Significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China


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Abstract

Nitrous acid (HONO) can strongly affect atmospheric photochemistry in polluted regions through the production of hydroxyl radical (OH). In January 2017, a severe pollution episode occurred in the Pearl River Delta (PRD) of China, with maximum hourly PM$_{2.5}$, ozone and HONO levels reaching 400 µg/m$^3$, 150 ppb, and 8 ppb, respectively, at a suburban site. The present study investigated the sources/processes generating such high HONO concentrations and the role of HONO chemistry in this severe winter episode. Four recently reported HONO sources were added to the Community Multi-scale Air Quality (CMAQ) model, including RH-dependent and light-enhancing effects on heterogeneous reactions, photolysis of particulate nitrate in the atmosphere, and photolysis of HNO$_3$ and nitrate on surfaces. The revised model reproduced the observed HONO and significantly improved its performance for O$_3$ and PM$_{2.5}$. The model simulations showed that the heterogeneous generation on surfaces (with RH and light effects) was the largest contributor (72%) to the predicted HONO concentrations, with the RH-enhancing effects more significant at nighttime and the light-enhancing effects more important in the daytime. The photolysis of total nitrate in the atmosphere and deposited on surfaces was the dominant HONO source during noon and afternoon, contributing above 50% of the simulated HONO. The HONO photolysis was the dominant contributor to HO$_X$ production in this episode. With all HONO sources, the daytime average O$_3$ at Heshan site was increased by 24 ppb (or 70%), compared to the simulation results without any HONO sources. Moreover, the simulated mean concentrations of TNO$_3$ (HNO$_3$ + fine particle NO$_3^-$) at Heshan site, which was the key species for this haze formation, increased by about 17µg/m$^3$ (67%) due to the HONO chemistry, and the peak enhancement reached 55 µg/m$^3$. This study highlights the key role of HONO chemistry in the formation of winter haze in a subtropical environment.
1 Introduction

Nitrous acid (HONO) can significantly affect atmospheric photochemistry through its photolysis producing hydroxyl radical (OH) (R1) and subsequent reactions of OH with other gases (Alicke et al., 2003; Kleffmann et al., 2005). OH radical oxidizes volatile organic compounds (VOC) and converts nitric oxide (NO) into nitrogen dioxide (NO₂) without consuming ozone (O₃), leading to the generation of O₃ (R2 to R6). The oxidation of oxides of nitrogen (NOₓ=NO+NO₂), sulfur dioxide (SO₂) and VOC by OH, O₃ and H₂O₂ also produce secondary aerosols, which are the key components of haze (e.g., Cao et al., 2012).

\[ \text{HONO} + hv \rightarrow \text{NO} + \text{OH} \quad (\text{R1}) \]
\[ \text{OH} + \text{VOC} \rightarrow \text{RO} + \text{H}_2\text{O} \quad (\text{R2}) \]
\[ \text{RO} + \text{NO} \rightarrow \text{NO}_2 + \text{HO} + \text{OVOC} \quad (\text{R3}) \]
\[ \text{NO}_2 + \text{NO} \rightarrow \text{NO}_3 + \text{OH} \quad (\text{R4}) \]
\[ \text{NO}_2 + hv \rightarrow \text{NO} + \text{O}_3 \quad (\text{R5}) \]
\[ \text{O}_3 + \text{O}_2 \rightarrow \text{O}_5 \quad (\text{R6}) \]

The impact of HONO on atmospheric photochemistry varies under different environmental conditions. In general, the effect of HONO is more significant in polluted conditions than clean conditions. For example, calculations constrained by field measurements of HONO have suggested that the contributions of HONO photolysis to the daytime HOₓ (HOₓ = OH + HO₂) production can reach 56% in an urban area (Ren et al., 2003) and 87% at a roadside (Yun et al., 2017), which are higher than the contributions in rural and forested areas (30% to 40%) (Acker et al., 2006; Kleffmann et al., 2005). Simulations by chemistry transport model which considered major sources of HONO showed that the maximum enhancements of O₃ concentrations due to HONO were mostly less than 10 ppb in the US and other western countries (Sarwar et al., 2008; Czader et al., 2012; Li et al., 2010; Goncalves et al., 2012), but more significant impacts have been reported in China due to more intense NOₓ and VOC emissions. For example, the reported maximum hourly O₃ enhancement can be more than 30 ppb in Beijing (Li et al., 2011; Xu et al., 2006) and up to 25 ppb in Hong Kong (Zhang et al., 2016). The previous studies mostly focused on summertime.

Limited attention has been paid to the winter season when the observed HONO
concentrations can also be high (Hou et al., 2016; Li et al., 2018a; Wang et al., 2016; Xu et al., 2015).

The source and formation mechanism of HONO are still not fully understood. Most previous studies suggest that heterogeneous reaction of NO$_2$ on surface is dominant, especially at night (Li et al., 2012; Wang et al., 2017a; Zhang et al., 2016). In the daytime, the long-known gas-phase reaction of NO and OH explains less than 10% of the daytime HONO production (Sarwar et al., 2008; Li et al., 2010; Zhang et al., 2016). Other daytime sources include direct traffic emissions (Kurtenbach et al., 2001; Liang et al., 2017), humidity and light-dependent heterogeneous generation (Finlayson-Pitts et al., 2003; Ndour et al., 2008; Monge et al., 2010), soil emissions (Oswald et al., 2013; Su et al., 2011; Meusel et al., 2018), photolysis of particle nitrate in the atmosphere (Ye et al., 2016b, 2017), and photolysis of deposited HNO$_3$ and nitrate on the ground (Ye et al., 2016a; Zhou et al., 2011), etc.

During 4-8 January 2017, a severe winter air pollution event occurred in the Pearl River Delta (PRD), a region long known to suffer from photochemical pollution due to its fast industrialization (Chan and Yao, 2008; Wang et al., 1998, 2003, 2017b; Xue et al., 2014; Zhang et al., 2008; Zheng et al., 2010). During this multi-day episode, an hourly peak value of ~150 ppb for O$_3$ and ~400 µg/m$^3$ for PM$_{2.5}$ were observed, and the HONO levels reached 8 ppb, with an average value of 2.9 ppb at night (18:00 to 6:00) and 2.4 ppb in daytime (7:00 to 17:00). The HONO values were among the highest ever reported in China (Bernard et al., 2016; Huang et al., 2017; Li et al., 2012; Qin et al., 2009; Su et al., 2008; Wang et al., 2017a; Wang et al., 2013; Li et al., 2018a; Xu et al., 2015). It is of great interest to find out how such a high level of HONO was produced and what impact it had on the radical levels and secondary pollutants during this severe winter pollution event.

The present study utilizes the CMAQ model with up-to-date HONO sources, including those in the original CMAQ model (gas-phase generation, heterogeneous reaction, and vehicle emissions) and four newly added sources (RH-enhancing effects on heterogeneous reactions, light-enhancing effects on heterogeneous reactions, photolysis of particulate nitrate in the atmosphere, and photolysis of HNO$_3$ and nitrate adsorbed on surfaces). The updated model was then used to analyze the contributions of different HONO sources, and also to quantify the contributions of HONO to secondary pollutants during this severe winter.
pollution event. Our study reveals the very large impact of HONO on winter-time chemistry at this subtropical site.

2 Materials and Methods

2.1 Model description

2.1.1 CMAQ model configurations and inputs

CMAQ version 5.1 with the updated carbon bond 2005 e51 (CB05e51) gas mechanism and AERO6 aerosol mechanism (Appel et al., 2017) was used in this study. One-way triple nesting domains were used with their horizontal resolutions being 36, 12, and 4 km, respectively, and the innermost domain covers the PRD region (Fig. 1). These domains are based on a Lambert projection with two true latitudes of 25° N and 40° N. The objective simulation period was 4 to 8 January 2017, with three days before as a spin-up time.

The Weather Research & Forecasting Model (WRF) version 3.7 was applied to generate the meteorological fields for the CMAQ simulations. The physical options used in the WRF model were the Lin microphysics scheme (Lin et al., 1983), Rapid Radiative Transfer Model for GCMs (RRTMG) shortwave and longwave radiation scheme (Mlawer and Clough, 1998; Mlawer et al., 1997), Noah land surface scheme (Chen and Dudhia, 2001), YSU PBL scheme (Hong et al., 2006), and Kain–Fritsch cumulus scheme (Kain, 2004). To improve the meteorological modeling performance, the nudging was performed using the NCEP Automated Data Processing (ADP) data (ds351.0 and ds461.0) and surface observation data from China Meteorological Administration (Zhang et al., 2016). Table S1 summarizes the statistical performance for the meteorological predictions.

The anthropogenic emission input was generated based on three emission inventories covering different regions. For the PRD region, a local emission inventory with high resolution for 2010 (Pan et al., 2014) was used. For other regions in China, the emission data for 2013 were from Ma et al. (2017). For other Asian countries, the INTEX-B dataset was used. HONO emissions from transportation sources were calculated based on the HONO/NOX...
ratios and NOX emissions from the transportation sources in the anthropogenic emission inventory. The HONO/NOX ratios were set as 0.8% and 2.3% for gasoline and diesel engines, respectively (Zhang et al., 2016). Natural biogenic emissions were estimated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006).

2.1.2 Parameterization of HONO Sources

In addition to the direct anthropogenic emissions, the default CMAQ model has two HONO more sources, including the gas-phase homogeneous reaction of NO and OH (R7) and the heterogeneous reactions of NO2 on surfaces (R8) (Sarwar et al., 2008). The heterogeneous formation of HONO on the surfaces of particle, urban and leaves was estimated with a reaction rate $k = 5 \times 10^{-5} \times (S/V)$ as measured by Kurtenbach et al. (2001) under dark conditions with a relative humidity (RH) of 50%.

$$NO + OH \rightarrow HONO \quad (R7)$$

$$2NO_2 + H_2O_{surface} \rightarrow HONO + HNO_3 \quad (R8)$$

In the present study, we incorporated four additional HONO sources, as described below.

(1) RH-enhancing effects on heterogeneous reaction of NO2 on surfaces

The default heterogeneous reaction rate was based on measurements at a relative humidity of 50%. However, previous field and lab studies found that surface adsorbed water played a key role in the heterogeneous conversion and the reaction rate was highly dependent on the RH level (Finlayson-Pitts et al., 2003; Stutz et al., 2004; Qin et al., 2009). The laboratory measurements over an RH range of 0% to 80% conducted by Finlayson-Pitts et al. (2003) showed that the heterogeneous conversion rate increased much faster when RH≥50% than that when RH<50%. Based on this result, the RH dependence of the heterogeneous reaction was considered through scaling the default reaction rate by a factor of $f_{RH}$ in this study, as shown in the following equation:

$$k_{het} = 5 \times 10^{-5} \times f_{RH} \times (S/V) \quad (E1)$$

$$f_{RH} = \begin{cases} 
    RH / 50 & (RH < 50) \\
    RH / 10 - 4 & (50 \leq RH < 80) \\
    4 & (RH \geq 80)
\end{cases}$$
(2) Light-enhancing effects on heterogeneous reaction of NO$_2$ on surfaces

The default reaction rate coefficient for the heterogeneous reaction was based on measurements under dark conditions. However, it has been reported that sunlight significantly boosts the heterogeneous generation of HONO (Ndour et al., 2008; Monge et al., 2010; Stemmler et al., 2007). To consider the photo-enhancing effect, we applied a higher reaction rate at daytime (Li et al., 2010; Czader et al., 2012), as shown in the following equation:

$$k_{het} = 1 \times 10^{-3} \times \frac{\text{light intensity}}{400} \times (S/V)$$  \hspace{1cm} (E2)

where light intensity means the total downward irradiance at the surface, measured in watts per meter squared (W/m$^2$).

(3) Photolysis of particulate nitrate in the atmosphere

Evidence from recent aircraft observations and laboratory measurements suggested that particulate nitrate in the atmosphere can undergo photolysis to produce HONO and NO$_2$ (R9) (Ye et al., 2016b, 2017).

$$pNO_3 \rightarrow 0.67HONO + 0.33NO_2$$  \hspace{1cm} (R9)

Ye et al. (2017) reported the photolysis rates ranging from $6.2 \times 10^{-6}$ s$^{-1}$ to $5.0 \times 10^{-4}$ s$^{-1}$, with a median of $8.3 \times 10^{-5}$ s$^{-1}$, at noontime tropical conditions. The reported value was much higher than the photolysis rate of gaseous HNO$_3$ ($\sim 7 \times 10^{-7}$ s$^{-1}$) under the typical tropical noontime conditions (Finlayson-Pitts and Pitts., 2000; Ye et al., 2017). Similar to the methodology of Sarwar et al. (2008), the photolysis rate of particulate nitrate was estimated as the following equation:

$$J_{pNO_3} = \frac{8.3 \times 10^{-5}}{7 \times 10^{-7}} \times J_{HNO_3-CMAQ}$$  \hspace{1cm} (E3)

where $J_{HNO_3-CMAQ}$ is the photolysis rate of gaseous HNO$_3$ calculated online in CMAQ.

(4) Photolysis of HNO$_3$/nitrate deposited on surfaces

Field observations and lab studies also indicated that the photolysis of HNO$_3$/nitrate deposited on the surface could be an important daytime HONO source (R10) (Zhou et al., 2003, 2011; Baergen et al., 2013). Ye et al. (2016a) tested the photolysis of HNO$_3$/nitrate deposited on various natural and artificial surfaces in the laboratory, and reported the photolysis rates ranging from $6 \times 10^{-6}$ s$^{-1}$ to $3.7 \times 10^{-4}$ s$^{-1}$, with a median of $3.4 \times 10^{-5}$ s$^{-1}$. 

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This reaction was incorporated into the CMAQ model by assuming deposited HNO$_3$/nitrate on surfaces to equal the accumulation of dry deposition since the last precipitation event, referring to the method of Sarwar et al. (2008). The photolysis rate of deposited HNO$_3$/nitrate was estimated as the following equation:

$$ J_{DNO3} = \frac{3.4 \times 10^3}{7 \times 10^{-7}} \times J_{HNO3-CMAQ} $$  \hspace{1cm} \text{(E4)}

### 2.1.3 Simulation cases

Eight simulations were conducted considering different HONO sources, including:

- **NO_HONO**: without any HONO sources
- **G**: gas-phase homogeneous reaction (G)
- **GE**: G + vehicle emissions (E)
- **GEH (CMAQ-default)**: GE + heterogeneous reactions under dark conditions with a RH of 50% (H)
- **GEHR**: GEH + RH-enhancing effects on heterogeneous reactions (R)
- **GEHRL**: GEHR + light-enhancing effects on heterogeneous reactions (L)
- **GEHRLP**: GEHRL + photolysis of particulate nitrate in the atmosphere (P)
- **GEHRLPD (CMAQ-revised)**: GEHRLP + photolysis of HNO$_3$/nitrate deposited on the surface (D)

### 2.2 Observation data

Field observations of HONO and other major air pollutants were conducted at Heshan site (112°55′17″ E, 22°42′50″ N) in the PRD region (Fig. 1). Hourly HONO concentration was measured using a Long Path Absorption Photometer (LOPAP) (QUMA, Model LOPAP-03) (Heland et al., 2001; Xu et al., 2015). PM$_{2.5}$ concentrations were determined by a Multi Angle Absorption Photometer (Thermo Scientific, Model 5012). Sulfate, nitrate and ammonium in PM$_{2.5}$ were measured by a gas and aerosol collector coupled with an ion chromatography (GAC-IC) system. Gas HNO$_3$ concentrations were also measured by this GAC-IC system. O$_3$
concentrations were measured by a UV photometric analyzer (Thermo Scientific, Model 49i). NO\textsubscript{2} concentrations were measured using a chemiluminescence instrument (Thermo Scientific, Model 42i) coupled with a photolytic converter (Droplet Measurement Technologies, model BLC) (Xu et al., 2013). Additionally, hourly PM\textsubscript{2.5}, O\textsubscript{3} and NO\textsubscript{2} observation data at 56 official monitoring sites (Fig.1) in the PRD region were obtained from the Ministry of Environmental Protection (MEP). It should be noted that NO\textsubscript{2} concentrations in the national network were measured using the catalytic conversion method, which overestimates NO\textsubscript{2}, especially during the period with active photochemistry and at the location away from the primary emission sources (Xu et al., 2013). The NO\textsubscript{2} observation data were adjusted based on the method of Zhang et al. (2017).

3 Results and Discussion

3.1 Observed pollution in this winter episode

During 4-8 January 2017, a severe pollution episode was observed in the PRD region. As shown in Fig. S1, the episode average PM\textsubscript{2.5} concentrations observed at the Heshan site reached 142 \(\mu\)g/m\textsuperscript{3}, which is nearly twice the respective standard of China (75 \(\mu\)g/m\textsuperscript{3} for daily average PM\textsubscript{2.5} concentration). The hourly PM\textsubscript{2.5} concentration peaked at 382 \(\mu\)g/m\textsuperscript{3}, which was among the highest PM\textsubscript{2.5} concentrations ever reported in the PRD region (Tan et al., 2009; Wang et al., 2012; Yue et al., 2015). O\textsubscript{3} levels were also high, with a peak of ~150ppb. Fig. S2 presented the spatial distribution of observed PM\textsubscript{2.5} and O\textsubscript{3} on the two heaviest polluted days (5 and 6 January) based on the interpolation of the observation data at the 56 official monitoring sites. It can be seen that the whole western PRD region suffered from severe pollution. On 5 January, the highest PM\textsubscript{2.5} pollution occurred in Foshan city and its surrounding area, with a peak of 448 \(\mu\)g/m\textsuperscript{3}. On 6 January, the pollution expanded to wider areas.

3.2 Evaluation of model performance

Figure 2 compared the simulated HONO mixing ratios by the default CMAQ model
(GEH) and the revised CMAQ model (GEHRLPD) with the observations at Heshan site for
4-8 January. For the HONO simulation, the default CMAQ significantly underestimated the
levels, with a normalized mean bias (NMB) of -71.6%. The maximum underestimation was
6ppb in the early morning of 5 January. The simulated HONO levels in the afternoon were
lower than 0.1 ppb in the default CMAQ model. By considering the four additional HONO
sources, the model performance was improved considerably, with an NMB of -22.5%. The
simulated average daytime HONO mixing ratios increased from 0.37 to 1.44 ppb, and the
simulated nighttime HONO values increased from 1.10 to 2.63 ppb. The revised model
reproduced the HONO diurnal variation. Underestimation was found on the morning of 5-6
and 8 January. One possible reason was that some HONO sources were not considered in this
study. For example, previous studies have proposed that deposited HONO can be reserved in
dew water on the ground or vegetation during the nighttime and re-released when the dew
water evaporate in the morning (He et al., 2006). Overestimation was seen at the nighttime of
4 and 7 January, which may be related to the uncertainties of emission inventory, and
meteorological simulation, etc.

The inclusion of the four additional HONO sources also changed the model performance
for other air pollutants. As shown in Fig. S1, the O₃ prediction by the default CMAQ model
was not satisfactory, especially for the peak value. For example, on 6 January, the observed
maximum 1-h and 8-h O₃ mixing ratios at Heshan site reached 147 ppb and 125 ppb,
respectively, exceeding the respective standard of China (~93 ppb and 75 ppb for maximum
1-h and 8-h O₃ concentrations, respectively). The simulated levels by the default CMAQ
model were just 64ppb and 52ppb, respectively, which failed to predict the non-compliance of
O₃ for this episode). In contrast, the revised model was better to reproduce the magnitude. For
the episode average, the NMB values decreased from -32.9% to 5.5% for the maximum 8-h
O₃. Therefore, it is crucial to include these additional HONO sources into air quality models.
For NO₂, the revised model could reproduce its temporal variation in general, although
underestimation was seen for some peak NO₂ values. This under-prediction could also explain
partially the underestimation of HONO peak values. For PM₁.₅, improvements also can be
seen, especially for the peak values. For the sulfate, nitrate and ammonium components in
PM₂.₅, as shown in Fig.S3, the revised model performed well in reproducing their temporal
variations, with correlation coefficients (R value) of 0.5, 0.7 and 0.7, respectively. Compared to the default CMAQ model, the NMB values decreased from -29.8% to -10%, -53.8% to -41.2%, and -32.9% to -14.1% for fine particle sulfate, nitrate and ammonium, respectively. Underestimation could be seen for particle nitrate, especially on 5 January. The possible reason was underestimation of the emissions of NH$_3$ or other alkaline species (e.g. Ca, K, Na), which led to gas HNO$_3$ not being converted to particle nitrate sufficiently. The model performance for total nitrate (TNO$_3$ = gaseous HNO$_3$ + fine particle nitrate) was satisfactory, with an NMB of -3.2% and R of 0.8.

Regionally, as shown in Table 1, the simulation results of the revised CMAQ model were in better agreement with the observations, with the NMBs decreasing from -33.3% to 0.7%, -8.1% to 4.7%, and 20.6% to 9.4% for 8-hour maximum O$_3$, hourly average PM$_{2.5}$ and hourly average NO$_2$ values, respectively.

The above results indicated the satisfactory performance of the revised CMAQ model to simulate HONO and other major pollutants. It could be used to analyze the formation and impact of HONO in this episode.

### 3.3 Contributions of different sources to HONO concentrations

Figure 3 presents the contributions of different HONO sources to the HONO mixing ratios at Heshan site. Heterogeneous generation on surfaces (including RH and light effects, H+R+L) was the largest contributor, representing 72% of the average predicted HONO for the whole day. It contributed up to 81% of the average predicted HONO values during the nighttime (18:00 to 6:00) and ~52% during the daytime (7:00 to 17:00). These findings on the dominant contribution from heterogeneous generation were similar to those in the previous modeling studies (Sarwar et al., 2008; Zhang et al., 2016) and field measurements (Li et al., 2012; Wang et al., 2017a). High relative humidity and solar radiation were two important driving factors for the formation of the high HONO concentrations in this pollution episode. During the nighttime and early morning (18:00 to 8:00), RH-enhancing effects on the heterogeneous generation were significant, due to high relative humidity (70% to 90%) (Fig. S4). The heterogeneous generation of HONO had a ~2-fold increase by considering
RH-enhancing effects, compared to that under the uniform relative humidity of 50%. From 9:00 to the afternoon, light-enhancing effects became important, contributing approximately 25% to HONO levels, due to strong radiation with a maximum of \(~450\) W/m\(^2\) (Fig. S4). In addition to enhancing the heterogeneous generation, the existence of light also increased HONO values through the photolysis of particle nitrate in the atmosphere and total nitrate deposited on the surface. Due to the high total nitrate concentrations in this pollution episode, these two photolysis sources were dominant during noon and afternoon (11:00 to 17:00), contributing 31% and 36% to the HONO levels, respectively. Vehicle emissions contributed approximately 8% of the daily average HONO values. The gas-phase homogeneous reaction was the smallest source, contributing approximately 3% and 7% of the daily and daytime average HONO values, respectively. Our model simulations suggest that the three additional light-dependent sources (L+P+D) could be an important part of missing daytime sources for the present case.

### 3.4 Impacts of HONO chemistry on \(\text{HO}_x\) and \(\text{O}_3\)

The \(\text{HO}_x\) (OH+HO\(_2\)) radical plays a key role in the atmospheric photochemical process. The photolysis of HONO can produce OH radical, and fast reactions exist between OH and HO\(_2\) radical. Therefore, the photolysis of HONO can affect the abundance of \(\text{HO}_x\) radical. Figure 4 presents the average diurnal OH and HO\(_2\) variations based on the simulations with and without the HONO sources (NO\_HONO vs. GEHRLPD). The diurnal pattern and magnitude of the simulated OH and HO\(_2\) mixing ratios in the GEHRLPD case were comparable to the previous observations in the PRD region and other areas (Lu et al., 2012; Mao et al., 2010). Compared to the results of the NO\_HONO simulation, the daytime average OH and HO\(_2\) values were increased by 175% and 336%, respectively. The integrated reaction rate (IRR) analysis tool available in CMAQ was utilized to explore the contribution of HONO photolysis to \(\text{HO}_x\) radical production relative to other \(\text{HO}_x\) radical sources in the surface layer (~0 to 30 m), including the reaction of H\(_2\)O with O (1D) which comes from the photolysis of O\(_3\), HCHO photolysis, H\(_2\)O\(_2\) photolysis, and the reaction of O\(_3\) with alkenes and biogenic VOCs. As shown in Fig. 5, HONO photolysis was the dominant \(\text{HO}_x\) source during
the daytime at Heshan site. The daytime average contribution of HONO photolysis to HO\textsubscript{X} production was approximately 74%, and the contribution during the morning could be above 90%. With the increasing of O\textsubscript{3} concentrations from sunrise to afternoon, the contribution of the O\textsubscript{3} photolysis began to increase and reached a peak of 33.4% at 14:00. Compared to the reported results in the previous studies (Czader et al., 2012; Mao et al., 2010; Tham et al., 2016; Xue et al., 2016; Li et al., 2018c), the contribution of HONO photolysis to HO\textsubscript{X} was much larger in the present study, mainly due to the high HONO concentrations in this episode. For example, Xue et al. (2016) and Li et al. (2018c) reported daytime average contributions of less than 30% from HONO photolysis at two sites in Hong Kong. Tham et al. (2016) showed a contribution of less than 50% in the morning at a site in the North China Plain. In these cases, the HONO levels were relatively low, with the peak HONO levels ranging among 1-3 ppb. The high HONO concentrations at Heshan increased the contribution of HONO photolysis to the formation of HO\textsubscript{X} in this winter pollution episode.

The enhanced HO\textsubscript{X} formation due to HONO chemistry could increase O\textsubscript{3} concentrations. As shown in Fig. 6, the simulated daytime average O\textsubscript{3} mixing ratio at Heshan site in the GEHRLPD case was approximately 24 ppb (70%) higher than that in the NO\textsubscript{3}HONO case, with a peak increase up to 60 ppb. The O\textsubscript{3} enhancement was much higher than the previous simulation results for the summer cases (Sarwar et al., 2008; Li et al., 2010; Zhang et al., 2016). In addition to higher HONO concentrations, another possible reason was that the VOC/NO\textsubscript{X} ratio was lower in winter than that in summer, due to less biogenic VOC emissions and more NO\textsubscript{X} emission from fuel combustion in winter. For example, Zou et al. (2015) reported VOC/NO\textsubscript{X} values higher than 10:1 in summer and about 5:1 for winter based on 1-year observation in Guangzhou, which is about 60 km from the Heshan site. The lower VOC/NO\textsubscript{X} ratio increased the sensitivity of O\textsubscript{3} concentrations to HO\textsubscript{X} changes through reaction 2 to 4. Therefore, the enhancement of O\textsubscript{3} concentrations was more significant (Li et al., 2018b). Figure 7 presents the spatial distribution of simulated surface O\textsubscript{3} concentrations at 15:00 LTC in the NO\textsubscript{3}HONO and GEHRLPD cases. With HONO sources, the increase of regional average O\textsubscript{3} mixing ratio at 15:00 LTC was 34% (~17 ppb). The above results indicated the significant impacts of HONO chemistry on the atmospheric oxidation capacity and O\textsubscript{3} pollution in the PRD region during this heavy winter episode.
3.5 Impacts of HONO chemistry on secondary inorganic aerosol formation

Secondary inorganic aerosols, including nitrate, sulfate and ammonium, contributed approximately 50% to PM$_{2.5}$ concentrations during this episode (Fig. S5). Among them, nitrate was the dominant component, with peak concentrations reaching ~110µg/m$^3$, which was much higher than the sulfate and ammonium concentrations. Particle nitrate can be generated through the partition of HNO$_3$ to particle phase. The major formation pathway of HNO$_3$ is the oxidation of NO$_2$ by OH during the daytime (R11). HNO$_3$ can also be produced via heterogeneous reactions of N$_2$O$_5$ on the particle surface at night (R12 to R14). Therefore HONO chemistry can accelerate the formation of nitrate through the enhancement of atmospheric oxidation capacity (HO$_X$ and O$_3$).

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad \text{(R11)} \]
\[ \text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 \quad \text{(R12)} \]
\[ \text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \quad \text{(R13)} \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad \text{(R14)} \]

Considering the uncertainty of the partition of gaseous HNO$_3$ to particle nitrate (see section 3.2), we assessed the impact of HONO chemistry on the sum of HNO$_3$ and fine particle NO$_3^-$ (TNO$_3$). As shown in Fig. 8, the average TNO$_3$ concentrations at Heshan site increased by about 17µg/m$^3$ (67%), and the peak enhancement reached 55µg/m$^3$ at 10 am on January 6, when the observed PM$_{2.5}$ and nitrate concentration was at its respective highest level. Figure 9 presents the distribution of simulated average surface TNO$_3$ concentrations in the NO$_3$HONO and GEHRLPD case. With HONO sources, the regional average TNO$_3$ concentrations were increased by 8.4 µg/m$^3$ for the entire episode. The absolute enhancement was more significant in the areas with higher aerosol concentrations. The highest increase for TNO$_3$ was above 25µg/m$^3$ for the episode average. Meanwhile, the HONO chemistry also accelerated the formation of other secondary inorganic aerosols. Particle sulfate can be generated through the partition of H$_2$SO$_4$ to the particle phase. The major formation pathways of H$_2$SO$_4$ include the gaseous oxidation of SO$_2$ by OH, and the aqueous oxidation of S(IV) by O$_3$, H$_2$O$_2$ and other oxidants. The partition of gaseous NH$_3$ to particle ammonium was based on the H$_2$SO$_4$-HNO$_3$-NH$_3$ thermodynamic equilibrium. The simulated enhancements of the
average sulfate and ammonium concentrations at Heshan site were 32% and 33%, respectively. The above results indicated that the HONO chemistry also aggravated the particulate pollution during this episode.

4 Conclusion

This study has identified the major contributors to the observed high HONO levels during a severe winter pollution episode and highlighted the importance of HONO chemistry in the combined photochemical and haze pollution in a subtropical region. Including up-to-date HONO sources in the widely used CMAQ model significantly improved its capability in simulating ambient concentrations of HONO and other major pollutants (e.g. O₃ and PM₂.₅). The model simulations suggested a predominant contribution from NO₂ heterogeneous reactions enhanced by humidity and solar radiation. The high HONO concentration significantly increased the atmospheric oxidation capacity and the levels of ozone and secondary aerosols, especially total nitrate. Our study highlights the critical need to include/update HONO sources in regional air quality models in order to predict ozone and other secondary pollutants during heavy pollution events in southern China and similar regions.

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### Table 1. Model performance of the default and revised CMAQ model for O₃, PM₂.₅ and NO₂ at 56 monitoring sites in the PRD region

<table>
<thead>
<tr>
<th></th>
<th>OBS (µg/m³)</th>
<th>SIM (µg/m³)</th>
<th>Bias (µg/m³)</th>
<th>NMB (%)</th>
<th>NME (%)</th>
<th>R</th>
</tr>
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<tr>
<td><strong>8h_max O₃</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>GEH (CMAQ-default)</td>
<td>84.79</td>
<td>56.55</td>
<td>-28.24</td>
<td>-33.3</td>
<td>42.69</td>
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<tr>
<td>GEHRLPD (CMAQ-revised)</td>
<td>85.42</td>
<td>0.63</td>
<td>0.74</td>
<td>41.76</td>
<td>0.31</td>
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<tr>
<td><strong>hourly PM₂.₅</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GEH (CMAQ-default)</td>
<td>78.75</td>
<td>72.34</td>
<td>-6.40</td>
<td>-8.13</td>
<td>46.6</td>
<td>0.60</td>
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<tr>
<td>GEHRLPD (CMAQ-revised)</td>
<td>82.44</td>
<td>3.69</td>
<td>4.68</td>
<td>50.64</td>
<td>0.61</td>
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<tr>
<td><strong>hourly NO₂</strong></td>
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<td></td>
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<tr>
<td>GEH (CMAQ-default)</td>
<td>53.39</td>
<td>64.39</td>
<td>11.00</td>
<td>20.61</td>
<td>49.51</td>
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<td>GEHRLPD (CMAQ-revised)</td>
<td>58.42</td>
<td>5.03</td>
<td>9.42</td>
<td>43.75</td>
<td>0.67</td>
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</table>
Figure Captions

Fig.1. Model domains and locations of the monitoring sites. Green star represents Heshan site and red dots represent official monitoring sites in the PRD region from the Ministry Environmental Protection of China.

Fig.2. Observed and simulated HONO mixing ratios by the default and revised CMAQ model at Heshan site during 4-8 January 2017.

Fig.3. Average diurnal variations of contributions of different HONO sources to the simulated HONO mixing ratios at Heshan site for 4-8 January 2017. The HONO sources include gas-phase homogeneous reaction of NO and OH (G), vehicle emissions (E), heterogeneous reactions under dark condition with the RH of 50% (H), RH-enhancing effects on heterogeneous reactions (R), light-enhancing effects on heterogeneous reactions (L), photolysis of particulate nitrate in the atmosphere (P) and photolysis of HNO3/nitrate deposited on the surface (D).

Fig.4. Average diurnal variations of OH and HO2 mixing ratios simulated in the NO_HONO and GEHRLPD case at Heshan site during 4-8 January 2017.

Fig.5. Average diurnal variations of contributions of different reactions to HOX generation at Heshan site.

Fig.6. Temporal variation of observed and simulated O3 mixing ratios in the NO_HONO and GEHRLPD case at Heshan site during 4-8 January 2017.

Fig.7. Spatial distributions of O3 mixing ratios at 15:00 LTC simulated in the NO_HONO and GEHRLPD case, and their difference for domain 3.

Fig.8. Temporal variation of observed and simulated total nitrate, sulfate, and ammonium concentrations in the NO_HONO and GEHRLPD case at Heshan site during 4-8 January 2017.

Fig.9. Spatial distributions of average TNO3 concentrations simulated in the NO_HONO and GEHRLPD case, and their difference for domain 3 during 4-8 January 2017.
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Fig. 4. Average diurnal variations of OH and HO$_2$ mixing ratios simulated in the NO$_2$HONO and GEHRLPD case at Heshan site during 4-8 January 2017.
Fig. 5. Average diurnal variations of contributions of different reactions to HOX generation at Heshan site.

Fig. 6. Temporal variation of observed and simulated O₃ mixing ratios in the NO_HONO and GEHRLPD case at Heshan site during 4-8 January 2017.
Fig. 7. Spatial distributions of O₃ mixing ratios at 15:00 LTC simulated in the NO_HONO and GEHRLPD case, and their difference for domain 3.

Fig. 8. Temporal variation of observed and simulated total nitrate, sulfate, and ammonium concentrations in the NO_HONO and GEHRLPD case at Heshan site during 4-8 January 2017.

Fig. 9. Spatial distributions of average $\text{NO}_3$ concentrations simulated in the NO_HONO and GEHRLPD case, and their difference for domain 3 during 4-8 January 2017.