Impacts of additional HONO sources on $O_3$ and PM$_{2.5}$
chemical coupling and control strategies in the Beijing–Tianjin–Hebei region of China

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ABSTRACT

The objective of this work is to examine the impacts of additional HONO sources on the chemical interaction between ozone ($O_3$) and particulate matter with a diameter $\leq 2.5$ $\mu$m (PM$_{2.5}$). Three additional HONO sources, i.e. HONO emissions, the reaction of photo-excited nitrogen dioxide (NO$_2^*$) with water vapour (H$_2$O), and NO$_2$ heterogeneous reaction on aerosol surfaces, were inserted into the fully coupled Weather Research and Forecasting-Chemistry model to evaluate $O_3$ and PM$_{2.5}$ concentration enhancements in the Beijing–Tianjin–Hebei (BTH) region during August 2007. Results show that the additional HONO sources significantly increase $O_3$ and PM$_{2.5}$ concentrations during daytime. Up to 9 ppb enhancements of $O_3$ and 32 $\mu$g m$^{-3}$ increases in PM$_{2.5}$ are found at seven urban sites over the BTH region. $O_3$ increases are closely connected to PM$_{2.5}$ increases over urban areas during daytime when the additional HONO sources are taken into account. PM$_{2.5}$ inorganic components of SO$_2^-$, NO$_3^-$ and NH$_4^+$ are increased by 5–18, 10–58 and 10–40%, respectively, over urban areas during daytime. The simultaneous increment of $O_3$ and PM$_{2.5}$ during daytime due to the additional HONO sources is related to the increasing oxidants (OH, H$_2$O$_2$ and $O_3$) that enhance the atmospheric oxidising capacity. The concentration variations of $O_3$ and PM$_{2.5}$ under a variety of NOx, volatile organic compound and ammonia (NH$_3$) emission control scenarios show that the additional HONO sources increase the sensitivity of $O_3$ and PM$_{2.5}$ concentrations to the changes of NOx emissions. An increase of the PM$_{2.5}$ sensitivity to changes in NH$_3$ emissions is also found. This indicates that without considering the additional HONO sources, the effectiveness of emission control strategies in reducing $O_3$ and PM$_{2.5}$ concentrations would be significantly underestimated.

Keywords: HONO sources, $O_3$ and PM$_{2.5}$ chemical coupling, control strategy, WRF-Chem model

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1. Introduction

Nitrous acid (HONO) plays an important role in enhancing $O_3$ and particulate matter (PM) concentrations in the polluted atmospheric boundary layer due to its photolysis into the hydroxyl radical (OH), which is a primary daytime oxidant (Alicke et al., 2002; Kleffmann et al., 2005). Jenkin et al. (2008) showed that increasing HONO emissions by 5% resulted in $O_3$ enhancements of 11 ppb in the southern UK during a heat-wave period of August 2003. Besides direct emissions, HONO can also be formed through gas-phase or heterogeneous reactions. The homogeneous gas-phase reaction between excited nitrogen dioxide (NO$_2^*$) and H$_2$O (NO$_2^*$ + H$_2$O $\rightarrow$ HONO + OH, hereafter referred to as NO$_2^*$ chemistry) has gained interest since its reaction rate
has been found at an order of magnitude faster than the previously estimated upper limit (Crowley and Carl, 1997), thus can substantially enhance OH production (Li et al., 2008). However, the atmospheric significance of this new mechanism is highly controversial. Carr et al. (2009) argued that the NO2 chemistry would not be important under normal atmospheric conditions and they estimated the reaction rate similar to the result of Crowley and Carl (1997) (1.2 × 10^{-14} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}). Amedro et al. (2011) claimed that no OH radicals were observed using an unfocused excitation laser beam at 565 nm, but OH formation was observed by focusing the laser beam. Recently, Wu and Chen (2012) concluded that the reaction of two photon absorbed NO2 with H2O makes negligible contributions to the formation of OH radicals while single photon absorption at <554 nm is a possible process.

The uncertainties in the NO2 chemistry did not prevent the evaluation of its potential impact on tropospheric air quality using chemical transport models. Simulations conducted in the South Coast Air Basin of California during the summer of 1987 showed that the NO2 chemistry increased O3 and PM2.5 (PM with a diameter ≤2.5 μm) concentrations by as much as 55 ppb and 20 μg m⁻³, respectively (Wennberg and Dabdub, 2008). However, due to the lower ambient NOx and volatile organic compound (VOC) levels, the impact of the NO2 chemistry on O3 enhancement was found to be smaller in the U.S. after the year of 2000. The maximum increases of O3 concentrations in urban areas in the U.S. less than 10 ppb (Sarwar et al., 2009; Ensberg et al., 2010) suggest that the effect of the NO2 chemistry on pollution levels may be more significant in some industrialised regions with elevated levels of ambient NOx and VOCs, such as mega-cities in China. Thereafter studies reported that O3 enhancements were more than 30 ppb in Beijing (Li et al., 2011) and Taiwan (Jorba et al., 2012), and 10 ppb over the urban areas of the Pearl River Delta region of China (Zhang et al., 2013).

Along with the direct emissions and the homogeneous formation of HONO, NO2 heterogeneous reaction on wet surfaces (2NO2 + H2O → HNO3 + HONO) is commonly considered as one of the major HONO heterogeneous sources (Jenkin et al., 1988; Kleffmann et al., 1998; Finlayson-Pitts et al., 2003). The NO2 heterogeneous reaction has been included previously in the Community Multiscale Air Quality (CMAQ) modelling system (Foley et al., 2010). The CMAQ simulations showed that the NO2 heterogeneous reaction was found to be the most significant source of nocturnal HONO formation during the project of the Northeast Oxidant and Particle Study in the U.S. (Sarwar et al., 2008). The simulations conducted over the Beijing–Tianjin–Hebei region (referred as BTH region), as the most polluted areas in China, suggested that the largest enhancements of the monthly mean daytime O3 and PM2.5 during August 2007 were about 12 and 16%, respectively, and this was mostly due to the NO2 heterogeneous reaction on aerosol surfaces (An et al., 2013).

In addition to direct emissions, homogeneous gas-phase formation and heterogeneous reactions, a recent study has demonstrated that ammonia-oxidising bacteria in soil can directly release HONO (Oswald et al., 2013). The soil HONO emissions may play an important role in the biogeochemical and atmospheric nitrogen cycles. This finding helps understand how the biosphere affects the atmosphere and global climate. Before this new mechanism can be incorporated into chemical transport models, continuous and comprehensive field measurements are needed, including simultaneous monitoring of soil, ecosystem and atmospheric processes.

Previous studies mainly focused on the impacts of HONO sources on O3 and PM2.5 concentrations but rarely considered the relationship between O3 and PM2.5 enhancements due to HONO sources. Meng et al. (1997) pointed out that there was a complex chemical coupling between O3 and PM2.5 components because they shared the same precursors as NOx and VOCs. In-situ observations also proved that severe PM pollution was often accompanied with high O3 concentrations. Positive correlation between the daily PM2.5 and maximum 8-h O3 (O3_8h,max) concentrations was also observed over the BTH region during the Beijing 2008 Olympic Games (Xin et al., 2010). When additional HONO sources were considered in the O3 and PM2.5 interaction, another level of complexity was added into the chemical coupling system (Wennberg and Dabdub, 2008) and this impacted O3 and PM2.5 emission control strategies (Meng et al., 1997). Ensberg et al. (2010) studied the impacts of the NO2 chemistry on O3 and PM control strategies over the South Coast Air Basin of California during two emission episodes that occurred for 1987 and 2005. They showed that the NO2 chemistry increased the sensitivity of O3 and secondary PM concentrations with respect to changes in NOx emissions (Ensberg et al., 2010). Notable changes in O3 responses to NOx and VOC emission controls were also found in the Pearl River Delta of China due to the NO2 chemistry (Zhang et al., 2013). These studies suggested that the additional HONO sources had significant implications for polluted areas to achieve ozone and PM air quality standards.

In spite of considerable improvements in air quality indexes over the last decade, the BTH region continues to suffer from severe O3 and PM pollution as well as haze (Chan and Yao, 2008; Sun et al., 2013; Zhao et al., 2013). Significant O3 and PM2.5 enhancements over the BTH region during August 2007 due to three additional HONO sources (including HONO emissions, the NO2 chemistry and NO2 heterogeneous reaction on aerosol surfaces) were also reported by Li et al. (2011) and An et al. (2013).
These works suggested that more strict conditions on O₃ and PM concentration standards were needed to be set up. Presently, the China’s Grade-2 Standard list¹ includes the daily O₃₈h;max at 160 µg m⁻³ and 24-h average PM₂.₅ at 75 µg m⁻³.

There are two main objectives in this study: (1) to analyse the relationship between the enhancements of daytime O₃ and PM₂.₅ as a function of the additional HONO sources and (2) examine the reductions of daily O₃₈h;max and 24-h averaged PM₂.₅ concentrations as functions of NOₓ, VOC and NH₃ emission reductions when the additional HONO sources are considered. Section 2 is introduced for the numerical experiments conducted in this study. Section 3 describes observation data used in the model evaluation. The effects of the additional HONO sources on O₃ and PM₂.₅ chemical coupling and control strategies are discussed in Section 4 and the conclusions are presented in Section 5.

2. Model description

2.1. WRF-Chem model and new parameterisation of HONO

This study utilised a fully coupled Weather Research and Forecasting-Chemistry (WRF-Chem) model (Grell et al., 2005; Fast et al., 2006) with the gas phase chemical Carbon-Bond Mechanism Z (CBM-Z; Zaveri and Peters, 1999) and aerosol module of the Model for Simulating Aerosol Interactions and Chemistry (MOISAC; Zaveri et al., 2008). The physical schemes for simulations were identical to those chosen by Li et al. (2011).

Figure 1 shows the domains of the simulations. Domain 1, 2 and 3 primarily cover the Eastern Asia, Northern China and BTH region, respectively. Domain 3 contains 54 × 54 grids with a grid resolution of 9 km and centres at 40°N, 116°E. The 28 vertical layers extend from the surface to 50 hPa with the first level at 28 m above the ground. Meteorological initial and boundary conditions were obtained from the US National Centers for Environmental Prediction (NCEP; 6-h, 1° × 1°) final operation global analysis dataset. Chemical initial and boundary conditions were interpolated from the Model for OZone And Related chemical Tracers version 4 (MOZART-4; Emmons et al., 2010) outputs at every 6 h. Monthly anthropogenic emissions covering East Asia with a grid resolution of 0.5° × 0.5° were adopted from Zhang et al. (2009). Future emission inventory over this region requires a finer grid resolution to help air quality models better capture the localised photochemistry in the atmosphere. Biogenic emissions were calculated based on Guenther et al. (1993) and Simpson et al. (1995).

The following input for model reference simulation and test runs was considered. Besides HONO gas-phase production from OH and NO, three additional HONO sources...
(i.e. HONO emissions, the NO$_2$ chemistry and NO$_2$ heterogeneous reaction on aerosol surfaces) were coupled into the WRF-Chem model. Li et al. (2011, 2014) and An et al. (2013) have described the parameterisation schemes in detail. Briefly, HONO emissions included direct emissions estimated as 0.8% of NO$_x$ emissions (Kurtenbach et al., 2001) and 2.3% of the NO$_x$ emitted in diesel exhaust gases converted to HONO via heterogeneous reaction with semi-volatile organics (Gutzwiller et al., 2002). The ratio of HONO/NO$_x$ used in the model set up was about 1.18% in the urban centre of Beijing (Li et al., 2011; An et al., 2013). The rate constant for the reaction of NO$_2$ with H$_2$O was estimated as 9.1 x 10$^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ which was similar to the mean values of Li et al. (2008) and Crowley and Carl (1997). The NO$_2$ heterogeneous reaction on aerosol surfaces followed Jacob (2000) recommendations. To compute the reaction rate, the total aerosol surface area ($S_a$) per unit volume of air is derived from aerosol mass concentrations and number density in eight size bins set by the MOSAIC aerosol module. The mean calculated $S_a$ was 1367 µm$^2$ cm$^{-3}$ in Beijing during August 2007, within the observed range of 1000–2500 µm$^2$ cm$^{-3}$ (Spataro et al., 2013).

2.2. Experimental design

Five simulations given in Table 1 were conducted in this study. The first one was a reference case (Case R) that was performed using the standard CBM-Z mechanism and the MOSAIC module. Case Emis, Case NO$_2$ and Case Het were extensions of Case R by inclusion of HONO emissions, the NO$_2$ chemistry and the NO$_2$ heterogeneous reaction, respectively. The last simulation referred as an enhanced case (Case E) contained all the three additional HONO sources. The simulation period was August 2007, during which an extensive observed dataset was obtained, including highly time-resolved ambient gas phase species and aerosols (see Section 3).

**Table 1.** Design of WRF-Chem simulations to evaluate the effects of the additional HONO sources

| Case ID | HONO sources included in the WRF-Chem simulations |
|---------|--------------------------------------------------|
| Case R  | Reference case with HONO gas-phase production from OH and NO |
| Case Emis | Case R + HONO emissions |
| Case NO$_2$ | Case R + NO$_2$ chemistry |
| Case Het | Case R + NO$_2$ heterogeneous reaction on aerosol surfaces |
| Case E  | Enhanced case with all the three additional HONO sources |

Additional sensitivity runs for the impacts of the three additional HONO sources on O$_3$ and PM$_{2.5}$ control strategies were conducted on 17 August 2007 when the BTH region experienced exceedingly high ozone and PM levels. The daily O$_{3,8h}$ in Beijing violated China’s Grade-2 Standard values. In order to save the computational time, four emission scaling factors, i.e. 1, 0.75, 0.5 and 0.25, are employed. The reference case emissions (Zhang et al., 2009) of NO$_x$, VOCs and NH$_3$ were multiplied by the scaling factors individually, leading to 64 emission scenarios. The 128 (64 x 2) sensitivity simulations were conducted for Domain 3. The first 64 scenarios employed the standard CBM-Z and MOSAIC modules and the remaining 64 scenarios included the three additional HONO sources. All of the simulations started with the initial conditions at 00:00/16/8/2007 (UTC) using the standard CBM-Z and MOSAIC modules for the reference case emissions, then they were integrated from 00:00/16/8/2007 to 00:00/18/8/2007 (UTC) under different emission scenarios.

3. Observations and data

The HONO concentrations were measured on a 24-h basis by the annular denuder system at the campus of Peking University (39.99° N, 116.28° E) from 2 to 31 August 2007 as part of the CAREBeijing-2007 Experiment (2007 Campaigns of Air Quality Research in Beijing; Spataro et al., 2013). Measurements of NO$_2$, nitrate (NO$_3$) and ammonium (NH$_4$) were also used in this study (Ianniello et al., 2011). Hourly HONO concentrations were taken from Differential Optical Absorption Spectroscopy (DOAS) measurements in Beijing from 13 to 25 August 2007 (Zhu et al., 2009). The retroreflector array was placed on a platform at 15 m of the 325 m Meteorological Tower located at the Institute of Atmospheric Physics (IAP; 39.97° N, 116.37° E). The fixed light path was 470 m (one way) across an expressway (Li et al., 2011). Hourly measurements of meteorological parameters including air temperature (T), relative humidity (RH), wind speed (WS) and direction (WD) from 13 to 20 August were adopted from the Olympic Village (40.00° N, 116.37° E) site close to IAP because the observed meteorological data at the tower site were unavailable within the studied period. There was no precipitation happening during this period. Observations of the surface NO$_2$, O$_3$ and PM$_{2.5}$ concentrations over the BTH region were obtained from the Beijing Atmospheric Environmental Monitoring Action which was supported by the Beijing Olympic Technological Project (Xin et al., 2010; Gao et al., 2011). Hourly measurements of NO$_2$, O$_3$ and PM$_{2.5}$ at seven urban sites shown in Fig. 1 (Li et al., 2011) were used in the analysis.
4. Results and discussion

4.1. Model validation

Previously, the comprehensive model evaluations have been conducted for Case Emis, Case NO$_2$ and Case Het (Li et al., 2011; An et al., 2013; Tang et al., 2014). In this section, the simulation results for Case R and Case E are evaluated to examine the performance of the extended WRF-Chem model with the three additional HONO sources. Figure 2 shows the simulations of 24-h average concentrations of HONO, NO$_2$, NO$_3^-$ and NH$_4^+$ compared to the measurements conducted at Peking University in Beijing during August 2007. The mean simulated HONO concentration is only 0.08 ppb in Case R. When the additional HONO sources are considered for Case E, the mean HONO concentration is improved up to 1.36 ppb. This value is very close to the observed mean of 1.43 ppb (Fig. 2a). The NO$_2$ concentrations in Case E are approximately 2–10 ppb lower than those in Case R (Fig. 2b), which is mostly due to the NO$_2$ heterogeneous reaction on aerosol surfaces. Although the simulated NO$_2$ agrees reasonably well with most of the observations (Fig. 2b), the simulated NO$_3^-$ overestimates the observations by 5–20% (Fig. 2c) for both Case R and Case E. This NO$_3^-$ overestimation was found in the whole Northeast Asian region (Kajino et al., 2012, 2013) and further investigation with additional observations is required. Both Case R and Case E well reproduce NH$_4^+$ variations and quantities (Fig. 2d). The correlation coefficient (R) is found as 0.59. The simulated mean NH$_4^+$ in Cases R and E are 8.55 and 10.27 µg m$^{-3}$, respectively.

The observed mean is 12.27 µg m$^{-3}$. The additional HONO sources significantly enhanced NO$_3^-$ and NH$_4^+$ concentrations (Fig. 2c, d), and this resulted in an increase for PM$_{2.5}$ concentrations (An et al., 2013).

The comparison between the simulated and observed hourly concentrations of HONO and OH at the Meteorological Tower in Beijing, NO$_2$, O$_3$ and PM$_{2.5}$ at the seven urban sites over the BTH region are shown in the Supplementary file and our previous studies (Li et al., 2011; An et al., 2013; Tang et al., 2014). The simulations generally captured the diurnal variations of pollutants at different sites of the BTH region. The comparative statistics for Case E are given in Table 2. The variations of T, RH, WS and WD near the Meteorological Tower site are generally simulated well. During 13–20 August 2007 the high temperature and humidity values during low speed of southerly wind existed in Beijing. The meteorological conditions as well as the large emissions of NOx from the heavy traffic (An et al., 2009) nearby the sampling site resulted in the high HONO concentrations. The Case E average predicted HONO concentrations of 1.69 ppb agreed reasonably with the measured concentration of 1.27 ppb. The simulations of Case E also generally captured the hourly variations of NO$_2$, O$_3$ and PM$_{2.5}$ at the seven urban sites over the BTH region, with the correlation coefficients being 0.52, 0.87 and 0.51, respectively. The FAC2 (fractions of simulated values within a factor of two of the observed values) for NO$_2$, O$_3$ and PM$_{2.5}$ are 0.50, 0.62 and 0.64, respectively (Table 2).

For daytime (7:00–19:00, LT) and night (20:00–6:00, LT) conditions, HONO simulations for Case R and

![Fig. 2. Comparison of simulated 24-h average (a) HONO, (b) NO$_2$, (c) NO$_3^-$ and (d) NH$_4^+$ concentrations with observations at Peking University during August 2007 (Ianniello et al., 2011; Spataro et al., 2013). Case R is a reference case; Case E includes the HONO emissions, NO$_2$ chemistry and NO$_2$ heterogeneous reaction on aerosol surfaces.](image-url)
Case E are compared with the observations for the Meteorological Tower (Fig. 3a). The additional HONO sources significantly improved HONO simulations for both daytime and night-time. The simulated mean concentration of HONO for daytime increased from 0.10 ppb in Case R to 0.51 ppb in Case E, and for night-time, it increased from 0.21 ppb to 0.46 ppb. The observed mean concentration of HONO was 0.49 ppb for daytime and 0.25 ppb for night-time. The model results for Case E show a better agreement with the observations, as indicated by the higher mean and median concentrations and the lower mean bias (MB) and root mean square error (RMSE) values.

Table 2. Statistics for comparison of the observed (Obs.) and simulated (Sim.) hourly data during August 13–20, 2007

| Units | T | RH | WS | WD | HONO | NO₂ | O₃ | PM₂.₅ |
|-------|---|----|----|----|------|-----|----|-------|
|       | °C | %  | m s⁻¹ | deg | ppb  | ppb | ppb | μg m⁻³ |
| Number of data | 184 | 184 | 184 | 117 | 1304 | 1194 | 1340 |
| Median (Obs.) | 28.00 | 68.00 | 1.40 | 135.0 | 0.89 | 17.02 | 37.23 | 94.78 |
| Median (Sim.) | 29.15 | 41.11 | 2.11 | 190.7 | 1.49 | 20.79 | 32.77 | 143.86 |
| Mean (Obs.) | 28.05 | 66.45 | 1.46 | 136.35 | 1.27 | 19.29 | 44.61 | 100.11 |
| Mean (Sim.) | 28.92 | 43.29 | 2.34 | 185.74 | 1.69 | 24.62 | 38.62 | 161.18 |
| MB | 0.87 | 23.15 | 0.87 | 49.40 | 0.42 | 5.33 | 61.07 |
| NMB | 34 | 52 | 36 | 33 | 28 | 13 | 61 |
| RMSE | 1.85 | 24.78 | 1.60 | 133.56 | 1.05 | 19.01 | 18.59 | 96.84 |
| R | 0.94 | 0.88 | 0.47 | 0.42 | 0.71 | 0.52 | 0.87 | 0.51 |
| FAC² | 1.0 | 0.98 | 0.55 | 0.58 | 0.60 | 0.50 | 0.62 | 0.64 |

Observations of HONO are from the Beijing Meteorological Tower and the meteorological parameters are from the Olympic Village near to the tower site (see Section 3). NO₂, O₃ and PM₂.₅ measurements are from the seven urban sites over the BTH region (Fig. 1). Model results are for Case E.

The unit of NMB is in %.

Fraction of simulations within a factor of two of observations.

Case E are compared with the observations for the Meteorological Tower (Fig. 3a). The additional HONO sources significantly improved HONO simulations for both daytime and night-time. The simulated mean concentration of HONO for daytime increased from 0.10 ppb in Case R to 0.51 ppb in Case E, and for night-time, it increased from 0.21 ppb to 0.46 ppb. The observed mean concentration of HONO was 0.49 ppb for daytime and 0.25 ppb for night-time. The model results for Case E show a better agreement with the observations, as indicated by the higher mean and median concentrations and the lower mean bias (MB) and root mean square error (RMSE) values.

Fig. 3. Observed and simulated (a) daytime (D, 7:00–19:00) and night-time (N, 20:00–6:00) mean concentrations of HONO at the Beijing Meteorological Tower site and (b–h) daytime mean concentrations of O₃ and PM₂.₅ at the seven urban sites over the BTH region during 13–20 August, 2007. The unit used is μg m⁻³ (at 1.01325 × 10⁵ Pa and 25°C, 1 μg m⁻³ is ~0.52 ppb for HONO and ~0.51 ppb for O₃).
0.06 ppb to 2.05 ppb. Figure 3b–h shows the daytime simulations of O₃ and PM₂.₅ at the seven urban sites over the BTH region. Both Cases R and E performed well for predicting O₃ and PM₂.₅ daytime concentrations. The observed and simulated means, the mean bias (MB), the normal mean bias (NMB), the root mean square error (RMSE) and FAC2 of O₃ for Case E are 64.97 ppb, 63.05 ppb, -1.92 ppb, -2.95%, 12.48 ppb, and 0.98, respectively; corresponding PM₂.₅ values for Case E are 94.01 μg m⁻³, 119.24 μg m⁻³, 25.23 μg m⁻³, 26.83%, 36.05 μg m⁻³ and 0.91, respectively.

4.2. Daytime enhancements of O₃ and PM₂.₅ due to the additional HONO sources

4.2.1. The chemical coupling between O₃ and PM₂.₅. The chemical coupling between O₃ and PM₂.₅ was emphasised in previous studies (Meng et al., 1997; Nguyen and Dabdub, 2002; Wennberg and Dabdub, 2008). This is of profound importance in understanding processes that control the concentrations of both O₃ and PM₂.₅. As shown in Fig. 4, OH is the essential oxidant during daytime. The OH oxidises VOC to produce O₃ in presence of NOₓ and oxidises SO₂ and NOₓ to produce secondary inorganic particulate in presence of NH₃. OH and O₃ attack on organic molecules can generate semivolatile secondary organic aerosol (SOA). HONO sources add another level of complexity to this mechanism. When the HONO emissions, NO₂ chemistry and NOₓ heterogeneous reaction on aerosol surfaces are considered, the OH formation is increased via the HONO photolysis and reaction of NO₂* with H₂O. The increases in OH concentrations simultaneously enhance O₃ and PM₂.₅ production. In addition, increasing O₃ concentration further increases the daytime formation of OH. The OH in turn reacts with NO₂ to form gas nitric acid (HNO₃). The NO₂ heterogeneous reaction on aerosol surfaces also contributes to HNO₃ enhancement, which eventually increases nitrate concentrations.

Although O₃ and PM₂.₅ are subjected to a complex series of common emissions and photochemical production pathways, the coupling between O₃ and PM₂.₅ is in a non-linear manner. O₃ production is related mainly to the VOCs and NOₓ gas-phase chemistry while PM₂.₅ production is contributed mostly to the gas-to-particle conversion processes, involving chemical reactions and mass transport in the gas and particle phases (Shiraiwa et al., 2014). The impacts of the additional HONO sources on O₃ and PM enhancements are found to be more significant over urban and coastal areas with high NOₓ emissions. On the other hand, the impacts are small in rural and background areas where NOₓ emissions are relatively low (Wennberg and Dabdub, 2008; Sarwar et al., 2009; An et al., 2011; Li et al., 2011; Elshorbany et al., 2012, 2014; Jorba et al., 2012; Zhang et al., 2013). In the regions with high VOCs to NOₓ ratios (e.g. rural areas), O₃ production is sensitive to NOₓ concentrations. The NOₓ reductions due to the NO₂ heterogeneous reaction can decrease O₃ production in rural areas. Therefore, the additional HONO sources are more likely to enhance O₃ and PM₂.₅ simultaneously in urban areas with a low ratio of VOCs to NOₓ. In those areas, decreasing NO₂ alone likely leads to increasing O₃ concentrations (Wennberg and Dabdub, 2008; Ensberg et al., 2010).

In order to investigate the impacts of the additional HONO sources on O₃ and PM₂.₅ chemical interactions, the enhancements of daytime mean concentrations of O₃ and PM₂.₅ at the seven urban sites during 13–20 August 2007 shown in Fig. 3 are demonstrated in scatter diagrams (Fig. 5). Both O₃ and PM₂.₅ daytime enhancements (Fig. 5a) due to the NO₂ chemistry are mostly less than 5 μg m⁻³ (for O₃, 1 μg m⁻³ = 0.51 ppb at 1.01325 x 10⁵ Pa and 25°C). Among the three additional HONO sources, the NO₂ heterogeneous reaction is the largest contributor to O₃ and PM₂.₅ enhancements. Up to 14 μg m⁻³ (7 ppb) and 28 μg m⁻³ increases are found for O₃ and PM₂.₅, respectively (Fig. 5b). The contributions of HONO emissions to O₃ and PM₂.₅ enhancements are relatively small (<2 μg m⁻³; not shown). The largest enhancements of daytime concentrations of O₃ and PM₂.₅ due to all the three additional HONO sources are estimated to be 17.27 μg m⁻³ (8.79 ppb) for O₃ and 31.54 μg m⁻³ for PM₂.₅ (Fig. 5c). Figure 5 also clearly shows that the daytime O₃ increases are closely related to the daytime PM₂.₅ increases. The correlation coefficients between O₃ and PM₂.₅ enhancements are 0.71 and 0.75, respectively, when the NO₂ chemistry and NO₂

Fig. 4. Impacts of the additional HONO sources on the chemical coupling between ozone and particulate matter. HONO sources increase OH concentrations and subsequently promote O₃ and PM production. HNO₃ produced from the NO₂ heterogeneous reaction on aerosol surfaces enhances nitrate concentrations in presence of NH₃.
heterogeneous reaction are individually included in the WRF-Chem model.

The correlation coefficient between the daytime enhancement of O3 and PM2.5 over the BTH region for the whole month was estimated. As shown in Fig. 6a, the correlation coefficients between O3 and PM2.5 daytime enhancements due to the additional HONO sources are greater than 0.6 in many urban areas and greater than 0.8 over Beijing and Tianjin areas. The high correlation is found mainly over the urban areas where the values of the linear-fitting slope for O3 and PM2.5 enhancements are above zero (Fig. 6b), indicating that the additional HONO sources increase O3 and PM2.5 concentrations simultaneously. The increases in both O3 and PM2.5 are because of the enhanced OH concentrations as demonstrated in Fig. 4. The significant increases in O3 concentrations occur in urban areas also
because O₃ production is mainly sensitive to VOC concentrations in those areas, where the NOₓ decreases due to the NOₓ heterogeneous reaction increase O₃. As shown in Fig. 6c, 2−5 ppb increases in the monthly mean daytime O₃ concentrations are found in Beijing, Tianjin and south of Hebei Province.

The ratio of H₂O₂/HNO₃ is often used as an indicator to identify VOC-sensitive or NOₓ-sensitive regimes (Sillman, 1995; Lam et al., 2005). The transition value of 0.4−0.8 is adopted in this study according to the field measurements conducted in Beijing (He et al., 2010): a value < 0.4 indicates a VOC-sensitive regime, a value > 0.8 indicates a NOₓ-sensitive regime, and otherwise it indicates an intermediate regime (Fig. 6d). Comparing Fig. 6a and d, it is found that the low correlation ( < 0.2) between O₃ and PM₂.₅ daytime enhancements occurs mainly over the rural areas, such as Taishan Mountains to the west of Hebei Province, and Yan Mountains to the north of Beijing. Those rural areas are within the NOₓ-sensitive regimes where NOₓ decreases due to the NOₓ heterogeneous reaction (see Fig. 2b and Li et al., 2011) will reduce O₃ (Fig. 6c). Daytime enhancements of O₃ and PM₂.₅ for all the simulated grids within the BTH region during August 2007 are presented in Supplementary Fig. 5. The correlation coefficients between O₃ and PM₂.₅ daytime enhancements are estimated as 0.83, 0.91 and 0.90, for the NOₓ chemistry, NO₂ heterogeneous reaction and the three additional HONO sources included in the simulations, respectively.

4.2.2. Impacts on concentrations of PM₂.₅ and its major components. The additional HONO sources enhance O₃ production mainly through increasing OH concentrations which will enhance PM₂.₅ production as well. However, the coupling between O₃ and PM₂.₅ production is in a non-linear way. As stated in Fig. 4, PM₂.₅ production also involves complex gas precursors that go through multi-phase chemical evolution. Figure 7 shows that the impacts of the additional HONO sources on individual PM₂.₅ components during daytime. NOₓ has the largest enhancements (10−58%, 4−9 µg m⁻³), followed by NH₄⁺ (10−40%, 1−3 µg m⁻³) and SO₄²⁻ (5−18%, 0.5−1.5 µg m⁻³). The large increment is found mainly in areas with high NOₓ levels, e.g. Beijing, Tianjin and south of Hebei Province. The HONO-related enhancement of NO₃⁻ is due to the enhanced OH level (10−40%, Fig. 7e) and the NOₓ heterogeneous reaction that produces more HONO (Fig. 7f). The reason for the enhancement of SO₄²⁻ is that the increasing OH can oxidise SO₂ to produce gas-phase H₂SO₄ and enhance H₂O₂ (Fig. 7g) and O₃ (Fig. 6c), which can oxidise dissolved SO₂ to produce SO₄²⁻ through aqueous phase reactions. The increases in HNO₃ and H₂SO₄ can be neutralised by NH₃ to form NH₄⁺. The NOₓ heterogeneous reaction and H₂O₂ enhancements are major reasons for night-time enhancements of PM₂.₅ and its major components (Supplementary Fig. 6) and the contributions of the individual HONO sources to PM₂.₅ and its major inorganic components can be found in An et al. (2013).

Monthly-mean concentrations of PM₂.₅ and its major components characterised by the MOSAIC aerosol module in the WRF-Chem are shown in Supplementary Fig. 7. It should be noted that the formation of SOA is not taken into account in this study. Organic aerosol, especially SOA could contribute significantly to PM₂.₅. In-situ observations showed that OA on average accounted for approximate 40% of submicron aerosols in Beijing during summertime, and SOA dominated OA, contributing 64% (Sun et al., 2012 and references therein). However, the complexity involved in SOA formation makes SOA difficult to be simulated well. Current air quality models have generally underpredicted observed SOA concentrations, with model-measurement discrepancies of a factor of two or more. More recent modelling efforts incorporating a number of additional factors such as new SOA precursors and particle phase chemistry, have begun to close the gap between predicted and measured SOA concentrations. But even for cases when simulations show reasonable agreement with measurements, the agreement may not be for the right reasons (Hallquist et al., 2009). The impacts of the additional HONO sources on SOA concentrations will be considered in following studies since the enhancement of the oxidants augments the production of semi-VOCs, which are apt to partition more to particle phase and further escalates the SOA concentrations (Li et al., 2010).

4.3. Sensitivity of O₃ and PM₂.₅ to the additional HONO sources

Impacts of the additional HONO sources on the O₃ and PM₂.₅ chemical coupling require rethinking of their control strategies. Meng et al. (1997) suggested that attempts to reduce PM levels required control of the NOₓ and VOC emissions that are also precursors to O₃ formation. The O₃ control strategies rely primarily on NOₓ and VOC emission variations. The urban areas of Beijing are often in a VOC-sensitive regime for ozone chemistry (see Fig. 6d and Wang et al., 2006). This section mainly presents the simulation results for Beijing Meteorological Tower, where the traffic emissions are large (An et al., 2009).

The resulting peak 8-h average ozone isopleths are shown in Fig. 8. Figure 8a shows that with decreased VOC emissions, O₃ max concentrations are reduced steadily, whereas a decrease in NOₓ emissions over 50% is necessary to obtain the O₃ reduction. Figure 8b shows the differences in O₃ max concentrations between Cases E and R.
Fig. 7. Percentage increases of monthly-mean daytime (a) NO$_3^-$, (b) NH$_4^+$ and (c) SO$_4^{2-}$ in PM$_{2.5}$ and (d) PM$_{2.5}$, (e) OH, (f) HNO$_3$, (g) H$_2$O$_2$ and (h) H$_2$SO$_4$ concentrations over the BTH region during August 2007 due to the three additional HONO sources.
The additional HONO sources increase O$_{3\,8h_{\text{max}}}$ concentrations but the enhancements decline as NO$_x$ emissions decrease, indicating that the impacts of the additional HONO sources on O$_3$ are significant in areas with high NO$_x$ emissions (Sarwar et al., 2009; Ensergh et al., 2010).

In regulatory applications, the relative reduction factors (RRF) can be used to reflect control strategy effectiveness. RRF for a given pair of VOCs and NO$_x$ reduction factors, $f_{\text{VOC}}$, $f_{\text{NOx}}$, are calculated as the ratio of O$_{3\,8h_{\text{max}}}$ resulting from that particular pair ($f_{\text{VOC}}, f_{\text{NOx}}$) divided by O$_{3\,8h_{\text{max}}}$ from $f_{\text{VOC}} = 1.0$ and $f_{\text{NOx}} = 1.0$ (Hogrefe et al., 2008). Figure 8c presents the ratio of the RRF obtained in Case E divided by that obtained in Case R. The RRF ratios are below one under nearly all control scenarios, illustrating that the enhanced HONO sources increase the effectiveness of the control strategies in reducing O$_3$ concentrations, especially through NO$_x$ emission decreases. For example, when the additional HONO sources are considered, a reduction of 75% in emitted NO$_x$ leads to an O$_3$ reduction of 6.5% more than the O$_3$ reduction obtained in a case without the additional HONO sources. The RRF in Case E is up to 7% lower than that in Case R, similar to the results obtained in Los Angeles where the NO$_2$ chemistry produced RRF 5% lower than that in the reference case (Ensergh et al., 2010).

The additional HONO sources also affect PM$_{2.5}$ control strategies. Figure 9 shows isopleths of the 24-h average concentrations of PM$_{2.5}$ for Cases R and E. Although PM$_{2.5}$ decreases with any reductions of NO$_x$, VOCs or NH$_3$ emissions in both cases, the additional HONO sources induce more reductions of PM$_{2.5}$ in Case E than those in Case R. For example, when the NO$_x$ reduction factor declines from 1 to 0.25, PM$_{2.5}$ is decreased from 143.1 µg m$^{-3}$ to 123.8 µg m$^{-3}$, with a reduction of 13.5% in Case R (Fig. 9a), whereas PM$_{2.5}$ is decreased from 163.1 µg m$^{-3}$ to 128.6 µg m$^{-3}$, with a reduction of 21.1% in Case E (Fig. 9d).

The present results are found to be in agreement with previous studies. Ensergh et al. (2010) showed that the NO$_2$ chemistry increases the sensitivity of particle formation to changes in NO$_x$ emissions. In addition, the results in this study show that the three additional HONO sources also increase the sensitivity of PM$_{2.5}$ formation to changes in NH$_3$ emissions. Comparing Fig. 9b and e, the number of isopleths in Case E is more than that in Case R as NH$_3$ emissions are reduced, indicating that a decrease in NH$_3$ emissions leads to more PM$_{2.5}$ reduction in Case E than that in Case R. Figure 9c and f show that reducing NO$_x$ and NH$_3$ emissions simultaneously results in significant decreases in PM$_{2.5}$ concentrations. When NO$_x$ and NH$_3$ reduction factors decrease from 1 to 0.25, the PM$_{2.5}$ reduction in Case E is found to be 8% larger than that in Case R.

To better understand the effects of the additional HONO sources on PM$_{2.5}$ and O$_3$ control strategies, Fig. 10 illustrates how many times the concentration reductions of PM$_{2.5}$ and O$_3$ fall in a certain range due to the emission reductions of NO$_x$, VOCs and NH$_3$. Among the 64 sensitivity simulations (see Section 2.2), the number of large reductions of PM$_{2.5}$ or O$_3$ in Case E is more than that in Case R. For example, the number of PM$_{2.5}$ reductions in the range of −25 to −20% is 17 in Case E, whereas that in Case R is 4. The number of O$_3$ reductions in the range of −15 to −10% is 20 in Case E, much larger than that of 8 in Case R. Figure 11 further shows that within the same range of PM$_{2.5}$ or O$_3$ reductions in Cases R and E, the frequency of large decreases in pollutant emissions is much
Fig. 9. Twenty four-hour average PM$_{2.5}$ concentrations for Case R (a–c) and for Case E (d–f) in Beijing on 17 August 2007.

Fig. 10. The number of concentration reductions ($C$, with unit of %) of (a) PM$_{2.5}$ in Case R, (b) PM$_{2.5}$ in Case E, (c) O$_3$ in Case R, and (d) O$_3$ in Case E in a certain reduction range among the sensitivity simulations using the 64 emission scenarios (see Section 2.2).
less in Case E than that in Case R. For example, the frequency of NOx, VOC and NH3 reduction factors of 0.25 is less in Case E than that in Case R in a certain range of PM2.5 or O3 concentration reductions. The frequency of 50% decreases in NOx and NH3 emissions in Case E for the PM2.5 reductions between −10 and −5% is also much smaller than that in Case R (Fig. 11d). These results further indicate that the additional HONO sources enhance the effectiveness of control strategies for reducing PM2.5 and O3 concentrations.

5. Conclusions

Three additional HONO sources, i.e. the HONO emissions, NOx\textsuperscript{2} chemistry and NO\textsubscript{2} heterogeneous reaction on aerosol surfaces, were added into a fully coupled meteorology-chemistry model called WRF-Chem to examine how the additional HONO sources influence O3 and PM2.5 chemical coupling and their control strategies. The following main conclusions are obtained from the current study:

(1) The three additional HONO sources significantly increased daytime O3 and PM2.5 concentrations over the urban areas of the BTH region. The enhancements of up to 9 ppb for O3 and 32 µg m\textsuperscript{-3} for PM2.5 are found at the seven urban sites during August 2007. The NO\textsubscript{2} heterogeneous reaction on aerosol surfaces is the largest contributor to the enhancements of O3 and PM2.5 during daytime.

(2) The O3 increases are found to be closely associated with PM2.5 increases over VOC-sensitive regimes during daytime when the additional HONO sources are considered. The correlation coefficient between O3 and PM2.5 daytime enhancements is estimated to be greater than 0.6 in many urban areas of the BTH region and > 0.8 over Beijing and Tianjin areas.

(3) The additional HONO sources enhance PM2.5 components of SO\textsubscript{4}\textsuperscript{2−}, NO\textsubscript{3} and NH\textsubscript{4}, which are increased by 5–18, 10–58 and 10–40%, respectively, over urban areas during daytime. The simultaneous increment of O3 and PM2.5 during daytime due to the additional HONO sources is related to the increasing oxidants (OH, H\textsubscript{2}O\textsubscript{2} and O3) that enhance the atmospheric oxidising capacity. The 20–40%
enhancements of the monthly mean daytime OH concentrations are found over Beijing, Tianjin and south of Hebei Province.

(4) The changes in O3 and PM$_{2.5}$ concentrations under a variety of NO$_x$, VOC and NH$_3$ emission reduction scenarios revealed that the additional HONO sources enhanced the effectiveness of control strategies for reducing O$_3$ and PM$_{2.5}$ concentrations.

(5) A decrease in NO$_x$ emissions produced more decreases in O$_3$ concentrations when the additional HONO sources were included. The additional HONO sources resulted in the O$_3$ RRF 7% lower than that in the reference case and this is consistent with the recent study conducted for the South Coast Air Basin of California (Ensberg et al., 2010).

(6) The additional HONO sources significantly increased PM$_{2.5}$ sensitivity to the changes in NO$_x$ and NH$_3$ emissions.

The results presented in this study suggest that the complex chemical interactions between O$_3$ and PM$_{2.5}$ need better explanations when the additional HONO sources are considered. Without considering the additional HONO sources, the effectiveness of emission control strategies in reducing O$_3$ and PM$_{2.5}$ concentrations would be underestimated significantly. The effects of HONO sources on SOA concentrations will be evaluated in the following studies.

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