^* chemistry yields 30–50 ppb enhancements in daily maximum 1-h surface O_3 concentrations in major cities and 3–10 ppb increases in monthly mean daily maximum 8-h surface O_3 concentrations in most areas of the BTH region. Heterogeneous reactions on aerosol surfaces lead to 5–20 ppb decreases in monthly mean NO_y concentrations in major cities over the BTH region. Heterogeneous reactions and HONO emissions are the largest, and the second largest contributor, accounting for ~59% and 26% of simulated HONO concentrations, respectively. The three HONO sources produce enhancements in monthly mean daytime (10:00–17:00) concentrations of NO_y (total reactive N-containing compounds), NO_2, HNO_3, HONO, and HO_x being −1 to −5 ppb, −1 to −3 ppb, −0.3 to 0.5 ppb, 20–50 ppt, and 1–3 ppt, respectively. Comparison with observations shows that inclusion of the three HONO sources into the WRF–Chem model can considerably improve HONO and O_3 simulations in the BTH region. For HONO the mean, the normal mean bias, the root mean square error, and the correlation coefficient is greatly improved from 0.04 to 0.56 ppb, from −97% to −39%, from 1.10 ppb to 0.51 ppb, and from −0.56 to 0.86, respectively, by comparison with the gas chemical mechanism only considered in the WRF–Chem model. This suggests that the three important HONO sources be included in air quality models, particularly in the areas with high emissions of NO_x and particulate matter.

1. Introduction

Nitrous acid (HONO) plays an important role in the photochemistry of the troposphere due to its photolysis by solar ultraviolet radiation into the hydroxyl radical (OH), which is one of the most significant oxidants in the atmosphere (Alicke et al., 2002). Recent observations indicated unexpected high HONO levels of up to several ppb in urban or rural areas in China (Su et al., 2008a,b; An et al., 2009; Qin et al., 2009) but the state-of-the-art WRF–Chem model (Grell et al., 2005) and CMAQ model (Byun and Schere, 2006) severely underestimated HONO observations due to only inclusion of gas-phase chemical mechanisms (Sarwar et al., 2008; An et al., 2011). Su et al. (2008b) proposed an unknown HONO source to explain observed high HONO levels during the daytime. Sarwar et al. (2008) added a heterogeneous reaction, a surface photolysis reaction, and HONO emissions to the CMAQ model and simulations still showed HONO underestimation by comparison with observations, particularly in the daytime. Li et al. (2008) suggested an additional HONO daytime source through the reaction of electronically excited nitrogen dioxide with water vapor,

$$NO_2 + h\nu(\lambda > 420\ \text{nm}) \rightarrow NO_2^* \qquad (R1)$$

---

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

1352-2310/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2011.04.086

Table 1
Options in the WRF–Chem model used in this study.

Options	WRF–Chem
Advection scheme	Runge–Kutta 3rd order
Cloud microphysics	Lin et al.
Long-wave radiation	RRTM
Short-wave radiation	Goddard
Surface layer	Monin–Obukhov
Land-surface model	Noah
Boundary layer scheme	YSU
Cumulus parameterization	New Grell scheme
Photolysis scheme	Madronich (1987)
Chemistry option	CBM-Z
Aerosol option	MOZAIC

$$NO_2^* + H_2O \rightarrow HONO + OH \qquad (R2)$$

$$NO_2^* + M \rightarrow NO_2 + M \text{ (where M is } N_2, O_2, \text{ or } H_2O) \qquad (R3)$$

The reaction rate for Reaction R2 given by Li et al. (2008) is 1.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, which is an order of magnitude higher than that found by Crowley and Carl (1997). Although further experiments are needed to be done in order to reduce the uncertainty of the rate constant, the HONO increase due to Reaction R2 may potentially play a significant role in some industrialized areas with elevated emissions of NO_x ($=NO + NO_2$). Wennberg and Dabdub (2008) coupled the NO_2^* chemistry into an air quality model and found that ozone (O_3) simulations were increased by as much as 55 ppb in the South Coast Air Basin of California for a summer episode in 1987. Sarwar et al. (2009) did similar work but illustrated that simulated O_3 enhancements were considerably smaller than those reported by Wennberg and Dabdub (2008) due primarily to much lower emissions of NO_x and volatile organic compounds (VOCs) in 2001/2002 than those in 1987. Compared with those in California, current emissions of NO_x and particulate matter in Beijing, Tianjin, and Hebei Province (BTH region) are very high (Zhang et al., 2009), so contributions of the NO_2^* chemistry and heterogeneous reactions on aerosol surfaces to O_3, NO_y ($=NO_x + HONO + HNO_3 + PAN +$ other reactive N-containing compounds), HONO, NO_x, HO_x ($=OH + HO_2$), and HNO_3 in the BTH region could be significant and will be quantified in this paper by using the WRF–Chem model, which couples the newly developed modules of the NO_2^* chemistry, heterogeneous reactions on aerosol surfaces, and HONO emissions.

2. Model description

2.1. WRF–Chem model

The model used in this study is the Weather Research and Forecasting/Chemistry (WRF–Chem) model version 3.2 (Grell et al., 2005; Fast et al., 2006). The WRF–Chem model has two components: a meteorological module and a chemistry module. Both components use the same mass and scalar preserving flux scheme, the same physics schemes for subgrid-scale transport, the same horizontal and vertical resolutions, and the same time step (Grell et al., 2005). More detailed description of the WRF–Chem model can be found on the websites http://ruc.noaa.gov/wrf/WG11/ and http://www.wrf-model.org. The parameterization schemes used in this study are listed in Table 1. For gas chemistry used is the CBM-Z, an updated lumped-structure gas-phase photochemical mechanism (Zaveri and Peters, 1999). Photolysis rates are calculated by the TUV scheme (Madronich, 1987). The chosen aerosol module is MOSAIC (Zaveri et al., 2005a,b, 2008; Fast et al., 2006) with an 8-size-bin representation.

Two nested domains shown in Fig. 1 are employed for WRF–Chem simulations. Domain 1, 2, and 3 contains 83 × 65, 58 × 55 and 55 × 55 grid cells, with horizontal resolutions of 81, 27, and 9 km, respectively. Domain 3 primarily covers Beijing, Tianjin, and Hebei Province (BTH region). Twenty-eight vertical model layers from the surface to 50 hPa are used with nonuniform thickness. The lowest model layer is ~28 m above the ground. Meteorological initial and boundary conditions are from NCEP 1° × 1° reanalysis data, which are also used for nudging every 6 h. The chemical initial and boundary conditions are updated by the output of a global chemical transport model MOZART-4 (Emmons et al., 2010) every 6 h. The detailed description of mapping species concentrations from the MOZART to the WRF–Chem can be found on the website http://www.acd.ucar.edu/wrf-chem/. Anthropogenic emissions in 2006/2007 were from Zhang et al. (2009). Considered were monthly variations of the emissions of SO_2, NO_x, CO, VOCs, PM_{10}, $PM_{2.5}$, BC, and OC. NH_3 emissions were provided by Streets et al. (2003). Biogenic emissions were calculated based on suggestions of Guenther et al. (1993, 1994) and Simpson et al. (1995). Model

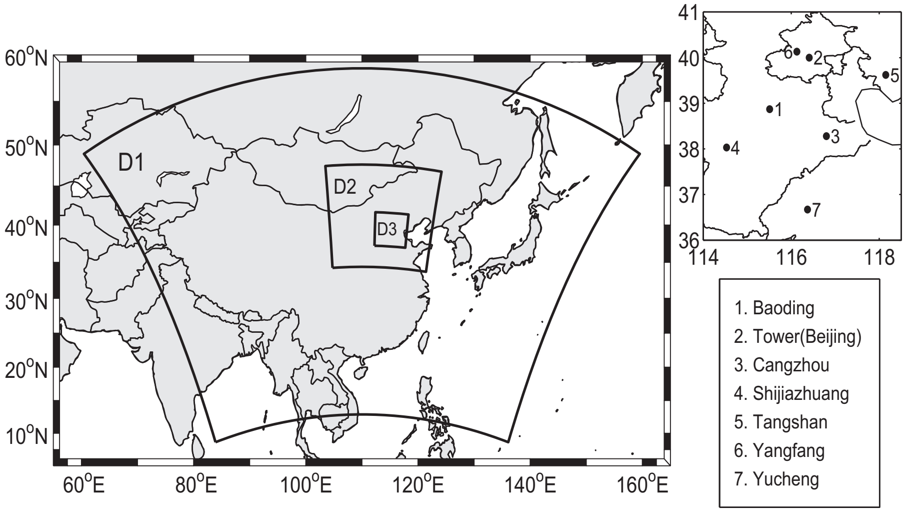

Fig. 1. Modeling domains used in this study and the seven measurement sites.