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Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China
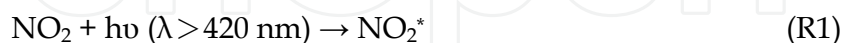
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1. Introduction

Nitrous acid (HONO) plays a significant role in the photochemistry of the troposphere, especially in the polluted urban atmosphere, due to its photolysis by solar UV radiation into the hydroxyl radical (OH), which is one of the most important oxidant in the atmosphere (Alicke et al., 2002). Some previous observations showed unexpected high HONO concentrations up to several ppb at urban or rural sites during the daytime or nighttime (Qin et al., 2009; Su et al., 2008a, 2008b; Yu et al., 2009) but gas-phase chemical models usually underestimated HONO observations, particularly in the daytime. HONO sources are thought to be direct emissions, homogeneous gas reactions, and heterogeneous reactions on aerosol surfaces. Sarwar et al. (2008) incorporated gas-phase reactions, direct emissions, a heterogeneous reaction, and a surface photolysis reaction into the CMAQ model, and simulations still indicated HONO underestimation by comparison with measurements, especially in the daytime. Li et al. (2008) suggested a reaction of electronically excited nitrogen dioxide (NO$_2^*$) with water vapor as follows,

$$NO_2 + h\upsilon \ (\lambda > 420 \ nm) \rightarrow NO_2^* \qquad (R1)$$

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

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

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 larger than that found by Crowley and Carl (1997). Although further experiments to reduce uncertainty in the rate constant need to be conducted, the HONO increase due to Reaction R2 may be potentially significant in some industrialized regions with elevated emission levels of NO$_x$ (= NO + NO$_2$) and volatile organic compounds (VOCs). Wennberg and Dabdub (2008) implemented the NO$_2^*$ chemistry into an air quality

model and found that simulated ozone (O_3) were enhanced by as much as 55 ppb in the southern California for a summer episode in 1987. However, Sarwar et al. (2009) did similar work and illustrated that the simulated increases were considerably smaller than those reported by Wennberg and Dabdub (2008) due primarily to the current low emissions of NO_x and VOCs compared to the emission levels in 1987. Ensberg et al. (2010) then used the emissions in both 1987 and 2005 to assess impacts of the NO_2^* chemistry on air pollution in the south coast air basin of California showed that the NO_2^* chemistry increased the effectiveness in reducing O_3 through NO_x emissions reductions alone. Li et al. (2010) coupled the NO_2^* chemistry, four heterogeneous reactions on aerosol surfaces recommended by Jacob (2000), and secondary HONO formation from the NO_2 heterogeneous reaction with semivolatile organics suggested by Gutzwiller et al. (2002) into the WRF-CHEM model version 3.2, and found that the additional HONO sources significantly improved HONO simulations by comparison with differential optical absorption spectroscopy (DOAS) observations (Zhu et al., 2009), especially in the daytime.

The purpose of this study is to use the state-of-the-art WRF-CHEM model version 3.2 to assess effects of the photoexcited NO_2 chemistry and heterogeneous reactions on concentrations of O_3 and NO_y(total reactive N-containing compounds) in Beijing, Tianjin and Hebei Province of China (BTH region), where emissions of NO_x and particulate matter (PM) are high (Zhang et al., 2009).

2. Model description

2.1 WRF-CHEM model

Used in this research is the Weather Research and Forecasting/Chemistry (WRF-CHEM) model version 3.2 (Fast et al., 2006; Grell et al., 2005). The WRF-CHEM model contains two components: a meteorological module and a chemistry module. The two modules use the same mass and scalar preserving flux scheme, the same horizontal and vertical resolutions, the same physics schemes for subgrid-scale transport, and the same time step (Grell et al., 2005). A detailed description of the WRF-CHEM model can be found on the website http://ruc.noaa.gov/wrf/WG11/ and http://www.wrf-model.org. In this study, the WRF-CHEM model employs the microphysics scheme of Lin et al. (1983), the Yonsei University (YSU) PBL scheme (Noh et al., 2001), the Noah land-surface model (Chen & Dudhia, 2001), the RRTM long wave radiation parameterization (Mlawer et al., 1997), and the Goddard short wave scheme (Chou & Suarez, 1994). For gas chemistry chosen is an updated lumped-structure photochemical mechanism CBM-Z (Zaveri & Peters, 1999). Photolysis rates are calculated by the TUV scheme (Madronich, 1987). The chosen aerosol module is MOSAIC (Fast et al., 2006; Zaveri et al., 2008) with an 8-size-bin representation and the biogenic module is based on the description of Guenther et al. (1993, 1994), Simpson et al. (1995), and Schoenemeyer et al. (1997).

Two nested domains shown in Fig. 1. are employed in the simulation. Domain 1, 2, and 3, consists of 83×65, 58×55 and 55×55 horizontal grid cells with 81 km, 27 km and 9 km, primarily covering East Asia, North China, and the BTH region, respectively. The stretched vertical coordinate in the model that extends up to approximately 50 mb uses 28 vertical model layers with nonuniform thickness and a 28 m first layer above the ground. Meteorological initial and boundary conditions are from NCEP reanalysis data, which are also used for nudging every 6 h. The chemical initial and lateral boundary conditions are constrained by the output of a global chemical transport model MOZART-4 (Emmons et al., 2009) every 6 h. The detailed description of mapping species concentrations from the

Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on
Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China

199

MOZART to the WRF-CHEM can be found on the website http://www.acd.ucar.edu/wrf-chem/. Monthly anthropogenic emissions of SO$_2$, NO$_x$, CO, VOCs, PM$_{10}$, PM$_{2.5}$, BC, and OC in 2006/2007 were obtained from (Zhang et al., 2009) and those of NH$_3$ from Streets et al. (2003) and monthly emissions of other species were derived from Zhang et al. (2009). Model simulations were performed in August 1-31, 2007 with a spin-up period of 7 days (July 25-31).
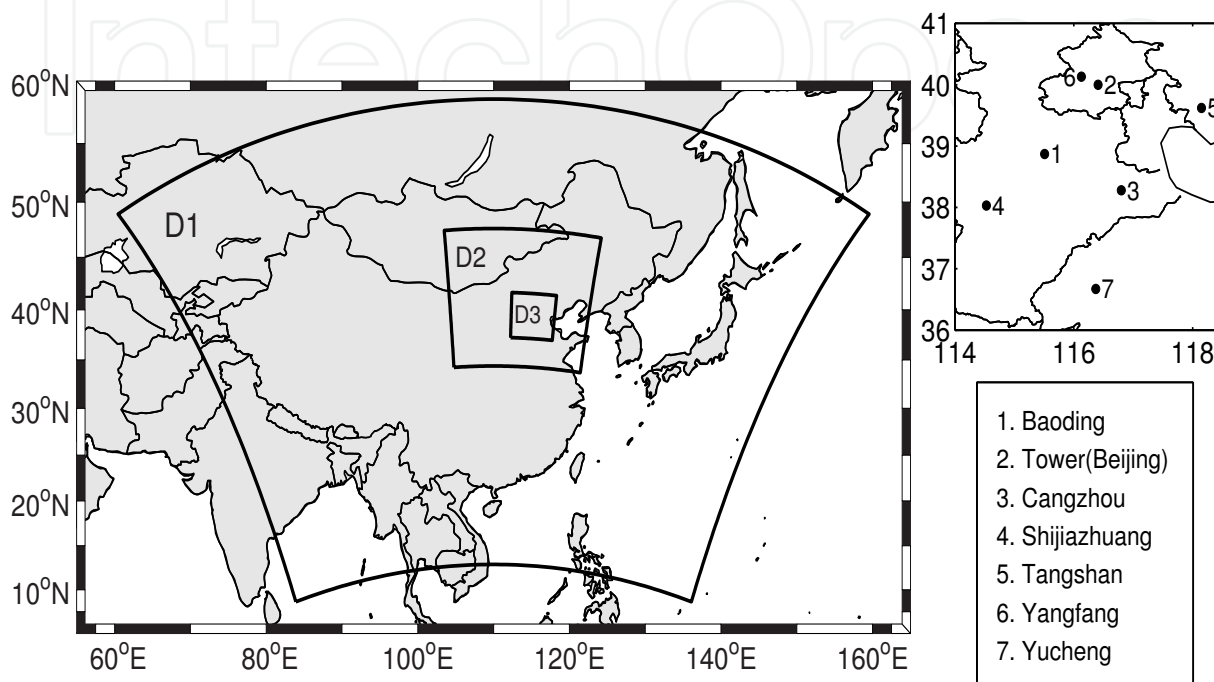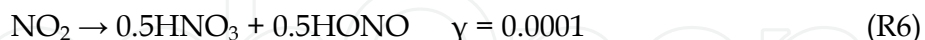

Fig. 1. Modeling domains used in this study and seven measurement sites in Beijing, Tianjin, and Hebei Province in Domain three.

Four different model simulations, i.e., Cases R, S, T and E, were conducted to assess impacts of the NO$_2^*$ chemistry and heterogeneous reactions on O$_3$ and NO$_y$ in the BTH region. Case R is a reference, using the standard CBMZ mechanism and the MOSAIC module. Case S contains Case R with Reactions R1-R3. Case T is the same as Case S besides inclusion of 3.1% emissions of HONO/ NO$_x$ (See Section 2.2). Case E includes Case T with Reactions R4-R7 (See Section 2.2).

2.2 Parameterization of HONO sources

The NO$_2^*$ chemistry (Reactions 1-3) (Li et al., 2008) is added to the CBM-Z mechanism. The rate of photoexcitation is simplified as 3.5 times the photolysis of NO$_2$ because the former is 3~4 times higher than the latter (Ensberg et al., 2010). The quenching rate constants for Reaction (R3) are 2.7×10^{-11}, 3.0×10^{-11}, and 1.7×10^{-10} cm^3 molecule^{-1} s^{-1} for N$_2$, O$_2$, and H$_2$O, respectively (Li et al., 2008). The uncertainty in the rate constant for Reaction (R2) is ±50% (Li et al., 2008), so the rate constant (R2) is chosen as 9.1×10^{-14} cm^3 molecule^{-1} s^{-1}, which is the mean value of 1.7×10^{-13} cm^3 molecule^{-1} s^{-1} from Li et al. (2008) and 1.2×10^{-14} cm^3 molecule^{-1} s^{-1} from Crowley and Carl (1997).

For heterogeneous reactions on aerosol surfaces we follow Jacob (2000) recommendations as below,

$$HO_2 \rightarrow 0.5H_2O_2 \quad \gamma = 0.2 \tag{R4}$$

$$NO_3 \rightarrow HNO_3 \quad \gamma = 0.001 \tag{R5}$$

$$NO_2 \rightarrow 0.5HNO_3 + 0.5HONO \quad \gamma = 0.0001 \tag{R6}$$

$$N_2O_5 \rightarrow 2HNO_3 \quad \gamma = 0.1 \tag{R7}$$

The reactive uptake of HO_2, NO_3, NO_2, and N_2O_5 by aerosols is depicted by using a simple reaction probability parameterization (Jacob, 2000),

$$k = \left(\frac{a}{D_g} + \frac{4}{v\gamma} \right)^{-1} A \tag{1}$$

where k is the first-order rate constant, a, the aerosol equivalent radius (m), D_g, the gas-phase molecular diffusion coefficient being 10^{-5} m^2s^{-1} (Dentener & Crutzen, 1993), v, the mean molecular speed (ms^{-1}), A, the aerosol surface area per unit volume of air, and γ, the uptake coefficient of reactive species. Considered aerosols are sulfate, nitrate, organic carbon, and black carbon. Taken from Chin et al. (2002) are parameters for aerosol density, size distributions, and hygroscopic growth rates at ambient relative humidity. A fraction of 2.3% of the NO_x emitted in diesel exhaust is assumed to be heterogeneously converted to HONO (Gutzwiller et al., 2002). Additionally, direct HONO emissions are estimated by 0.8% emissions of NO_x (Kurtenbacha et al., 2001), which is also adopted in other studies (Aumont et al., 2003; Sarwar et al., 2008). Thus, 3.1% (= 2.3% + 0.8%) of NO_x emissions is used to reflect HONO direct emissions and secondary HONO formation from the NO_2 heterogeneous reaction with semivolatile organics in diesel exhaust.

3. Results and discussion

3.1 Impacts of the NO_2^* chemistry and heterogeneous reactions on O_3 and NO_y

Shown in Fig. 2. are the largest differences in simulated daily maximum 1-h O_3 concentrations between Cases S and R. Typically 10~20 ppb increases in daily maximum 1-h O_3 concentrations are found in suburban areas and 30~50 ppb enhancements in major cities, i.e., Beijing, Tianjin, Shijiazhuang, and Baoding, over the BTH region. The values are much higher than the results (1~13 ppb) given by Sarwar et al. (2009). This demonstrates that the NO_2^* chemistry can play a key role in some industrialized regions with elevated emissions of NO_x and VOCs. The conclusion is consistent with the suggestion of Sarwar et al. (2009). Monthly mean daily maximum 8-h O_3 concentrations near the surface are enhanced in the range of 8~18 ppb in most areas of the BTH region due to the NO_2^* chemistry and the largest increase is located close to Shijiazhuang (Fig. 3.). The enhanced concentration range in the BTH region is much higher than that of 1~6 ppb in some urban areas and in the vicinity of isolated large NO_x sources in the United States of America (Sarwar et al., 2009).
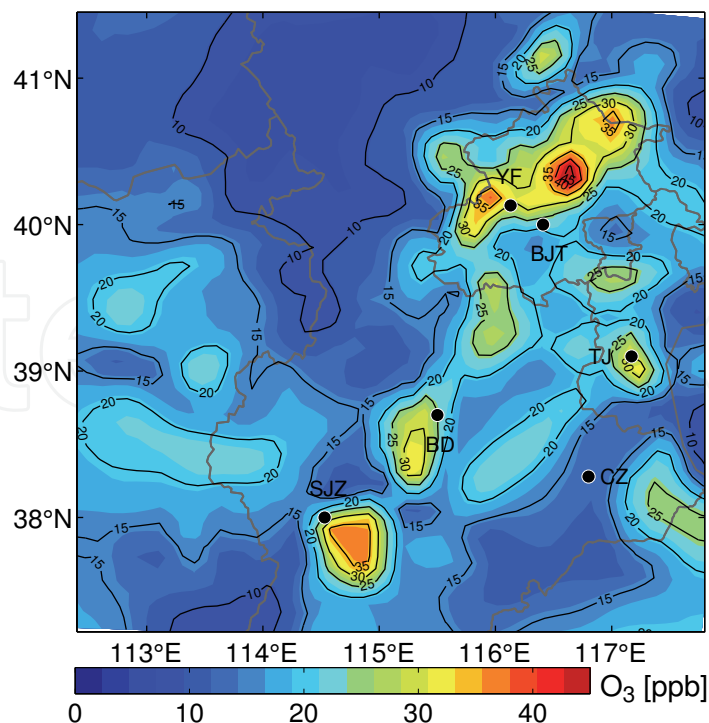
Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on
Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China
201

Fig. 2. Largest enhancements of daily maximum 1-h O$_3$ (ppb) in Beijing, Tianjin, and Hebei Province in August of 2007 due to the NO$_2^*$ chemistry (Case S – Case R). YF, BJT, TJ, CZ, BD, and SJZ denotes Site Yangfang, Beijing Tower, Tianjin, Cangzhou, Baoding, and Shijiazhuang, respectively.
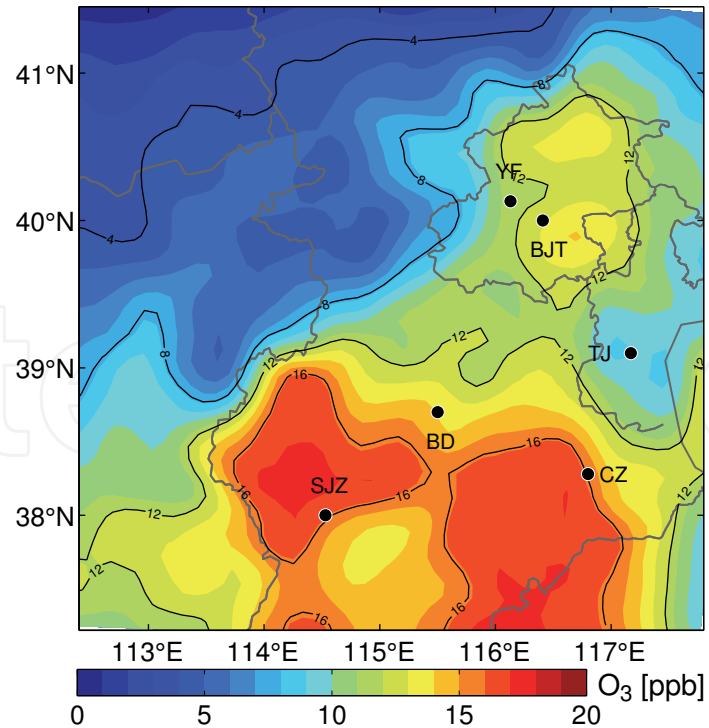

Fig. 3. Monthly mean enhancements of daily maximum 8-h O$_3$ (ppb) near the surface in August 2007 due to the NO$_2^*$ chemistry (Case S – Case R). YF, BJT, TJ, CZ, BD, and SJZ are the same as mentioned in Fig. 2.
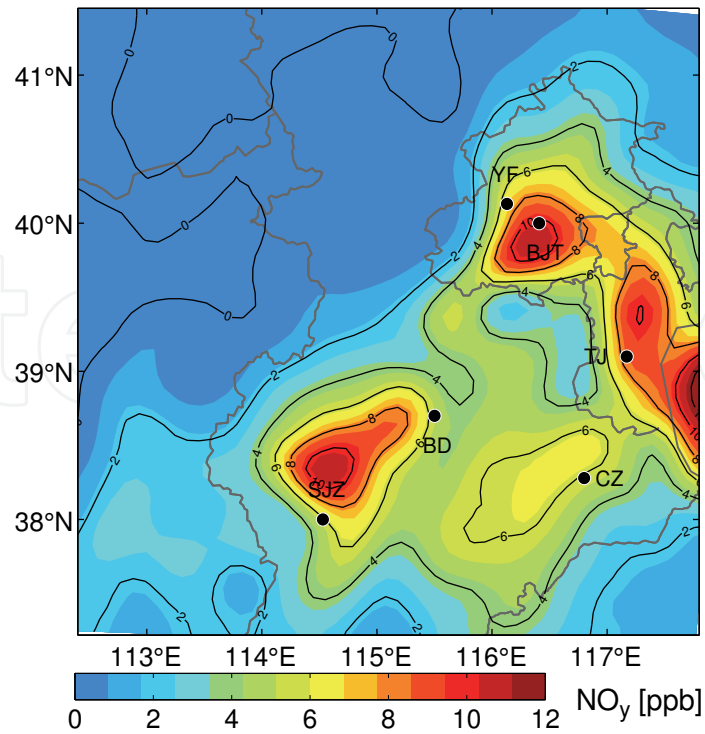
Fig. 4. Monthly mean daytime NO_y concentration differences (ppb) near the surface in August 2007 due to the NO_2^* chemistry (Case S – Case R). YF, BJT, TJ, CZ, BD, and SJZ are the same as mentioned in Fig. 2.

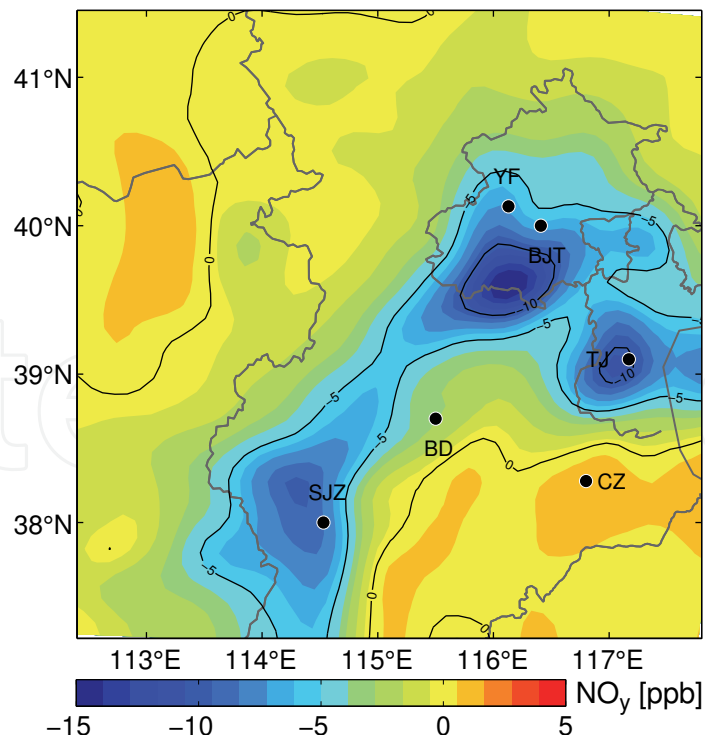Fig. 5. Monthly mean daytime NO_y concentration differences (ppb) near the surface in August 2007 due to heterogeneous reactions on aerosol surfaces (Case E – Case T). YF, BJT, TJ, CZ, BD, and SJZ are the same as mentioned in Fig. 2.

Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on
Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China

203

For monthly mean daytime surface NO$_y$ concentrations the NO$_2^*$ chemistry causes 4~15 ppb increases in the BTH region and the largest enhancement is found near the Bohai Bay (Fig. 4.) due to much lower heights of the planetary boundary layer (PBL) and much higher values of relative humidity around the Bohai Bay than those in the other areas of the BTH (Figures are not shown here). This agrees with the results of Sarwar et al. (2009).

Elevated PM concentrations in Beijing, Tianjin, and Shijiazhuang lead to 5~15 ppb decreases in monthly mean daytime NO$_y$ concentrations near the surface when heterogeneous reactions on aerosol surfaces are considered (Fig. 5.). Comparatively, during the nighttime high relative humidity, low heights of the PBL, and stable atmospheric conditions are favorable for enhancements in PM concentrations and PM hygroscopic growth rates and finally result in 10~29 ppb decreases in the nighttime NO$_y$ concentrations in Beijing, Tianjin, and Shijiazhuang cities and increases in areas with the reduced nighttime NO$_y$ concentrations being larger than 10 ppb over the BTH region (Fig. 6.).
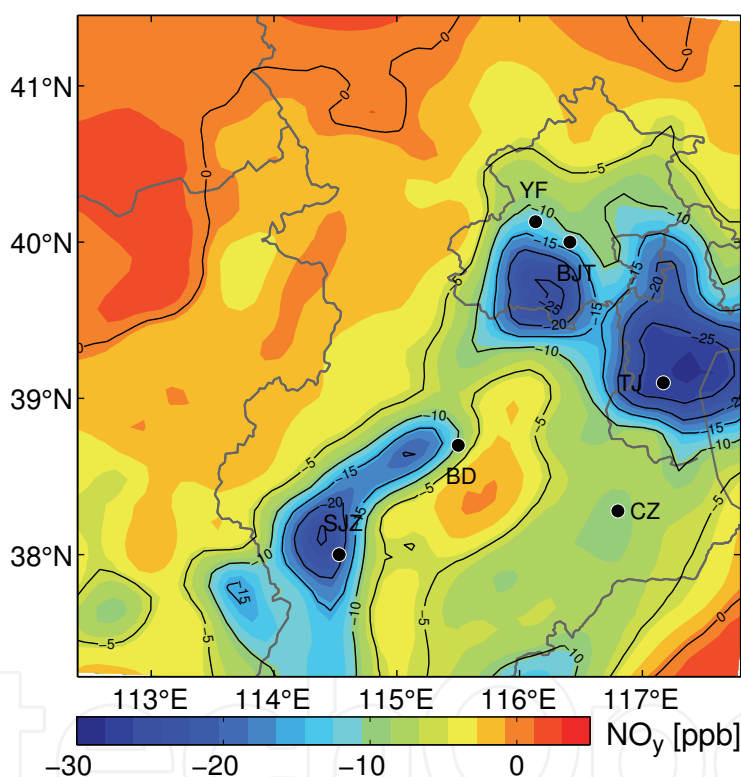

Fig. 6. Monthly mean nighttime NO$_y$ concentration differences (ppb) near the surface in August 2007 due to heterogeneous reactions on aerosol surfaces (Case E – Case T). YF, BJT, TJ, CZ, BD, and SJZ are the same as mentioned in Fig. 2.

3.2 Comparison of simulations and observations
3.2.1 Observed data used for model comparison

HONO observations in Beijing in August 13-25 of 2007 were from Zhu et al. (2009). HONO concentrations were measured by the differential optical absorption spectroscopy (DOAS), which was described in detail by Zhu et al. (2009) and Qin et al. (2006). The specific detection limits are 0.41 ppb for HONO, 2.17 ppb for O$_3$, and 0.63 ppb for NO$_2$, respectively (Zhu et al., 2009). O$_3$ and NO$_x$ were also simultaneously monitored at seven sites across

Beijing, Tianjin, and Hebei Province (BTH region), partially as the Beijing Atmospheric Environmental Monitoring Action conducted by Chinese Academy of Sciences. The detection limit of a Thermo Environmental Instrument (TEI) model 49 analyzer is 2 ppb for O_3, and that of a conventional chemiluminescent gas analyzer (TEI Model 42C) is 0.05 ppb for NO_2. Li et al. (2010) find that there is a nice agreement between O_3 and NO_2 measurements from DOAS and Chemiluminescence in Beijing. The correlation coefficient is 0.97 for O_3 and that is 0.83 for NO_2. The intercept of 0.75 for NO_2 is much better than that of 12.0 given by An et al. (2009). This is due to inclusion of heavy emissions from the Badaling expressway for DOAS measurements, and also confirms the suggestions of An et al. (2009).

3.2.2 Comparison of simulated and observed HONO concentrations

For Case R simulated hourly HONO concentrations are always considerably underestimated by comparison with observations in the period of August 13-25, 2007 (Fig. 7a). Diurnal averages in 13 days (August 13-25, 2007) are approximately 25 times lower than observations (Fig. 7b). The mean bias (MB), the normal mean bias (NMB), the root mean square error (RMSE), the normal mean error (NME), and the correlation coefficient (RC) is -0.98 ppb, -97%, 1.10 ppb, 97%, -0.56, respectively. When the four HONO sources are included (Case E), the WRF-CHEM model well simulates observed HONO daily variations within the studied period (Fig. 7a) and simulated daytime HONO concentrations are also considerably improved (Fig. 7b). This leads to significant improvements in diurnal averaged HONO levels, and the corresponding MB, NMB, RMSE, NME, and RC is improved to -0.28 ppb, -28%, 0.37 ppb, 29%, 0.91, respectively.
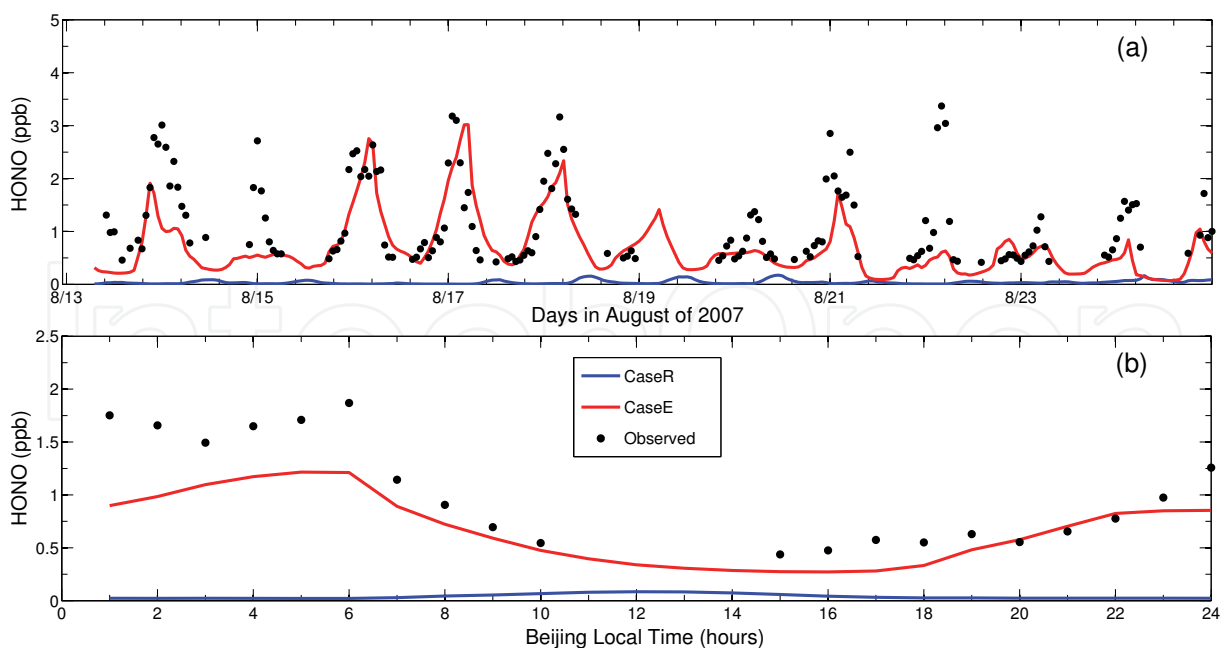

Fig. 7. Comparison of simulated hourly mean (a) and (b) diurnal-mean HONO concentrations (ppb) with observations from DOAS in August 13-25 of 2007.

Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on
Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China

205

3.2.3 Comparison of simulations and observations of O$_3$ and NO$_2$

Daily O$_3$ peaks are substantially improved in most cases when the four HONO sources are included (Case E) although Cases R and E show similar daily O$_3$ variations (Fig. 8.). This further indicates the importance of the NO$_2^*$ chemistry, heterogeneous reactions on aerosol surfaces, secondary HONO formation from the NO$_2$ heterogeneous reaction with semivolatile organics, and direct emissions in the industrialized region with high emissions of NO$_x$, VOCs and PM. Daily NO$_x$ simulations also demonstrate certain improvements at some sites, e.g., Sites Baoding and Shijiazhuang, in different days (Fig. 9.). For diurnal averages in 13 days (August 13-25, 2007) the O$_3$ peak is improved (Case E, Fig. 10a), with an increase of 25.5 ppb (= 64.2 - 38.7 ppb). NO variations are excellently reproduced both in the day and at night (Fig. 10c). NO$_2$ levels are well simulated in the nighttime whereas those are underestimated in the daytime (Fig. 10b).
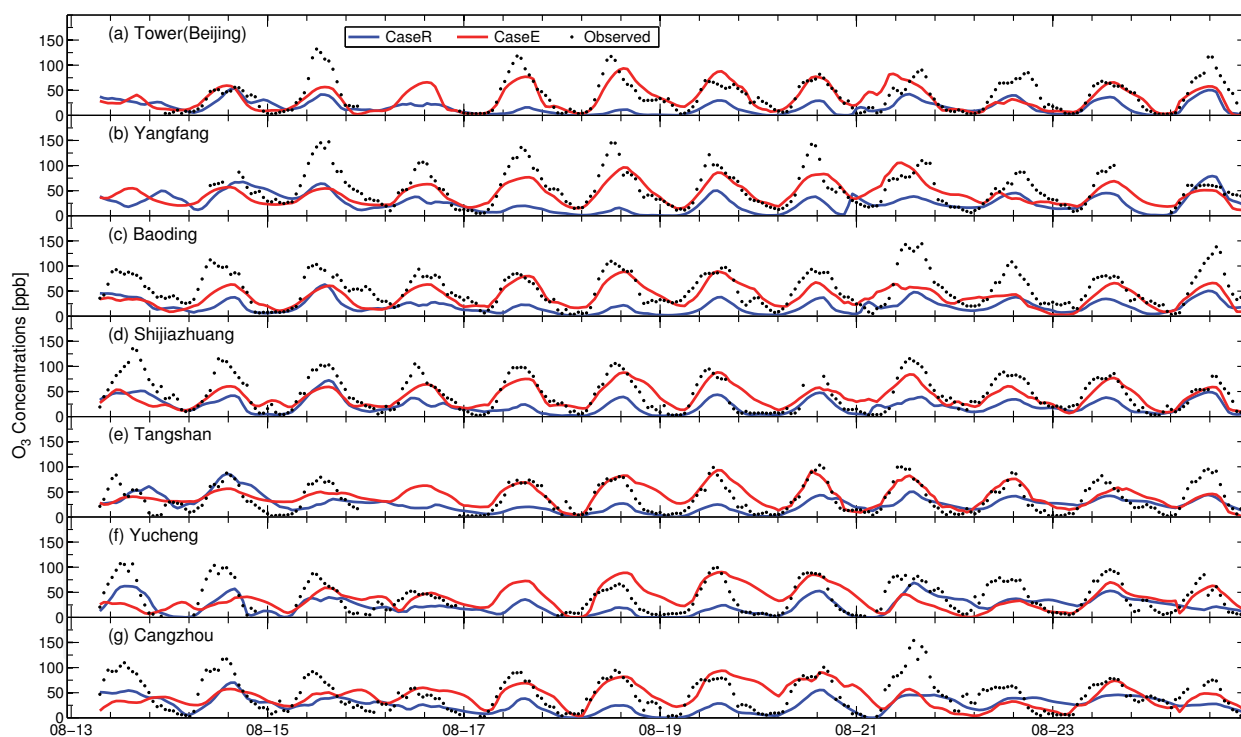

Fig. 8. Simulated and observed O$_3$ concentrations (ppb) at seven sites in Beijing, Tianjin, and Hebei Province in August 13-25 of 2007. O$_3$ measurements are from Chemiluminescence.
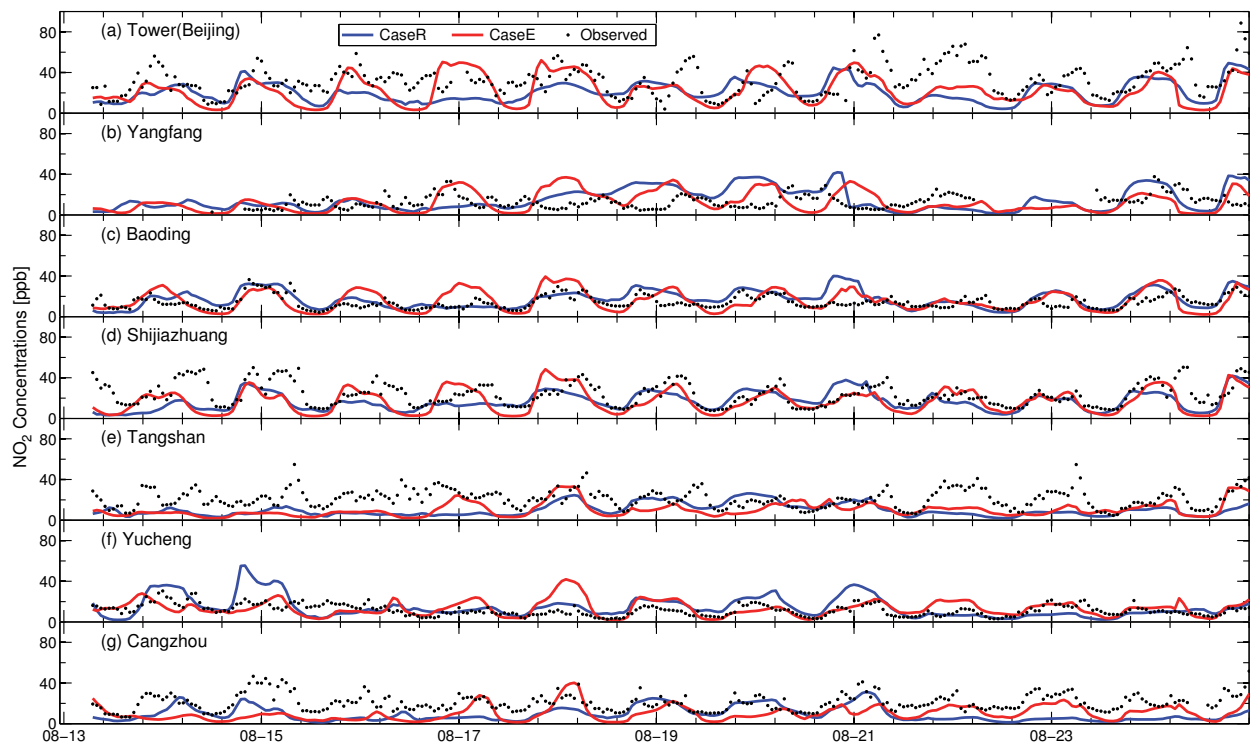
Fig. 9. Simulated and observed NO_2 concentrations (ppb) at seven sites in Beijing, Tianjin, and Hebei Province in August 13-25 of 2007. NO_2 measurements are from Chemiluminescence.

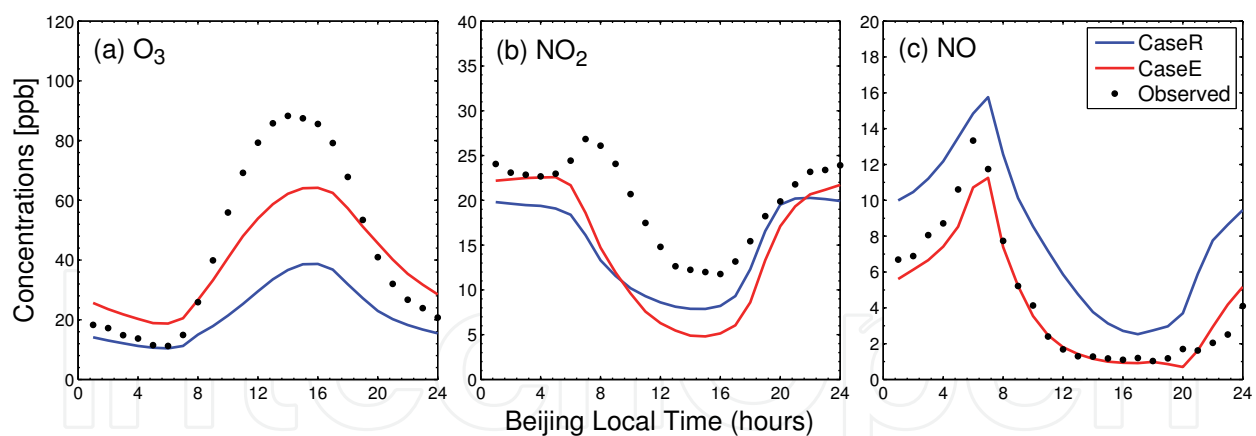Fig. 10. Comparison of simulated diurnal-mean O_3 (a), NO_2 (b), and NO (c) concentrations with observations (ppb) averaged over all monitoring sites in August 13-25 of 2007.

4. Conclusions

Incorporated into the state-of-the-art WRF-CHEM model were four sources of HONO, i.e., photoexcited NO_2 (NO_2^*) chemistry, heterogeneous reactions on aerosol surfaces, secondary HONO formation from the NO_2 heterogeneous reaction with semivolatile organics, and direct emissions, and simulations were conducted in Beijing, Tianjin, and Hebei Province (BTH region) in August of 2007. Results indicate that the NO_2^* chemistry and heterogeneous

Impacts of Photoexcited NO₂ Chemistry and Heterogeneous Reactions on
Concentrations of O₃ and NOᵧ in Beijing,Tianjin and Hebei Province of China

207

reactions on aerosol surfaces have considerable impacts on concentrations of O_3 and NO_y (total reactive N-containing compounds) in the BTH region. The NO_2^* chemistry produces 30~50 ppb enhancements in daily maximum 1-h surface O_3 concentrations in major cities, 8~18 ppb enhancements in monthly mean daily maximum 8-h surface O_3 concentrations, and 4~15 ppb increases in monthly mean daytime surface NO_y concentrations over the BTH region. Heterogeneous reactions on aerosol surfaces lead to 5~15 ppb decreases in monthly mean daytime NO_y concentrations and further substantial decreases in monthly mean nighttime NO_y concentrations, with a maximum decrease of nearly 29 ppb in major cities over the BTH region. This suggests that inclusion of the four HONO sources could aggravate acid deposition in industrialized areas with high emissions of NO_x (NO + NO_2), volatile organic compounds, and particulate matter. Comparison with observations indicates that HONO simulations are significantly improved and O_3 concentrations are well simulated in most cases when the four sources of HONO are included in the WRF-CHEM model.

5. Acknowledgement

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Impacts of Photoexcited NO$_2$ Chemistry and Heterogeneous Reactions on
Concentrations of O$_3$ and NO$_y$ in Beijing,Tianjin and Hebei Province of China

209

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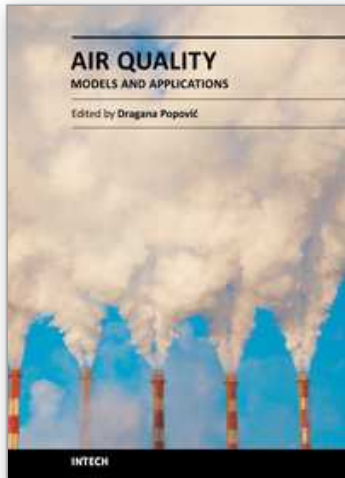
Air Quality-Models and Applications

Edited by Prof. Dragana Popovic

Air pollution has been a major transboundary problem and a matter of global concern for decades. High concentrations of different air pollutants are particularly harmful to large cities residents, where numerous anthropogenic activities strongly influence the quality of air. Although there are many books on the subject, the one in front of you will hopefully fulfill some of the gaps in the area of air quality monitoring and modeling, and be of help to graduate students, professionals and researchers. The book is divided in five sections, dealing with mathematical models and computing techniques used in air pollution monitoring and forecasting; air pollution models and application; measuring methodologies in air pollution monitoring and control; experimental data on urban air pollution in China, Egypt, Northeastern U.S, Brazil and Romania; and finally, the health effects due to exposure to benzene, and on the influence of air pollutants on the acute respiratory diseases in children in Mexico.

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Junling An, Ying Li, Feng Wang and Pinhua Xie (2011). Impacts of Photoexcited NO2 Chemistry and Heterogeneous Reactions on Concentrations of O3 and NOy in Beijing,Tianjin and Hebei Province of China, Air Quality-Models and Applications, Prof. Dragana Popovic (Ed.), ISBN: 978-953-307-307-1, InTech, Available from: http://www.intechopen.com/books/air-quality-models-and-applications/impacts-of-photoexcited-no2-chemistry-and-heterogeneous-reactions-on-concentrations-of-o3-and-noy-in

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