Impacts of Additional HONO Sources on Concentrations and Deposition of NO_y in the Beijing-Tianjin-Hebei Region of China

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Abstract

This study applies the chemistry version of the Weather Research and Forecasting model (WRF-Chem) to examine impacts of three additional HONO sources, i.e., the reaction of photo-excited NO₂ (NO₂^{*}) with water vapor (NO₂^{*} chemistry), the NO₂ heterogeneous reaction on aerosol surfaces and HONO emissions, on concentrations and deposition of individual NO_y species over the Beijing-Tianjin-Hebei region (BTH) in summer and winter periods of 2007. The results show that the three additional HONO sources produce a 20%–40% (> 100%) increase in monthly-mean OH concentrations in many urban areas in August (February), leading to a 10%–40% (10%–100%) variation in monthly-mean concentrations of NO_x, NO₃[−] and PAN, a 5%–10% (10%–40%) increase in the total dry deposition of NO_y, and an enhancement of 1.4 Gg N (1.5 Gg N) in the total of dry and wet deposition of NO_y over this region in August (February). These results suggest that the additional HONO sources aggravate regional-scale acid deposition, emphasizing the importance of the additional HONO sources in the NO_y budget.

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1. Introduction

Reactive nitrogen-containing compounds (NO_y) are involved in many important chemical processes in the atmosphere, including aerosol and ozone (O₃) formation (Kondo et al. 2008). Some NO_y species are soluble in water, e.g. HNO₃ and particulate nitrate (NO₃[−]), and easily undergo wet deposition. Dry deposition can happen for all the NO_y species. Previous studies have highlighted the significance of NO_y deposition on ecosystem eutrophication and the global nitrogen cycle (Galloway et al. 2008). Liu et al. (2013) found that the NO_y deposition was increasing rapidly in China during 1980s–2000s, suggesting control of NO_x (NO + NO₂) emissions from industrial and traffic sources is urgently needed.

HONO, an important component of NO_y, is a significant precursor of the hydroxyl radical (OH) that drives the formation of O₃ and fine particles (PM_{2.5}). Nevertheless, the detailed formation mechanisms of HONO remain unclear (Stemmler et al. 2006; Li et al. 2014a). Unknown HONO sources and their potential impacts on air quality have gained extensive interests (Sarwar et al. 2008; Li et al. 2011; Hendrick et al. 2014). An et al. (2013) found that HONO sources decreased concentrations of gaseous NO_y but to our current knowledge, the impact of HONO sources on regional-scale deposition of individual NO_y species has not been quantified up to date.

Air quality models usually severely underestimate HONO ob-

servations even though some new HONO formation mechanisms have been considered (Li et al. 2010; Gonçalves et al. 2012). Previously, the NO₂^{*} chemistry (Li et al. 2008), the NO₂ heterogeneous reaction on aerosol surfaces (Het), and HONO emissions (Emis) were implemented in the fully coupled WRF-Chem resulted in a significant improvement of HONO simulations over the BTH (Li et al. 2011; 2014b). In this study, we will evaluate the effects of the three additional HONO sources on concentrations and deposition of individual NO_y species as well as the NO_y budget.

2. Model setup

2.1 WRF-Chem model

Used was the WRF-Chem version 3.2.1 (Grell et al. 2005) with the CBM-Z gas phase chemistry (Zaveri and Peters 1999) and the MOSAIC aerosol module (Zaveri et al. 2008). The aerosol size distribution in MOSAIC is divided into eight bins. Dry deposition of trace gases and particles is calculated by multiplying concentrations in the lowest model layer by the spatially and temporally varying dry deposition velocity (V_d) (Wesley 1989). Wet deposition includes in- and below- cloud removal (Easter et al. 2004).

The model configuration and domains are described in detail in Li et al. (2011). Briefly, three domains are employed, covering East Asia, North China and the BTH, respectively. The horizontal resolution in Domain 3 is 9 km. There are 28 vertical layers from the surface to 50 hPa. Initial and boundary conditions of meteorological fields are from the US National Centers for Environmental Prediction analysis data, while those of trace gases and aerosols are provided by the Model for Ozone and Related chemical Tracers (Emmons et al. 2010). Monthly anthropogenic emissions are constructed from Zhang et al. (2009). Future emission inventory over this region requires a finer grid resolution to help air quality models better capture the localized photochemistry.

2.2 New parameterization of HONO

Augmented HONO sources are NO₂^{*} chemistry (Reactions 1–3), the Het (Reaction 4) and the Emis. We parameterize Reactions 1–3 following Li et al. (2008) and Ensberg et al. (2010), with the rate constant for Reaction 2 being 9.1×10^{-14} cm³ molecule^{−1} s^{−1}. The first-order rate constant k for Reaction 4 follows Jacob (2000):

$$k = \left(\frac{a}{D_g} + \frac{4}{\nu\gamma} \right)^{-1} A_s \quad (1)$$

where a is the particle radius; D_g is the gas-phase molecular diffusion coefficient (Dentener and Crutzen 1993); ν is the mean molecular speed (Pleim et al. 1995); A_s is the aerosol surface area per unit volume of air, and γ is the uptake coefficient of NO₂, taken as 10^{-4} (Jacob 2000). A_s is derived using mass concentrations and number density of aerosols in each size bin set by MOZAIC. The mean simulated A_s is 1577 μm² cm^{−3} during 17–21 August 2007 at Peking University, close to the observed value of 1450 μm² cm^{−3} (Spataro et al. 2013). The Eq. (1) can also reflect the effects of the relative humidity since the aerosol hygroscopic growth can increase A_s and thus enhance k .

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The Emis 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 heterogeneously converted to HONO (Gutzwiller et al. 2002). NO_x emissions are appropriately reduced so that the sum of NO_x and HONO equals to NO_x in the anthropogenic emissions of Zhang et al. (2009).

2.3 Experimental design

We conduct five sensitivity runs. The first was a reference (Case R). Case NO₂^{*}, Case Het and Case Emis were extensions of Case R by inclusion of the NO₂^{*} chemistry, the Het and the Emis, respectively. The last was an enhanced case (Case E), with augmentation of the three additional HONO sources. Simulations were conducted for the photo-chemically active season, August 2007, during which an extensive observed dataset was obtained. HONO effects in February were also analyzed (figures shown in the Supplement due to the space limitation) to show the difference in summer and winter periods.

3. Observed data

Measurements of NO_x, peroxyacyl nitrates (PAN), HONO, HNO₃, NO₃⁻, and total gas-phase NO_y (NO_y_g) were conducted at Peking University in August as part of the Campaign of Air Quality Research in Beijing (CAREBeijing-2007). For winter period, only 24-h averages of HONO, NO₂ and NO₃⁻ were obtained. Details were given in Liu et al. (2010) and Spataro et al. (2013).

HONO was measured on a 24-h basis with a liquid coil scrubbing/UV-Vis instrument. In summer, interferences on the order of 2–9% from nitrite-forming species were observed and corrected using sodium carbonate denuders (Spataro et al. 2013). The detection limit was 0.88 ppt (Spataro et al. 2013; Spataro and Ianniello 2014). The uncertainty for HONO measurements was ~10% (Liu et al. 2010). The 24-h averages of HONO (HONO/NO₂) were 0.44–2.91 ppb (0.01–0.09), with the mean of 1.45 ppb (0.05) (Spataro et al. 2013). Meantime hourly HONO were measured by the Differential Optical Absorption Spectroscopy (DOAS) at the Meteorological Tower in the Institute of Atmospheric Physics (39.97°N, 116.37°E), ~6 km away from Peking University, from 13 to 25 August 2007 (Zhu et al. 2009). The HONO detection limit was 0.41 ppb. The hourly HONO averaged was 1.17 ppb, with the maximum of 3.37 ppb and the minimum lower than the detection limit. The hourly HONO/NO₂ ranged from 0.01 to 0.43, with the mean of 0.05, similar to the in-situ observations conducted at Peking University. Note that the actual HONO concentrations may be overestimated by the wet-chemical techniques due to the sample artifacts and chemical interferences, especially in daytime (Pinto et al. 2014). The daytime (7:00–19:00) mean concentration of HONO measured by the DOAS was 0.66 ppb, while that of HONO measured by the UV-Vis instrument was 1.22 ppb.

4. Results and discussion

4.1 Model evaluation

a. Concentrations of NO_y species

The updated WRF-Chem performance has been evaluated in terms of near-surface O₃, NO_x, HONO, PM_{2.5} and its inorganic components (Li et al. 2011; Tang et al. 2014). The extended model with the additional HONO sources succeeded to capture the magnitude and the diurnal variations of the observed data (Table S1), e.g., promising improvement in the model performance is found for predictions of O₃ peaks in urban areas (Li et al. 2011). Our results agree with other studies (Li et al. 2010; Elshorbany et al. 2012; Gonçalves et al. 2012), showing that at least the Het and the Emis should be included in models, since their impact on second-

Fig. 1. Comparison of observed and simulated 24-h averages of (a) NO₂, (b) HNO₃, (c) NO₃⁻ and (d) HONO during 2–31 August 2007 and diurnal averages of (e) HONO, (f) PAN, (g) NO and (h) NO_y_g during 10–30 August 2007. Observations at Peking University in Beijing were from Liu et al. (2010) and Spataro et al. (2013). Case R is a reference case; Case E includes NO₂^{*} chemistry, the NO₂ heterogeneous reaction on aerosol surfaces and HONO emissions. The relative concentration changes due to the three additional HONO sources are also shown in red lines.

ary pollutants has been proven, especially in the areas with high emissions of NO_x and particulates (Liu et al. 2014).

Simulated NO_y includes NO_x, PAN, HONO, HNO₃, HNO₄ and N₂O₅. Shown in Fig. 1 are the simulations compared with observations at Peking University in August. Both Cases R and E agreed reasonably well with the observed NO₂ but overestimated HNO₃ and NO₃⁻ (Fig. 1a, b, c). This NO₃⁻ overestimation was found in the whole Northeast Asia (Kajino et al. 2013) and further investigation with additional observations is required. Compared to Case R, Case E significantly improved HONO simulations, especially in nighttime. However, HONO in Case E were only ~24% of the observed mean value in daytime (Fig. 1d, e). Comparison of observed and simulated HONO at the Meteorological Tower site also showed that the model underestimated daytime HONO (Fig. S1), suggesting further effort is needed to characterize unknown HONO daytime sources. Figure 1f showed that PAN observations were underestimated by more than 80% in both Cases R and E. It is likely because the model underestimated the concentrations of acetaldehyde (CH₃CHO) and methylglyoxal (MGLY, CH₂CHC(O)CH₃) (Fig. S2), which were found as the dominant PAN sources in urban Beijing (Liu et al. 2010). The additional HONO sources also increased daytime concentrations of CH₃CHO, MGLY and PAN. Figures 1g, h showed that the additional HONO sources decreased NO and NO_y_g, especially during the local 8:00–16:00.

Figure S3 showed the comparison of observed and simulated 24-h averages of HONO, NO₂ and NO₃⁻ in the winter period. HONO simulations were considerably improved in Case E and both Cases R and E reflected the daily variations of those species (Table S2). The above evaluation demonstrates that except for PAN, the updated WRF-Chem can generally well reproduce variations and quantities of the individual NO_y species.

b. Dry deposition of NO_y species

Dry deposition of chemical species is related to their concentrations and deposition velocities. Dry deposition evaluation is challenging because of the difficulty in performing direct flux measurements. For V_d , the simulated monthly-mean values of NO, NO₂, HONO, HNO₃, NO₃⁻ and PAN in Case E over the BTH in August are ~0.01 cm s⁻¹, 0.01–0.35 cm s⁻¹, 0.70–2.18 cm s⁻¹, 0.67–3.63 cm s⁻¹, 0.01–0.12 cm s⁻¹ and 0.02–0.26 cm s⁻¹, respectively. Those in February are ~0.01 cm s⁻¹, 0.01–0.16 cm s⁻¹, 0.54–2.00 cm s⁻¹, 0.61–3.11 cm s⁻¹, 0.01–0.10 cm s⁻¹ and 0.02–0.12 cm s⁻¹, respectively. V_d is found larger over mountainous terrain or where patchy forest conditions exist (Wesely and Hicks 2000). The simulations are generally within the observed range

(Pan et al. 2012), except the underestimation of V_d of PAN (0.2–1.5 cm s⁻¹ for the observed range), due mainly to the underestimation of nonstomatal uptake (Wu et al. 2012). Dry deposition of the total N in NO_y (NO_y-N) is 0.5–2 kg N ha⁻¹ in the BTH, comparable to the previous measurements (Pan et al. 2012).

c. NO₃⁻ wet deposition

Besides concentrations of chemical species, wet deposition is also related to the precipitation amount. Figure 2a showed that the model underestimated the observed precipitation over the highly polluted regions. Measurements of the total wet deposition of NO₃⁻ (W-NO₃⁻) were unavailable within the studied period. Pan et al. (2012) reported that the mean W-NO₃⁻ for August were 0.5–1.5 kg N ha⁻¹ at ten selected sites over the BTH during a three-year observation campaign (December 2007–November

2010). The simulated W-NO₃⁻ at those ten sites in August 2007 were 0.2–1.9 kg N ha⁻¹ (Fig. 2b). Although the simulations were generally within the range reported by Pan et al. (2012), considering the model underestimated daytime HONO concentrations (Fig. 1), the actual W-NO₃⁻ may be larger.

4.2 Impacts on concentrations of NO_y species

The impact in August is shown in Fig. 3. The monthly-mean simulated HONO levels are considerably enhanced over Beijing, Tianjin, and south of Hebei Province (Fig. 3a). The enhanced HONO as well as the NO₂^{*} chemistry leads to a 20%–40% increase in monthly-mean OH concentrations over many urban areas (Fig. 4). The OH enhancement is favorable for the formation of HNO₃, NO₃⁻ and PAN and lowering NO. As shown in Fig. 3, the monthly-mean concentrations of NO are decreased by 5%–20%,

Fig. 2. Simulated (a) precipitation amount and (b) wet deposition amount of nitrate in August 2007 from the reference run (Case R) and (c) percentage changes due to the additional HONO sources (Case E). Observations of the precipitation amount at seventeen meteorological stations over the BTH region are indicated by colored dots.

Fig. 3. Monthly-mean concentration changes of (a) HONO, (b) NO, (c) NO₂, (d) N₂O₅, (e) HNO₃, (f) NO₃⁻, (g) PAN, and (h) NO_y over the BTH in August 2007 due to the additional HONO sources (Case E).

while those of HNO₃, NO₃⁻, and PAN are increased by 2%–10%, 20%–50%, and 10%–30%, respectively, over urban areas. The large increment of NO₃⁻ and reduction of NO₂ (10%–20%) are attributed mainly to the NO₂ heterogeneous reaction on aerosol surfaces. The NO₂ heterogeneous reaction can decrease the monthly-mean concentrations of NO₂ by 10%–28% over urban areas (Table 1). Overall, NO_y concentrations are decreased by 6%–10% in large areas (Fig. 3h). These results are in agreement with Elshorbany et al. (2012).

The individual contributions of the three additional HONO sources are summarized in Table 1. The Het is the largest contributor to OH enhancements and the concentration changes of NO_y species. Table 1 also showed that the concentration changes of NO_y species are generally larger in winter than in summer, consistent with Elshorbany et al. (2014). The three additional HONO sources decreased the monthly-mean concentrations of NO and NO₂ by 10%–50% and 10%–30%, while increased HNO₃, NO₃⁻, and PAN by 20%–60%, 40%–100%, and 20%–80%, respectively, over urban areas in February (Fig. S4). The OH enhancements were > 100% over many urban areas (Fig. S5).

Fig. 4. Simulated monthly-mean (a) OH concentrations in Case R and (b) OH enhancements due to the additional HONO sources (Case E) in August 2007.

Changes in concentrations of NO_y components owing to the additional HONO sources may exert a paramount effect on the overall atmospheric lifetime of the oxidized nitrogen, thus will impact NO_y deposition.

4.3 Impacts on dry deposition of NO_y species

NO_x and HNO₃ usually dominate NO_y dry deposition. As shown in Fig. 5, dry deposition of NO_x, HONO, HNO₃, NO₃⁻ and PAN in August is approximately 20–200 mg m⁻², 1–4 mg m⁻², 100–400 mg m⁻², 20–100 mg m⁻² and 3–15 mg m⁻² over the BTH, respectively. When the additional HONO sources are considered, NO_x dry deposition is decreased by 10%–20% in urban areas (Fig. 5g). HONO dry deposition is significantly increased, with the increment being larger than 20 mg m⁻² (Fig. 5h). Dry deposition of HNO₃, NO₃⁻, PAN and NO_y-N is enhanced by 4%–10%, 10%–50%, 20%–50%, and 5%–10%, respectively (Fig. 5i, j, k, l). Changes in the dry deposition of NO_y species correspond to their concentration changes (Fig. 3). The individual contributions of the three additional HONO sources are shown in Table 2. The dominant contributor is the Het. Table 2 also showed that the impact on NO_y dry deposition in winter is larger than that in summer. Dry deposition of NO_x is decreased by 10%–30% while that of HONO, HNO₃, NO₃⁻, PAN and NO_y-N is enhanced by 10–50 mg m⁻², 20%–40%, 20%–100%, 20%–80%, and 10%–40%, respectively, over urban areas in February (Fig. S6).

4.4 Impacts on NO₃⁻ wet deposition

W-NO₃⁻ was found with ~20% increases in a few areas of the BTH in August (Fig. 2c). The enhancement of W-NO₃⁻ due to the additional HONO sources is smaller than that of the dry deposition. However, it should be noted that the model significantly underestimates the observed precipitation over the highly polluted regions (Fig. 2a) where W-NO₃⁻ enhancements are larger. And considering the model severely underestimated the daytime HONO concentrations (Fig. 1), the actual enhancement of W-NO₃⁻ due to the additional HONO sources could be larger than the current simulation. W-NO₃⁻ enhancements in winter are larger than those in summer, with a 40%–120% increment in urban areas (Fig. S7).

Table 1. Maximum enhancements of monthly-mean concentrations of OH, HONO, NO, NO₂, N₂O₅, HNO₃, HNO₄, NO₃⁻, PAN, and NO_y over the BTH, due to the NO₂^{*} chemistry (Case NO₂^{*}–Case R), the NO₂ heterogeneous reaction on aerosol surfaces (Case Het–Case R), HONO emissions (Case Emis–Case R), and the three additional HONO sources (Case E–Case R). The unit of OH is 10⁶ molecules cm⁻³, of HONO, NO, NO₂, HNO₃, PAN, and NO_y, ppb, of N₂O₅ and HNO₄, ppt, and of NO₃⁻, μg m⁻³. A percentage change is shown in parentheses.

Species	Case NO ₂ [*] –Case R	Case Het–Case R	Case Emis–Case R	Case E–Case R
August 2007				
OH	0.4 (17.8)	1.1 (53.6)	0.2 (8.0)	1.9 (108.9)
HONO	0.03 (66.0)	1.7 (5257.3)	0.5 (818.0)	2.4 (5882.0)
NO	–0.8 (–10.2)	–1.8 (–49.8)	–0.9 (–3.4)	–3.3 (–56.3)
NO ₂	0.3 (1.2)	–5.3 (–28.5)	0.1 (0.7)	–5.7 (–33.0)
N ₂ O ₅	1.2 (9.1)	–11.6 (–28.7)	0.2 (4.1)	–11.4 (–11.4)
HNO ₃	0.1 (4.6)	0.2 (9.3)	0.02 (1.5)	0.3 (16.0)
HNO ₄	0.6 (13.6)	2.0 (37.3)	0.4 (6.6)	3.8 (66.6)
NO ₃ ⁻	2.0 (5.9)	9.5 (47.1)	0.2 (1.0)	13.5 (48.1)
PAN	0.02 (10.4)	0.06 (31.8)	0.007 (2.1)	0.1 (52.7)
NO _y	–0.4 (–2.6)	–4.5 (–28.6)	–0.5 (–2.6)	–5.8 (–33.4)
February 2007				
OH	0.1 (5.0)	0.5 (231.8)	0.1 (20.4)	0.6 (246.2)
HONO	0.008 (27.9)	2.3 (7909.4)	0.7 (976.9)	3.1 (8565.8)
NO	1.3 (13.0)	–9.9 (–64.0)	1.0 (15.1)	–12.7 (–68.3)
NO ₂	–0.7 (–2.7)	–5.9 (–39.1)	–0.8 (–3.0)	–5.7 (–42.1)
N ₂ O ₅	–7.4 (–16.1)	30.4 (63.7)	–9.1 (–17.8)	41.1 (85.4)
HNO ₃	0.1 (4.6)	0.01 (83.6)	0.1 (5.2)	0.02 (82.3)
HNO ₄	–2.6 (–18.9)	26.5 (258.0)	–3.0 (–21.2)	34.4 (325.1)
NO ₃ ⁻	–1.0 (–3.7)	27.2 (115.6)	–1.4 (–5.5)	26.9 (122.2)
PAN	–0.2 (–16.6)	0.6 (63.6)	–0.2 (–18.0)	0.8 (88.9)
NO _y	0.5 (1.8)	–11.6 (–31.6)	0.5 (2.3)	–12.7 (–33.1)

Fig. 5 Simulated dry deposition of (a) NO_x , (b) HONO, (c) HNO_3 , (d) NO_3^- , (e) PAN, and (f) the total N in NO_y in August 2007 from the reference run (Case R) and (g–l) percentage changes due to the additional HONO sources (Case E).

4.5 Impacts on the NO_y budget

Table 2 summarizes the regional NO_x emissions and the dry and wet deposition amounts of each NO_y species. In August, emissions of NO_x were 54.3 Gg N and the total deposition of NO_y were 37.0 Gg N (20.2 Gg N for the dry and 16.8 Gg N for the wet deposition) over the BTH in Case R. The additional HONO sources increased the total deposition of NO_y to 38.4 Gg N. In February the total deposition of NO_y is increased by 1.5 Gg N. Even though the regional total increment is not exceedingly significant, the maximum change could be very large: the impact of the additional HONO sources on NO_y deposition amounts is considerably significant for some specific locations (see brackets in Table 2). This is because the dry deposition velocities, the wet scavenging efficiencies, and the concentrations of each NO_y species varied substantially over this region so that the horizontal pattern of NO_y depositions changed consequently.

5. Summary and discussion

Using an updated WRF-Chem, we simulated the contributions of three additional HONO sources to the concentrations and deposition of individual NO_y species. Results showed that the additional HONO sources significantly enhanced the atmospheric oxidation capacity. The increment of monthly-mean OH concentrations were 20%–40% in urban areas in August and > 100% in February, leading to a decrease in NO_x concentrations and an increase in HNO_3 , NO_3^- and PAN. The changes in monthly-mean concentrations of NO_x , NO_3^- and PAN were 10%–40% (10%–100%) in many urban areas in August (February). The additional HONO sources resulted in a noticeable increase in NO_y dry deposition, with a percentage increase of 5%–10% (10%–40%) in urban areas in August (February). Among the three additional HONO sources, the NO_2 heterogeneous reaction is the largest contributor. The total

Table 2. Regional dry and wet deposition amounts of each NO_y species (Gg N) and monthly-mean emissions of NO_x (Gg N) over the BTH. The maximum differences (%) of NO_y deposition amounts over the BTH between Case R and Case NO₂^{*}, Case Het, Case Emis, and Case E, respectively, are provided in parentheses.

Species	Case R	Case NO ₂ [*]	Case Het	Case Emis	Case E
August 2007					
Dry deposition amount over the BTH region					
NO	0.49	(-11.0)	(-53.2)	(-3.4)	0.46 (-57.8)
NO ₂	6.7	(1.3)	(-29.0)	(1.0)	5.7 (-30.6)
HONO	0.10	(61.3)	(2653.9)	(359.8)	1.4 (2762.3)
HNO ₃	11.4	(5.9)	(10.3)	(3.4)	11.9 (15.3)
NO ₃ ⁻	1.4	(30.9)	(40.1)	(27.1)	1.6 (54.3)
PAN	0.08	(10.7)	(36.3)	(2.9)	0.09 (45.2)
Total	20.2	(4.7)	(48.2)	(13.1)	21.1 (54.3)
Wet deposition amount over the BTH region					
HNO ₃	0.07	(98.5)	(190.5)	(125.3)	0.07 (205.9)
NO ₃ ⁻	16.7	(319.8)	(250.2)	(182.9)	17.2 (161.8)
Total	16.8	(309.2)	(244.2)	(180.1)	17.3 (161.3)
Total emissions over the BTH region					
NO	54.3	54.3	54.3	54.0	54.0
HONO	0	0	0	0.3	0.3
February 2007					
Dry deposition amount over the BTH region					
NO	0.08	(33.5)	(-69.5)	(25.5)	0.06 (-73.7)
NO ₂	2.9	(-2.0)	(-42.8)	(-2.3)	2.3 (-46.0)
HONO	0.05	(36.5)	(4549.7)	(489.3)	1.3 (4766.5)
HNO ₃	0.2	(6.4)	(62.3)	(5.6)	0.3 (73.8)
NO ₃ ⁻	0.7	(-13.5)	(110.8)	(-20.9)	0.9 (115.3)
PAN	0.08	(-16.1)	(63.2)	(-17.5)	0.1 (88.1)
Total	4.0	(3.6)	(148.6)	(14.9)	5.0 (166.0)
Wet deposition amount over the BTH region					
HNO ₃	1.0×10 ⁻³	(109.8)	(422.5)	(124.1)	1.0×10 ⁻³ (493.1)
NO ₃ ⁻	3.6	(56.8)	(165.8)	(30.1)	4.1 (173.8)
Total	3.6	(56.8)	(165.4)	(30.1)	4.1 (173.7)
Total emissions over the BTH region					
NO	54.3	54.3	54.3	54.0	54.0
HONO	0	0	0	0.3	0.3

deposition of NO_y is increased by 1.4 Gg N (1.5 Gg N) over the BTH in August (February), suggesting that the additional HONO sources aggravate regional-scale acid deposition.

The above results demonstrate the importance of the additional HONO sources in the NO_y budget in the atmosphere. Note that this study has not taken into account the HONO heterogeneous production occurring on ground (Aumont et al. 2003) and this mechanism is also found an important HONO source (Sarwar et al. 2008). Considering the HONO formation on ground, the discrepancy between the observed and modeled HONO in the daytime may be reduced and the effects of HONO on NO_y concentrations and deposition could be more significant.

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Supplement

Supplement shows comparison of the observed and simulated data. Effects of the additional HONO sources in February are also shown.

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