Environmental Research Letters

LETTER

Evidence of heterogeneous HONO formation from aerosols and the regional photochemical impact of this HONO source

Xingcheng Lu, Yuhang Wang, Jianfeng Li, Lu Shen and Jimmy C H Fung

Abstract

Large missing daytime HONO sources have been reported by many previous studies around the world. Possible HONO sources include ground heterogeneous conversion, aerosol heterogeneous formation, soil emission, and photochemical production. In this study, a consistent 1D framework based on regional and 3D chemical transport models (CTMs) was used to analyze the unknown daytime HONO sources in 14 cases worldwide. We assume that the source of HONO from aerosols is through NO₂ hydrolysis (not including its oxidation products) and that non-local mixing effect is negligible. Assuming all the missing unknown HONO source is from the ground, it would imply a NO₂-to-HONO ground heterogeneous conversion exceeding 100% in daytime, which is unphysical. In contrast, a strong R² reaching up to 0.92 is found between the unknown HONO sources and the products of aerosol wet surface area and short-wave radiation. Because the largest unknown daytime HONO sources are found in China due to high concentrations of aerosols and NO₂, we derive an optimized NO₂ uptake coefficient on the basis of these measurements. The 3D CTM simulations suggest that in some regions of central, eastern, and southwestern (e.g. SiChuan province) China, the aerosol HONO source has the greatest effects on ozone (> 10 ppbv) and OH (> 200%) in winter. In January, the simulated particulate sulfate level over these three regions increases by 6–10 μg m⁻³ after including the aerosol-HONO source, which helps reduce the previous model underestimation of sulfate production in winter. Additional measurement studies that target the daytime HONO sources will be essential to a better understanding of the mechanisms and resulting effects on atmospheric oxidants.

1. Introduction

Ozone (O₃) is one of the most notorious ambient photochemical pollutants worldwide. High concentrations of this pollutant can adversely affect human health and cause substantial reductions in crop yields (Avnery et al. 2011, Lu et al. 2016). O₃ formation is influenced by the photochemical reactions of ROₓ (OH + HO₂ + RO₂) and NOₓ in the atmosphere. Many recent studies have investigated the role of the ROₓ cycle in O₃ formation (Liu et al. 2012a, Lu et al. 2017). Known atmospheric sources of OH radicals include (but are not limited to) reactions between water vapor and electronically excited oxygen atoms (O³D), the photodissociation of some types of volatile organic compounds (Jaegle et al. 2011), and the photolysis of nitrous acid (HONO) (Liu et al. 2012a). According to Lu et al. (2017), HONO can contribute to over 30% of the O₃ production rate during the daytime at a site of central China in Wuhan City.

Many field campaigns have analyzed the ambient level, diurnal profile, and sources of HONO because of

© 2018 The Author(s). Published by IOP Publishing Ltd
its importance to atmospheric OH radical formation (Su et al 2008, Liu et al 2012a, Lee et al 2016). Short-wave radiation (SWR) induced photolysis has been acknowledged as the major sink of HONO during the daytime. However, the daytime source of HONO remains unknown based on current knowledge and cannot merely be explained by the gaseous reaction between atmospheric NO and OH. As a result, the performance of the 3D chemical transport model (CTM) simulations of OH radicals and O3 might be influenced by the missing HONO source (Zhang et al 2012). Hence, the missing daytime HONO source is highly significant and must be understood to achieve better 3D CTM simulations of O3. Several mechanisms have been proposed to explain the missing daytime HONO source. Su et al (2011) proposed that nitrates in low-pH fertilized soil may be a strong source of ambient HONO (Su et al 2011), whereas Vanden-Boer et al (2015) reported that surface acid displacement processes were an important potential HONO daytime source in both urban and vegetated regions. Zhou et al (2011) found that surface nitrate loading correlated with HONO flux in a forest environment. Furthermore, in the ambient environment, the heterogeneous conversion of NO2 to HONO on the soot surface was found to increase dramatically in response to solar radiation (Monge et al 2010).

Increasing attention has recently been directed to the heterogeneous conversion of NO2 to HONO on aerosol surfaces. Tong et al (2016) reported that the RH (relative humidity) and PM2.5 (atmospheric particulate matter with a diameter <2.5 mm) concentration might be important factors in the conversion of NO2 to HONO (Tong et al 2016). Combined with 1D model simulation and correlation analysis, Liu et al reported that rapid daytime HONO formation depended on the aerosol surface area and solar radiation strength (Liu et al 2014). They further proposed that dicarboxylic acid anions on the wet aerosol surface could catalyze the enhanced hydrolytic disproportionation of NO2. Given the high levels of dicarboxyl compounds and organic acid found in China (Hu et al 2010, Hu et al 2011, Kawamura et al 2013), aerosol might serve a more important role in HONO formation in this region than in other areas of the world. However, the importance of aerosol surface area with respect to heterogeneous HONO formation remains controversial. Some studies reported relatively low (10^-7 to 10^-6) NO2 uptake coefficients on the aerosol surface area (Stemmier et al 2007), whereas others observed uptake coefficients of 10^-4 to 10^-3 (Colussi et al 2013).

This study combined observational and 3D CTM simulation data to further investigate the role of aerosol in heterogeneous HONO formation. We applied observational data and output from models to calculate the unknown HONO production source and investigated the relative HONO contributions from aerosol, ground heterogeneous sources and soil emissions. The NO2 uptake coefficient was further estimated based on the calculated unknown HONO source, and the new coefficient was modified into the community multiscale air quality model (CMAQ) to further study the effects of aerosol-generated HONO on O3 concentrations in China.

2. Data and methods

2.1. Observational and model data

In this work, the average diurnal HONO concentrations from 14 different cases worldwide were extracted from the literature to calculate the unknown HONO source. Data from forest or Arctic regions, which have unique underlying surfaces, were excluded. Table 1 lists the locations of the campaigns investigated in this study. In general, the collected HONO data were sampled in China, the United States, Italy, Mexico, and France. The locations of the sampling sites can be found in figure 1 (green triangles). The sampling period as well as the HONO measurement method are listed in table S1 (available online at stacks.iop.org/ERL/13/114002/mmedia).

The wet aerosol surface area was used for correlation analyses (between unknown HONO source) and NO2 uptake coefficient calculations. The observed dry aerosol surface area was corrected using the ratio of the simulated wet surface area over the simulated dry surface area. For some areas with observed PM2.5 concentration data but no available aerosol surface area data, the simulated wet surface area was corrected by the ratio of the observed PM2.5 concentration over the simulated PM2.5 concentration. The availability of the aerosol surface area data for each case is listed in table 1. The wet aerosol surface areas of the sampling sites in China were simulated with the CMAQ model, whereas these surface areas of other sites were simulated using the GEOS-Chem global CTM. Cai et al (2017) reported that the R^2 between the active aerosol surface area and PM2.5 mass concentration reached a value of 0.85. Hence, the correction method is adequate for the analysis of correlating the unknown HONO source with aerosol surface area. The random errors in the aerosol surface area corrections will lead to a low bias in the R^2 between the unknown HONO source and aerosol surface area.

The OH concentration is needed to calculate HONO production from NO + OH. For study that did not contain OH concentration (e.g. Jiangmen), this value was calculated by the 3D CTM. The J(HONO) values were simulated with CMAQ (within China) and GEOS-Chem (outside China). In addition, SWR(W m^-2) data are required for an investigation of the photo-enhanced effect on HONO formation. Because most of the analyzed field campaigns did not report the SWR value, we adopted SWR values from Weather Research Forecast (WRF) corrected by a factor of exp(-AOD) (aerosol optical depth) and from the...
Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2) for cases within China and outside China, respectively. We used AOD data from the moderate resolution imaging spectroradiometer (MODIS) AOD 550 nm product. In short, the observation and model data used in this study includes: HONO data, aerosol surface area data, J values (HONO), SWR value (simulated), dry deposition velocities for HONO and NO₂ (simulated, section 2.3), and vertical diffusion coefficient (simulated, section 2.3).

### 2.2. Model configuration

WRF v3.2 was used to simulate the meteorology field for the CMAQ model. WRF has a domain resolution of 27 km, and the domain extent is shown in figure 1 (blue dash line). Final Operational Global Analysis (FNL) Data were used to drive the WRF model. CMAQ (v5.0.1) also has a domain resolution of 27 km, and its domain extent is plotted as a red line in figure 1. The CMAQ domain covers most of China and some neighboring countries, including Korea and Japan. CB05 and ISORROPIA were respectively selected as the gas-phase chemistry scheme and inorganic aerosol scheme for the simulation. The in-line photolysis module, which considers aerosol, ozone, and cloud attenuation effects, was selected for the chemical photolysis rate calculation. The dry deposition velocity in the CMAQ model is calculated using the M3Dry module (Plem and Byun 2004). The MEX emission inventory was used as the anthropogenic emission input for this simulation (Li et al 2017). More details about the WRF and CMAQ schemes settings have been reported by Lu et al (2015).

GEOS-Chem v10.01 was used in this work. This model was driven by the GEOS-FP met fields and has a worldwide domain extent with a spatial resolution of 2 × 2.5 degree. The GEOS-Chem model is run with full gaseous chemistry and an updated isoprene scheme (Mao et al 2013), and the simulated aerosol species included sulfate, nitrate, ammonium, black carbon (BC), sea salts, natural dust, and primary organic carbon. A non-local scheme (Lin and McElroy 2010) and a relaxed Arakawa-Schubert scheme (Suarez et al 2008) were selected for vertical mixing and convection, respectively, in the simulation. The model-based dry deposition velocity calculation was based on the Wesely resistance-in-series model (Wesely 1989). More details of the dry deposition calculations in GEOS-Chem and CMAQ can be found in the supplemental material.

### 2.3. Unknown HONO source estimation

We proposed an analytic 1D framework based on the equations shown below to analyze the unknown HONO source. The proposed equations consider the gaseous HONO source (NO + OH), daytime HONO sink, NO₂ heterogeneous conversion to HONO from the ground and an unknown source:

\[
\begin{align*}
\frac{\partial c}{\partial t} &= -K_z \frac{\partial^2 c}{\partial z^2} - K_c c + S', \\
- K_z \frac{\partial c}{\partial z} \bigg|_{z=0} &= F
\end{align*}
\]

where \(c\) is the HONO concentration, \(t\) is the time, \(K_z\) is the vertical eddy diffusion coefficient (table S2), \(K_c\) is the HONO chemical reaction coefficient \((\text{s}^{-1})\), \(F\) is the vertical HONO flux from the ground and \(S'\) is the combination of the unknown HONO source and the source from the reaction of NO and OH (molecule \(\text{cm}^3\ \text{s}^{-1}\)). The pseudo-steady state is assumed, \((\frac{\partial c}{\partial t} = 0)\), and hence we selected for analysis the period when the daytime HONO concentration reached a steady value (the period for each case is listed in table 1). The daytime HONO photochemical lifetime is on the order of 10–20 min. Therefore, when daytime HONO concentrations do not change, it suggests that mixing processes reached a steady state with HONO chemical sources and sinks. We assumed that the unknown HONO source would not change with the...

### Table 1. References analyzed for the HONO unknown source in this work.

| No. | References | Location | Time period | Aerosol surface area | Note |
|-----|------------|----------|-------------|----------------------|------|
| 1   | Liu et al (2014) | Beijing, China | 2007.08 | Observation | Average Case |
| 2   | Liu et al (2014) | Beijing, China | 2007.08 | Observation | Heavy Pollution Case |
| 3   | Hou et al (2016) | Beijing, China | 2014.02/03 | CMAQ | Clean Case |
| 4   | Hou et al (2016) | Beijing, China | 2014.02 | CMAQ | Heavy Pollution Case |
| 5   | Zhao et al (2015) | Shanghai, China | 2010.06 | CMAQ | |
| 6   | Yue et al (2015) | Jiangmen, China | 2013.10 | CMAQ | |
| 7   | Su et al (2008) | Guangzhou, China | 2004.10 | Observation | |
| 8   | Acker et al (2006) | Rome, Italy | 2001.05/06 | GEOS-Chem | |
| 9   | Michoud et al (2014) | Paris, France | 2009.07 | GEOS-Chem | Summer case |
| 10  | Michoud et al (2014) | Paris, France | 2010.01/02 | GEOS-Chem | Winter case |
| 11  | Li et al (2010) | Mexico City, Mexico | 2006.03 | GEOS-Chem | |
| 12  | VandenBoer et al (2014) | California, USA | 2010.05/06 | Observation | |
| 13  | VandenBoer et al (2013) | Colorado, USA | 2011.02 | GEOS-Chem | |
| 14  | Gall et al (2016) | Dallas, USA | 2011.06 | Observation | |

* The aerosol wet surface area was corrected by the ratio of the observed PM₂.₅ concentration over the simulated PM₂.₅ concentration.
height near the surface, allowing us to derive an analytical solution for equation (1):

\[ X = \frac{F}{\sqrt{K_c K_e}} + \frac{S}{K_c}, \]  

(2)

where \( X \) is the observed HONO concentration subtracted the HONO formed by NO + OH. Other unknown gas phase HONO formation reaction is not considered here. \( K_c \) is calculated based on the HONO photolysis rate and the reaction rate between HONO and OH, which determine the HONO lifetime during the daytime. \( F \) is the net HONO ground flux and is calculated as the upward HONO flux subtracted by the downward HONO flux (dry deposition). \( S \) is the unknown HONO source (molecule cm\(^{-3}\) s\(^{-1}\)), which is not the ground heterogeneous conversion or the gaseous phase formation. Zhang et al (2016) evaluated several PBL schemes in a 1D column model to investigate the boundary-layer vertical gradients of reactive nitrogen oxides using the DISCOVER-AQ 2011 campaign and reported that the ACM2 scheme is the best and that it can reproduce the profile of the deep turbulent mixing. Hence, in this work, ACM2 scheme was used to calculate the vertical diffusion coefficients for the 1D analytic framework. Non-local mixing is not considered here, which may cause biases in the computed HONO budget calculation. However, the differences among the different WRF boundary layer mixing schemes found by Zhang et al (2016) is considerably less than the uncertainties in unknown HONO aerosols.

In this analytic 1D framework, we assumed that as the NO\(_2\) molecules reached the ground via dry deposition, part of them would be converted to HONO and released to the atmosphere immediately (upward HONO flux). According to Liu et al (2014), we assumed that the ground heterogeneous conversion of NO\(_2\) and dry deposition of HONO were the major nighttime HONO source and sink, respectively. The NO\(_2\) ground conversion ratio \((f)\) during the nighttime could then be calculated by equation (3):

\[ \text{[HONO]} \times V_{\text{HONO}} = f \times [\text{NO}_2] \times V_{\text{NO}_2}. \]  

(3)

The dry deposition velocities of HONO and NO\(_2\) were calculated using the CMAQ (within China) and GEOS-Chem 3D models. The NO\(_2\) ground conversion ratio \((f)\) from equation (3) was then used to calculate the upward HONO flux during the daytime. Hence, the \( F \) term in equation (2) is calculated by subtracting the right-hand side by the left-hand side of equation (3). The conversion ratio \((f)\) for each case can be found in table S2 in the supplemental material. The parameter, \((f)\), is mainly dependent on the surface characteristics, e.g. surface area, surface type. Hence, it is reasonable to keep the value of \((f)\) constant when the sampling location did not change. Some of other works also applied the dry deposition rate of NO\(_2\) to calculate the NO\(_2\) ground conversion rate during the nighttime (Li et al 2012, Liu et al 2014).

After acquiring the unknown HONO source \( S \) (molecule cm\(^{-3}\) s\(^{-1}\)) from equation (1), the NO\(_2\) uptake coefficient for aerosol could then be calculated using equations (4) and (5) listed below:

\[ S = k_a \times [\text{NO}_2], \]  

(4)

\[ k_a = \sum_{i=1}^{n} \left[ \frac{r_i^2}{D_g} + \frac{4}{\gamma \omega} \right]^{-1} A_i, \]  

(5)

where \( k_a \) is the first-order NO\(_2\) uptake coefficient for aerosol (s\(^{-1}\)), \( A_i \) and \( r_i^2 \) are the aerosol surface area (\(\mu m^2\) cm\(^{-3}\)) and particle radius (\(\mu m\)) for the \(i\)th size bin, respectively, \( \omega \) is the NO\(_2\) mean molecular velocity (m s\(^{-1}\)), \( D_g \) is the gas molecular diffusion coefficient (m\(^2\) s\(^{-1}\)) and \( \gamma \) is the NO\(_2\) uptake coefficient.

We discuss the correlation between the unknown HONO source and aerosol wet surface area in section 3. The NO\(_2\) uptake coefficient, calculated using equation (5), was implemented into the CMAQ model.
Table 2. Calculated unknown HONO concentrations/sources for the selected campaigns.

| Time          | Unknown HONO concentration\(^a\) | Unknown HONO source\(^b\) |
|---------------|-----------------------------------|---------------------------|
| 1 14:00–16:00 | 1.78 \times 10^{10}              | 2.00 \times 10^{7}       |
| 2 15:00–17:00 | 4.07 \times 10^{10}              | 2.84 \times 10^{7}       |
| 3 15:00–16:00 | 1.25 \times 10^{10}              | 9.38 \times 10^{6}       |
| 4 13:00–14:00 | 4.00 \times 10^{10}              | 3.48 \times 10^{7}       |
| 5 14:00–15:00 | 5.76 \times 10^{9}               | 6.82 \times 10^{6}       |
| 6 10:00–14:00 | 2.39 \times 10^{10}              | 1.70 \times 10^{7}       |
| 7 12:00–14:00 | 1.98 \times 10^{10}              | 2.50 \times 10^{7}       |
| 8 14:00–15:00 | 3.25 \times 10^{9}               | 6.88 \times 10^{6}       |
| 9 14:00–16:00 | 2.09 \times 10^{9}               | 3.07 \times 10^{6}       |
| 10 15:00–17:00| 7.49 \times 10^{9}               | 1.75 \times 10^{6}       |
| 11 14:00–16:00| 3.86 \times 10^{9}               | 4.24 \times 10^{6}       |
| 12 16:00–17:00| 1.70 \times 10^{9}               | 1.90 \times 10^{6}       |
| 13 11:00–13:00| 7.17 \times 10^{9}               | 8.70 \times 10^{5}       |
| 14 9:00–11:00 | 5.19 \times 10^{9}               | 7.93 \times 10^{5}       |

\(^a\) Values are shown in molecules cm\(^{-3}\).

\(^b\) Values are shown in molecules cm\(^{-3}\) s\(^{-1}\).

and its effects on O\(_3\) and OH concentrations in China were investigated.

3. Results and discussion

3.1. Heterogeneous HONO formation from aerosol

The calculated unknown HONO concentration/source and time periods we selected for the study are shown in table 2. The calculated unknown HONO concentrations ranged from 7.17 \times 10^{6} (No. 13 for Colorado case) to 4.07 \times 10^{10} molecules cm\(^{-3}\) (No.2 for 2007 Beijing Heavy Pollution Case), and the unknown HONO sources ranged from 8.70 \times 10^{5} (No.13 for Colorado case) to 3.48 \times 10^{7} molecules cm\(^{-3}\) s\(^{-1}\) (No.4 for 2014 Beijing Heavy Pollution Case). The calculated unknown HONO concentrations were generally higher in China than in other countries. The unknown HONO sources in Beijing (cases No.1, 2 and 4), Jiangmen (No.6) and Guangzhou (No.7 for Xinken site) all exceeded 10^{7} molecules cm\(^{-3}\) s\(^{-1}\).

Figure 2(a) depicts the R\(^2\) between the calculated unknown HONO source and aerosol wet surface area. A total of 14 points were used for the correlation analysis, and each point represents an individual case listed in table 1. The R\(^2\) between these two parameters reached 0.87. Some studies have reported that SWR could enhance heterogeneous HONO formation by aerosol (Liu et al 2014, Lu et al 2017). Accordingly, the the R\(^2\) value between the unknown HONO source and aerosol wet surface area increased to 0.92 after multiplying by SWR (figure 2(b)). These results provide the evidence to support that the aerosol surfaces comprise an important medium for HONO formation. The OH radical concentrations for Jiangmen (No.6), Shanghai (No.5) and Rome (No.8) cases were calculated by the 3D CTM. A sensitivity test was performed by adding 50% more to the OH concentrations to these three cases and the changes of the calculated unknown HONO source are 2.9% (No.6 for Jiangmen case), 1.5% (No.8 for Rome case) and 3.2% (No.5 for Shanghai case) respectively, when compared to the original values. This shows that HONO production from the reaction of NO + OH is limited when compared to the unknown HONO source and the uncertainty caused by the OH radical computation in these three cases would not influence the results. Since the effect of multiple scattering by aerosols is not included, the attenuation effect of SWR may be overestimated. However, the biases do not lead to false correlations between the unknown HONO source and aerosol since the bias in SWR estimate is monotonic with aerosol AOD.

NO\(_2\) is the major gaseous precursor of both HONO and aerosol formation, and this might drive the strong correlation between the aerosol surface area and the unknown HONO source. As shown in figure 2(c), the R\(^2\) between NO\(_2\) and the unknown HONO source was only 0.62, much lower than the R\(^2\) between the unknown HONO source and aerosol wet surface area. Multiplication by SWR decreased the R\(^2\) value between the unknown HONO source and NO\(_2\) to 0.19. Therefore, figures 2(c) and (d) indicate that the strong R\(^2\) between the unknown HONO source and the aerosol surface area was not driven by NO\(_2\). However, the R\(^2\) between the unknown HONO source and the product of aerosol wet surface area \(\times\) NO\(_2\) \(\times\) SWR dropped down to 0.78. Except the cases of California, Colorado, Beijing 2007 and Shanghai, the NO\(_2\) data in the other datasets were measured by the chemiluminescence method, which might be influenced by the NO\(_y\) species (e.g. PAN). We further applied the observed seasonal ratios of coincident NO\(_2\) measurements of by the chemiluminescence instrument to the more selective photolytic instrument reported by Zhang et al (2018) to correct the NO\(_2\) data and found that the R\(^2\) (0.87) increased after the correction (figure 2(f)). Xu et al (2013) reported that this ratio varied in different seasons and locations. Hence, the applied correction ratios by Zhang et al (2018) may not be representative for the different campaigns in this study. By using a consistent NO\(_2\) dataset, the R\(^2\) between the unknown HONO source and the product of SWR \(\times\) NO\(_2\) \(\times\) aerosol surface area was the highest when compared to other correlations in Liu et al (2014). Therefore, figures 2(e), (f) implies that the decrease of R\(^2\) after adding NO\(_2\) might be caused by the inconsistent uncertainties in NO\(_2\) measurements in different campaigns. The decrease of the R\(^2\) value may reflect some of the approximations used in this study. However, we believe that the change may be more numerical than physical. Panel (b) of figure 2 shows much more evenly distributed data points without NO\(_2\) than panel (f) with NO\(_2\). In panel (f), there are effectively only 7 data points because the low NO\(_2\) \(\times\) SWR \(\times\) aerosol wet surface area data points are essentially lumped together. The large
deviations of the three data points (in red, black, and blue) from the regression line explain most of the decrease of the $R^2$ value. Recent studies pointed towards much faster photolysis of aerosol nitrate as a source of HONO (Ye et al. 2016, Ye et al. 2017). Our analysis cannot rule out that this pathway contributes significantly to daytime HONO formation. Given the relatively small amount of nitrate in aerosols, the supply of aerosol nitrate through the reaction of OH and NO$_2$ in daytime essentially balances out nitrate photolysis and therefore the production of HONO in aerosols has a similar daytime cycle as OH. Modeling analysis of summer data at Wangdu, China (e.g. Liu et al. 2017, Tan et al. 2017) suggests that if aerosol nitrate photolysis rate is ten times higher than that of gas-phase HNO$_3$ photolysis, the pathway will provide <10% of the daytime unknown HONO (Hang Qu 2018 personal communication). More research is required to understand if this mechanism can reproduce the observed daytime variation of HONO (Liu et al. 2014).

Besides the investigation of the averaged unknown HONO source around the world, the day-to-day unknown HONO source has also been analyzed for the Beijing 2007 case. During the sampling period in this campaign, eleven days’ data are available (e.g. valid aerosol surface area data, no precipitation, and at least 2 h stable daytime HONO concentrations). However, the MODIS AOD data are available for only five days and hence, the correlation between the unknown HONO source and aerosol wet surface area × NO$_2$ × SWR was not examined. Shown in figure S1, the unknown HONO source still has a relatively high $R^2$ with the aerosol wet surface area, which demonstrates that aerosol surface is possibly an important driver for the formation of HONO during daytime.

Ground heterogeneous conversion might also be an important potential source of heterogeneous HONO formation. Hence, we investigated whether ground heterogeneous conversion could sustain the daytime HONO level. We excluded the third term in

---

**Figure 2.** The $R^2$ values of calculated unknown HONO sources with the aerosol wet surface area (a), the aerosol wet surface area × SWR (W m$^{-2}$)(b), NO$_2$ (c), NO$_2$ × SWR (d), NO$_2$ × SWR × aerosol wet surface area (e) and corrected NO$_2$ × SWR × aerosol wet surface area (f).
equation (2) and set the unknown HONO as directly equal to the ground-generated HONO. The ground NO$_2$-to-HONO conversion ratio, ($f$), was then calculated by substituting all other parameters into this modified equation. The new $f$ values for different cases are shown in Table 3. Based on our calculation, the NO$_2$-to-HONO conversion ratios of all cases, except Beijing 2007 Heavy Pollution (99%), Mexico City (37%) and Colorado (87%), exceeded 100% if the aerosol heterogeneous formation was not considered. In other words, these results suggest the non-physical conversion of one NO$_2$ molecule to more than one HONO molecule on the ground. This result indicates that NO$_2$ ground heterogeneous conversion cannot be the only major unknown HONO source under most circumstances. We note that it is assumed that soil nitrate is not a source of atmospheric HNO$_2$.

The calculated unknown HONO concentrations at Chinese sites were large and possibly derived from soil emissions. Through laboratory experiments, Oswald et al. (2013) found that the ammonia-oxidizing bacteria in soil can directly emit HONO and reported HONO emission flux values from different types of soil. Notably, differences in emission were great, even for the same type of soil, as demonstrated by the >500% difference between two pasture soil samples taken from different locations. Sörgel et al. (2015) reported that acidic soil might not promote HONO emission and stated that the mechanisms of soil emission remained under debate. Given this uncertainty, the HONO emission flux for related soil types could not be applied to equation (1) when estimating the exact HONO budget from soil emissions based on current knowledge.

Hence, we discuss herein the relative importance of soil emissions compared to the aerosol heterogeneous source. Among the seven sites in China, the Beijing and Shanghai sites are located in urban areas, far from farmlands, whereas the Guangzhou (No.7 for Xinken site) and Jiangmen (No.6) sites are in rural areas. The urban areas mainly comprise concrete surfaces, with a small proportion of tree and grass coverage. Hence, soil emission is unlikely to be a major HONO source in urban areas. However, it remains interesting to compare the relative amounts of HONO generated by aerosol sources and estimates of soil HONO flux. Because the sites did not have homogeneous land-use types, we calculated the average HONO emission fluxes of pasture, woody savannah, and grassland according to Oswald et al. (2013) and added the optimum value ($\sim5.8 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$ at 25 °C) to the second term of equation (2). The HONO soil emission flux depends on the soil water content and can decrease to zero when the soil water content is near zero or exceeds 40%. For the soil flux, we used the peak value (optimum) for each soil type at an approximate soil water content of 15%. After adding the potential soil emission flux, the ratios of aerosol-generated HONO (the third term in equation (2)) versus observed HONO are 56.5%, 80.3%, 34.1%, 69.9%, 53.2%, and 60.9% for the Beijing 2007 average and heavy cases (No.1 and 2), Beijing 2014 clean and heavy cases (No.3 and 4), Guangzhou (No.7), and Jiangmen cases (No.6), respectively. The optimum soil emission could sustain the daytime HONO budget in the Shanghai case (No.5), for which the aerosol concentration was relatively low. At the optimum HONO soil flux, however, HONO from an aerosol source still accounted for more than 60% of the total HONO budget for both the Beijing heavy pollution cases. This further demonstrates that aerosol is an important HONO source in China in urban sites with high aerosol loading. Earlier soil studies found that N$_2$O correlated positively with soil temperature (Dobbe and Smith 2001, Schindlbacher et al. 2004). In a soil model, Parton et al. (2001) reported that at temperatures below 10 °C, the parameter used to characterize the nitrification process decreased dramatically. Oswald et al. (2013) also showed that the soil HONO emissions would decrease with decreasing temperature. In winter, low soil temperatures prohibit soil HONO emissions, and aerosol becomes a more important medium for heterogeneous HONO formation (e.g. No.4 case).

### 3.2. NO$_2$ reactive uptake coefficient

As introduced in section 1, the NO$_2$ reactive uptake coefficient can be calculated using equations (4) and (5) once the unknown HONO source has been acquired. Because high daytime HONO sources have been along with high aerosol loading are found in China (table 2), the NO$_2$ reactive uptake coefficients for the first seven cases were calculated and used to study the regional effect on O$_3$ in China (in section 3.3).

As shown in table 4, the calculated $\gamma$ values range from $1.0 \times 10^{-4}$ (Beijing 2014 heavy pollution case) to $7.9 \times 10^{-4}$ (Shanghai 2010 case). The magnitudes of our calculated $\gamma$ values are equivalent to those reported

| Conversion ratio | Table 3. NO$_2$-to-HONO ground conversion ratios without consideration of the aerosol source. |
|------------------|-----------------------------------------------------------------------------------------------|
| 1                | 118%                                                                                         |
| 2                | 99%                                                                                          |
| 3                | 320%                                                                                         |
| 4                | 290%                                                                                         |
| 5                | 232%                                                                                         |
| 6                | 250%                                                                                         |
| 7                | 195%                                                                                         |
| 8                | 208%                                                                                         |
| 9                | 100%                                                                                         |
| 10               | 195%                                                                                         |
| 11               | 37%                                                                                          |
| 12               | 131%                                                                                         |
| 13               | 87%                                                                                          |
| 14               | 450%                                                                                         |
by Colussi et al (2013) and those used by Liu et al (2014) and Wong et al (2012) for 1D/3D model simulations. As introduced in section 1, some aerosol components (e.g. dicarboxylic acid anions) can enhance HONO formation. Nie et al (2015) observed a high NO2/HONO ratio in the mixed plumes resulting from biomass burning and fossil fuel emission and concluded that this mixed aerosol could promote HONO formation. Other studies reported that the NO2–to–HONO conversion ratio could be influenced by mineral (e.g. Al2O3) (Romanias et al 2013) and metal (e.g. Fe2+) (Kebede 2015) compositions. According to an observation study, the metal compositions of aerosols in China exhibit large daily variations (Okuda et al 2004). Recently, Han et al (2016 and 2017) reported that the NO2 uptake coefficient and HONO yield would not change with light intensity on the humid acid; however, once the benzophenone was added, the HONO yield increased linearly with the light intensity. Hence, differences in γ values may be attributable to differences in aerosol components during different periods and at various locations. Another factor that influences the uptake coefficient calculation is the interference of the chemiluminescence measurements of NO2 as discussed in section 3.1. More field experiments are needed to verify the dominant factors that affect the magnitude of the reactive NO2 uptake coefficient in an ambient environment.

Liu et al (2014) assumed a linear dependence of γ on SWR. Using their method, we calculated the γ/SWR (γ′), as shown in the second column of table 4. Our γ′ values for the seven cases were on the order of 10^{-7} to 10^{-6}. In some modeling studies, such as that conducted by Zhang et al (2012), the reactive NO2 uptake coefficient was set to equal the magnitude of γ′ calculated in this work, without considering the photo-enhancement effect. Using such a parameterization, the NO2 uptake coefficient during daytime could be underestimated (Liu et al 2014). Accordingly, the aerosol contribution to heterogeneous HONO formation is negligible in some 3D modeling studies. Because the exact soil HONO flux could not be identified, the γ′ calculated in this work harbors some uncertainty.

| Case | γ (NO2 emission) | γ (SWR) |
|------|------------------|---------|
| 1    | 7.6 × 10^{-4}    | 2.2 × 10^{-6} |
| 2    | 1.9 × 10^{-4}    | 8.8 × 10^{-7} |
| 3    | 6.2 × 10^{-4}    | 1.8 × 10^{-6} |
| 4    | 1.0 × 10^{-4}    | 4.2 × 10^{-7} |
| 5    | 7.9 × 10^{-4}    | 1.5 × 10^{-6} |
| 6    | 2.3 × 10^{-4}    | 8.2 × 10^{-7} |
| 7    | 2.1 × 10^{-4}    | 4.5 × 10^{-7} |

3.3. Effect on O3 spatial distribution

The formation of HONO from heterogeneous NO2 conversion on aerosol and ground surfaces was implemented into the CMAQ model. The effects of aerosols on regional-scale ambient HONO, OH and O3 concentrations were also investigated. The following simulations were set for this comparison: (1) HONO formation mechanisms, including gaseous formation in CB05, tailpipe emission (0.8% of total NOx emission), and ground heterogeneous formation (f set as 0.1) and (2) the mechanism listed in the first set of simulations, together with the aerosol heterogeneous HONO formation based on equation (4). We used the same CMAQ domain shown in figure 1 for this sensitivity comparison. January, April, July, and October 2015 were selected for the simulation, representing four different seasons. To determine heterogeneous HONO formation on the aerosol surface, we parameterized the reactive NO2 uptake coefficient by γ = γ′ × SWR. As shown in table 4, the γ′ value differed for each case. Given the short lifetime of HONO for our analysis periods, HONO sources should be balanced by its chemical loss. We therefore obtain the optimal γ′ value by minimizing the squared difference between HONO sources and chemical sink for all data points in table 1. The value of the optimized γ′ is 5.0 × 10^{-7}.

The difference between the CMAQ baseline and updated HONO heterogeneous formation scheme is shown in figure 3. Following the update, during winter daytime (9:00 am–17:00 pm), a simulated HONO difference generally greater than 0.5 ppbv mainly appeared in central, southwestern (SiChuan Basin) and eastern China (Yangtze River Delta). The difference in OH was also centered in this region and reached approximately 200% after updating the scheme. The O3 differences in some areas of this region reached 10 ppbv. In summer, the differences in HONO, O3, and OH in the northern plain and eastern coast of China were relatively larger than those in other places. The simulated spatial difference in July in this study was similar to that in August as reported by Liu et al (2014). The differences in the spatial patterns of these three species between April (spring) and October (autumn) were similar. In the northern central plain of China, the differences for O3 and HONO were larger during October than during April. When an adequate HONO soil emission module is included, the simulation differences of HONO, O3, OH are expected to become larger.

The simulation over China yielded a much larger difference in winter than in summer, which can be attributed largely to two factors. (1) The aerosol concentration over the northern plain of China is higher in winter than in summer because of weaker, stable meteorology conditions (Zou et al 2017). (2) As noted by Liu et al (2014), the OH source generated by O (′D) + H2O is much smaller in winter than in summer because of the low RH in winter. Accordingly,
heterogeneous HONO formation from aerosol plays a more important role with respect to the radical budget and the O$_3$ ambient level during winter. Based on this result, the O$_3$ concentration would decrease if the particulate matter level decreases, especially during winter. However, the O$_3$ production rate would increase as the aerosol optical depth decreases, in contrast to the effect of aerosol on the formation of HONO (Lu et al. 2017). The HO$_2$ uptake by aerosol has not yet been included in the CMAQ model. If this mechanism is active, however, the HO$_2$ concentration would increase as the aerosol concentration decreases, which would promote O$_3$ formation (Liu et al 2012a). Hence, in the future, it is important to investigate the combined effects of aerosol on O$_3$ formation in China.

Two important factors are needed in future studies to improve the 3D CTM simulations of the ambient HONO concentrations in China: (1) the effects of aerosol components on the coefficient of NO$_2$ heterogeneous uptake and (2) the important factors determining HONO soil emissions. Liu et al (2012b) investigated satellite products and reported a relatively high concentration of glyoxal (dicarboxylic acid precursor) in central China. Colussi et al (2013) reported that the carboxylate anions can work as a catalyst to promote the disproportionation of NO$_2$ on water and HONO formation. This may have driven the heterogeneous HONO generation in the northern central plain of China. Yabushita et al (2009) also reported that the NO$_2$ uptake coefficient can be enhanced by

Figure 3. Monthly average changes in HONO (ppbv), O$_3$ (ppbv) and OH (%) levels during 9:00 am–17:00 pm in January, April, July and October 2015 (1–4 represent the cases in different seasons and (a)–(c) represent the changes of HONO, O$_3$ and OH).
several order of magnitude by the disproportionation of gas phase NO2 on the air/water interface. More experimental studies are needed to quantify the effect of the aerosol component on the production of HONO. Although Oswald et al (2013) reported the HONO emissions of different soil types, large emission differences were observed even for single soil type, and the factors that determine this process will require further identification in the future.

Several recent studies found that current mechanisms in 3D CTMs could not explain the observed sulfate production rates during winter in north and central China (Wang et al 2014, Zheng et al 2015). The following reactions could oxidize sulfur(IV) and produce particulate sulfate (R2–R4 are aqueous phase reactions):

\[
\begin{align*}
\text{SO}_2 + \text{OH} & \rightarrow \text{H}_2\text{SO}_4 + \text{HO}_2, \\
\text{SO}_2 + \text{O}_3 & \rightarrow \text{H}_2\text{SO}_4 + \text{O}_2, \\
\text{HSO}_3 + \text{O}_3 & \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2, \\
\text{HSO}_3^+ + \text{H}_2\text{O}_2 & \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{H}_2\text{O}. 
\end{align*}
\]

As shown in figure 3, the OH and O3 concentrations increased substantially after the heterogeneous HONO production in January was added. H2O2 would increase as a result of increases in OH and HO2. According to R1–R4, increases in OH and O3 could promote the formation of SO4^{2-}, which might partly explain the missing sulfate formation in the 3D CTMs. Spatially enhanced sulfate production in January is demonstrated in figure S2 in the supplemental material. Sulfate production increased by approximately 6–8 μg m^{-3} in the northern central plain and by 10 μg m^{-3} or more in the Sichuan Basin. Czader et al (2013) noted that the CMAQ underestimated the daytime OH and HO2 concentrations of a polluted air mass. In other words, the missing daytime OH could explain part of the missing particulate sulfate in the 3D CTMs.

### 3.4. Conclusion
In this study, a consistent 1D framework based on regional and 3D CTMs was used to analyze the unknown daytime HONO sources in 14 cases worldwide. We assume that the source of HONO from aerosols is through NO2 hydrolysis (not including its oxidation products) and that non-local mixing effect is negligible. We found that the daytime unknown HONO source correlated strongly with the aerosol wet surface area. If all unknown HONO were derived from NO2 ground heterogeneous formation, the NO2-to-HONO conversion fraction would exceed 100% in most cases, which is unphysical. After adding the optimized soil emission, heterogeneous HONO formation from aerosol still accounted for more than 60% in the two urban heavy pollution cases. Furthermore, low soil temperatures in winter could prohibit the emission of HONO from soils. Hence, our results indicate that aerosol should play an important role in daytime HONO heterogeneous formation, especially on days affected by heavy pollution and winter temperatures. This result contrasts with the general assumption that aerosols are insignificant with regard to daytime HONO formation. The NO2 uptake coefficient was estimated for seven cases in China, leading us to propose that variations in the uptake coefficients depend on the aerosol composition. According to the CMAQ simulation results, the aerosol generated HONO can contribute up to 10 ppbv of O3 in central China. Further investigations of the effects of different aerosol components on HONO production in China are warranted, because such efforts could improve O3 and PM2.5 simulations based on 3D CTMs.

### Acknowledgments
We thank the CalNex 2010 campaign for making the data public. We also thank the constructive comments from the anonymous reviewers. We appreciate the help from Prof Alexis Lau (HKUST) for the CMAQ model consultation. This work was supported by the Research Grants Council of Hong Kong Government (Project No. T24/504/17). Xingcheng Lu was supported by the Overseas Research Award from the Hong Kong University of Science and Technology. Yuhang Wang was supported by the Atmospheric Chemistry Program of the US National Science Foundation.

### ORCID iDs
Xingcheng Lu @ https://orcid.org/0000-0002-0962-9855
Lu Shen @ https://orcid.org/0000-0003-2787-7016

### References
Acker K, Febo A, Trick S, Perrino C, Bruno P, Wiesen P, Möller D, Wieprecht W, Auel R and Giusto M 2006 Nitrous acid in the urban area of Rome Atmos. Environ. 40 S12–S33
Avnery S, Mauzerall D L, Liu J and Horowitz L W 2011 Global crop yield reductions due to surface ozone exposure. 1. Year 2000 crop production losses and economic damage Atmos. Environ. 45 2284–96
Cai R, Yang D, Fu Y, Wang X, Li X, Ma Y, Hao J, Zheng J and Jiang J 2017 Aerosol surface area concentration: a governing factor in new particle formation in Beijing Atmos. Chem. Phys. 17 12327–40
Colusui A J, Enami S, Yabushita A, Hoffmann M R, Liu W-G, Mishra H and Goddard W A III 2013 Tropospheric aerosol as a reactive intermediate Faraday Discuss. 165 407–20
Czader B H, Li X and Rappenglück B 2013 CMAQ modeling and analysis of radicals, radical precursors, and chemical transformations J. Geophys. Res.: Atmos. 118 11376–87
Dobbie K and Smith K 2001 The effects of temperature, water-filled pore space and land use on N2O emissions from an imperfectly drained gleysol Eur. J. Soil Sci. 52 667–73
Gall E T, Griffin R J, Steiner A L, Dibb J, Schuerz E, Gong L, Rutter A P, Cevik B K, Kim S and Lefer B 2016 Evaluation of nitrous acid sources and sinks in urban outflow Atmos. Environ. 127 272–82
Han C, Yang W, Wu Q, Yang H and Xue X 2016 Heterogeneous photochemical conversion of NO2 to HONO on the humic
acid surface under simulated sunlight Environ. Sci. Technol. 50 5017–23
Han C, Yang W, Yang H and Xue X 2017 Enhanced photochemical conversion of NO₂ to HONO on humic acids in the presence of benzo[alpha]pyrene Environ. Pollut. 231 979–86
Ho K, Ho S, Lee S, Kwakamura K, Zou S, Cao J and Xu H 2011 Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM₁₀ in Pearl-delta river region, China Atmos. Chem. Phys. 11 2197–208
Ho K, Lee S, Ho S H, Kwakamura K, Tachibana E, Cheng Y and Zhu T 2010Dicarboxylic acids, keto dicarboxylic acids, α-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of air quality research in Beijing (CAREBeijing-2006) J. Geophys. Res.: Atmos. 115 19312
Hou S, Tong S, Ge M and An J 2016 Comparison of atmospheric nitric acid during severe haze and clean periods in Beijing, China Atmos. Environ. 124 199–206
Jaegle L, Jacob D J, Brune W H and Wennberg P O 2011 Chemistry of HO, radicals in the upper troposphere Atmos. Chem. Phys. 11 3469–89
Kawamura K, Okuzawa K, Aggarwal S, Irie H, Kanaya Y and Wang Z 2013 Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxycetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai Atmos. Chem. Phys. 13 5369–80
Kebede M A 2015 Nitric acid formation on environmental surfaces containing titanium and iron PhD Thesis Indiana University
Lee J, Whalley L, Heard D, Stone D, Dunmore R, Hamilton J, Young D, Allan J, Lauti S and Kleffmann J 2016 Detailed budget analysis of HONO in central London reveals a missing daytime source Atmos. Chem. Phys. 16 7247–64
Li G, Lei W, Zavala M, Volkamer R, Dusanter S, Stevens P and Molina L 2010 Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/ MILAGRO Campaign Atmos. Chem. Phys. 10 6531–67
Li M, Zhang Q, Kurokawa J-I, Wu J H, He K, Lu Z, Ohtara T, Song Y, Streets D G and Carmichael G R 2017 MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP Atmos. Chem. Phys. 17 933–63
Lin J-T and McElroy M B 2010 Impacts of boundary layer mixing on satellite remote sensing Chloride at a rural site on the North China plain Environ. Res. Lett. 5 124002
Lu X, Yao T, Fung J C H and Lin C 2016 Estimation of health and economic costs of air pollution over the Pearl river delta region in China Sci. Total Environ. 566 134–43
Mao J, Paulot F, Jacob D J, Cohen R C, Crounse J D, Wennberg P O, Keller C A, Hudman R C, Barkey M P and Horowitz L W 2013 Ozone and nitrate nitrates over the eastern United States: sensitivity to isoprene chemistry J. Geophys. Res.: Atmos. 118 11256–68
Michoud V, Colombe A, Borbon A, Miet K, Beekmann M, Camredon M, Aumont B, Perrier S, Zapf P and Siour G 2014 Study of the unknown HONO daytime source at a European suburban site during the MEGAPOLI summer and winter field campaigns Atmos. Chem. Phys. 14 2805–22
Monge M E, D’Anna B, Mazzri L, Giorno-Fendler A, Ammann M, Donaldson D and George C 2010 Light changes the atmospheric reactivity of soot Proc. Natl Acad. Sci. USA 107 6605–9
Nie W, Ding A, Xie Y, Xu Z, Mao H, Kerminen V-M, Zheng L, Q X, Huang X and Yang X-Q 2015 Influence of biomass burning plumes on HONO chemistry in eastern China Atmos. Chem. Phys. 15 1147–59
Okuda T, Kato J, Mori T, Tennmoku M, Suda Y, Tanaka S, He K, Ma Y, Yang F and Yu X 2004 Daily concentrations of trace metals in aerosols in Beijing, China, determined by using inducibly coupled plasma mass spectrometry equipped with laser ablation analysis, and source identification of aerosols Sci. Total Environ. 330 145–58
Oswald R, Behrendt T, Ermel M, Wu D, Su H, Cheng Y, Breuninger C, Moravek A, Mougin E and Delon C 2013 HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen Science 341 1233–5
Parton W, Holland E, DeGrosso S, Hartman M, Martin R, Mosier A, Ojima D and Schimel D 2003 Generalized model for NO₂ and N₂O emissions from soils J. Geophys. Res.: Atmos. 106 17403–19
Pleim J E and Byun D W 2004 Application of a new land-surface, dry deposition, and PBL model in the models-3 community multi-scale air quality (CMAQ) model system Air Pollution Modeling and Its Application XIV (Berlin: Springer) pp 297–303 (https://doi.org/10.1007/978-3-642-16530_33_30)
Romania N M, Bedjanian Y, Zaras A M, Andrade-Eiroa A, Shahla R, Dagaut P and Philippidis A 2013 Mineral oxides change the atmospheric reactivity of soot: NO₂ uptake under dark and UV irradiation conditions J. Phys. Chem. A 117 12897–911
Schindlhuber A, Zeichmeister-Boltenstein S and Butterbach-Bahl K 2004 Effects of soil moisture and temperature on NO₂, NO₃, and N₂O emissions from European forest soils J. Geophys. Res.: Atmos. 109 D123702
Stemmler K, Moravek A, Wittrock F, Burrow J P, Shao M, Chang C, Liu S C and Wang H 2012b Exploring the missing source of glyoxal Environ. Sci. Technol. 46 333–41
Su H, Cheng Y, Oswald R, Behrendt T, Trebs I, Meixner F X, Andreea M O, Cheng P, Zhang Y and Foschini U 2011 Soil nitrite as a source of atmospheric HONO and OH radicals Science 333 1616–8
Su H, Cheng Y F, Shao M, Gao D F, Yu Z Y, Zeng L M, Slanina J, Zhang Y H and Wiedensohler A 2008 Nitrous acid (HONO) and its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China J. Geophys. Res.: Atmos. 113 D14312
Suarez M J, Rienecker M, Todling R, Bacmeister J, Takacs L, Liu H, Gu W, Sienkiewicz M, Koster R and Gelaro R 2008 The GEOS-5 Data Assimilation System – Documentation of Versions 5.0, 1, 5.1.0, and 5.2.0 (https://ntrs.nasa.gov/search.jsp?R=20120011953)
Sörgel M, Trebs I, Wu D and Held A 2015 A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment Atmos. Chem. Phys. 15 9237–51
Tan Z et al 2017 Radical chemistry at a rural site (Wangdu) in the North China plain: observation and model calculations of OH, HO₂ and RO₂ radicals Atmos. Chem. Phys. 17 663–90
Tong S, Hou S, Zhang Y, Chu B, Liu Y, He H, Zhao P and Ge M 2016 Exploring the nitrous acid (HONO) formation mechanism in winter Beijing: direct emissions and heterogeneous production in urban and suburban areas Faraday Discuss. 189 213–30
VandenBoer T, Markovic M, Sanders J, Ren X, Pusede S, Browne E, Cohen R, Zhang I, Thomas J and Brune W 2014 Evidence for a nitrous acid (HONO) reservoir at the ground surface in Bakersfield, CA, during CalNex 2010 J. Geophys. Res.: Atmos. 119 9093–106
VandenBoer T C, Brown S S, Murphy J G, Keene W C, Young C J, Pszenny A, Kim S, Warneke C, Gouw J A and Maben J R 2013 Understanding the role of the ground surface in HONO vertical structure: high resolution vertical profiles during NACHTT-11 J. Geophys. Res.: Atmos. 118 10155–71
VandenBoer T C, Young C J, Talukdar R K, Markovic M Z, Brown S S, Roberts J M and Murphy J G 2015 Nocturnal loss and daytime source of nitrous acid through reactive uptake and displacement Nat. Geosci. 8 55–60
Wang J, Wang S, Jiang J, DING A, Zheng M, Zhao B, WONG D C, ZHOU W, ZHENG G and WANG I. 2014 Impact of aerosol–meteorology interactions on fine particle pollution during China’s severe haze episode in January 2013 Environ. Res. Lett. 9 094002
Wesely M 1989 Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models Atmos. Environ. 23 1293–304
Wong K, Tsai C, Lefer B, Haman C, Grossberg N, Brune W, Ren X, Luke W and Stutz J 2012 Daytime HONO vertical gradients during SHARP 2009 in Houston, TX Atmos. Chem. Phys. 12 635–52
Xu Z, Wang T, Xue L, Louie P, LUK C, Gao J, Wang S, CHAI F and WANG W 2013 Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China Atmos. Environ. 76 221–6
Yabushita A, Enami S, Sakamoto Y, Kawasaki M, Hoffmann M R and Colussi A J 2009 Anion-catalyzed dissolution of NO₂ on aqueous microdroplets J. Phys. Chem. A 113 4844–8
Ye C et al 2016 Rapid cycling of reactive nitrogen in the marine boundary layer Nature 532 489–91
Ye C, Zhang N, Gao H and Zhou X 2017 Photolysis of particulate nitrate as a source of HONO and NO₃ Environ. Sci. Technol. 51 6849–56
Yue D, ZHONG L, Shen J, ZHANG T, Xie Z, ZENG L and DONG H 2015 Effect of atmospheric HNO₃, and O₃ on OH radical formation during daytime in the Pearl River delta region China Sci. Paper 10 1387–91 (in Chinese)
Zheng B, Zhang Q, ZHANG Y, He K, Wang K, ZHENG G, Duan F, MA Y and Kimoto T 2015 Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China Atmos. Chem. Phys. 15 2031–49
Zhou X, Zhang N, Ter'Avest M, Tang D, Hou I, Bertman S, Aalghanand M, Shepson P B, Carroll M A and Griffith S 2011 Nitric acid photolysis on forest canopy surface as a source for tropospheric nitric acid Nat. Geosci. 4 440–3
Zou Y, Wang Y, ZHANG Y and Koo J-H 2017 Arctic sea ice, Eurasia snow, and extreme winter haze in China Sci. Adv. 3 e1602751