The promotion effect of nitrous acid on aerosol formation in wintertime Beijing: possible contribution of traffic-related emission

Yongchun Liu1*, Yusheng Zhang1, Chaofan Lian2,6, Chao Yan3, Zeming Feng1, Feixue Zheng1, Xiaolong Fan1, Yan Chen2,6, Weigang Wang2,6*, Biwu Chu3,4, Yonghong Wang3, Jing Cai3, Wei Du3, Kaspar R. Daellenbach3, Juha Kangasluoma1,3, Federico Bianchi1,3, Joni Kujansuu1,3, Tuukka Petäjä3, Xuefei Wang6, Bo Hu5, Yuesi Wang5, Maofa Ge2, Hong He4 and Markku Kulmala1,3*

1. Aerosol and Haze Laboratory, Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, China
2. State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
3. Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, P.O. Box 64, FI-00014, Finland
4. State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
5. State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China
6. University of Chinese Academy of Sciences, Beijing 100049, PR China

Correspondence to: liuyc@buct.edu.cn, wangwg@iccas.ac.cn or markku.kulmala@helsinki.fi
Abstract

Secondary aerosol is a major component of PM$_{2.5}$, yet its formation mechanism in the ambient atmosphere is still an open question. Based on field measurements in downtown Beijing, we show that the photolysis of nitrous acid (HONO) might promote the formation of organic and nitrate aerosol in wintertime Beijing as evidenced by the growth of the mass concentration of organic and nitrate aerosols linearly increasing as a function of consumed HONO from early morning to noon. The increased nitrate also leads to the formation of particulate matter ammonium by enhancing the neutralization of nitrate and sulfate by ammonia. We further illustrate that over 50% of the ambient HONO during pollution events in wintertime Beijing might be related to traffic-related emission including direct emission and formation via the reaction between OH and vehicle-emitted NO. Overall, our results indicate that the traffic-related HONO might play an important role in the oxidative capacity and in turn, contribute to the haze formation in winter Beijing. Mitigation of HONO and NO$_x$ emission from the vehicles might be an effective way to reduce secondary aerosol mass formation and severe haze events in wintertime Beijing.
1. **Introduction**

China is one of the countries suffering from severe pollution of fine particulate matter with diameter less than or equal to 2.5 μm (PM$_{2.5}$) (Lelieveld et al., 2015). Although the regional air quality has been continuously improving since the central government of China issued the Clean Air Act in 2013 (Vu et al., 2019), PM$_{2.5}$ concentration is still significantly higher than that in developed countries (Fu et al., 2014; An et al., 2019). Nowadays, a consensus has been reached that haze events are driven by local emissions (An et al., 2019), regional transport (Zheng et al., 2015b) and secondary formation (Huang et al., 2014; He et al., 2018) of pollutants under unfavorable meteorological conditions (stagnant atmosphere and high relative humidity) (Zhu et al., 2018; Liu et al., 2017c). A feedback loop between meteorological parameters and haze formation also plays an important role in the evolution of haze events (Zhang et al., 2018b).

Secondary aerosol can contribute ~70% to the aerosol mass concentration on polluted days (Huang et al., 2014). Several reaction pathways have been proposed, such as sulfate formation via heterogeneous oxidation of SO$_2$ promoted by H$_2$O$_2$ and/or NO$_2$ on mineral dust (Huang et al., 2015; He et al., 2014), aqueous oxidation of SO$_2$ promoted by NO$_2$ in the presence or absence of NH$_3$ in particle-bound water film (He et al., 2014; Wang et al., 2016), catalytic conversion of SO$_2$ to sulfate by black carbon (Zhang et al., 2020), nitrate formation via efficient hydrolysis of N$_2$O$_5$ on aerosol surfaces (Wang et al., 2017c; Wang et al., 2019; Kulmala, 2018; Li et al., 2017), and the haze formation initiated by new particle formation and growth (Guo et al., 2014; Guo et al., 2020). During the past years, strict control of coal combustion has successfully reduced
the SO$_2$ concentration, resulting in a reduction of sulfate (SO$_4^{2-}$) component in PM$_{2.5}$; in stark contrast, the contributions from organic and nitrate become increasingly more significant in China (Lang et al., 2017).

The formation of secondary organic aerosol (SOA) starts from the gas-phase oxidation of volatile organic compounds (VOCs) leading to various low-volatility and semi-volatile products (Bianchi et al., 2019), followed by partitioning into the particle phase (Hallquist et al., 2009). Similarly, the formation of nitrate aerosol in the daytime is largely due to the partitioning of gaseous nitric acid, which is formed via the oxidation of NO$_2$ by OH (Seinfeld and Pandis, 2006; Wang et al., 2019). It is traditionally believed that the wintertime atmospheric oxidation capacity is weak due to the weak solar radiation, which limits the formation of SOA and nitrate (Sun et al., 2013). However, it is very recently shown that the peak OH concentration on polluted days in winter Beijing varies from 2×10$^6$ to 6×10$^6$ molecules cm$^{-3}$, which is 6-10 times higher than what is predicted by the global model (Tan et al., 2018). This discrepancy can be largely reduced after accounting for other OH production processes in model simulations, which shows that the photolysis of nitrous acid (HONO) dominates the initiation of HO$_x$ (OH and HO$_2$) and RO$_x$ (RO and RO$_2$) radical chain in wintertime Beijing (Tan et al., 2018), and some other cities (Ren et al., 2006; Stutz et al., 2013).

More recently, modeling studies have suggested that nitrous acid (HONO) could enhance secondary aerosols formation in Beijing-Tianjin-Hebei (BTH) region (Zhang et al., 2019b), Pearl-River-Delta (PRD) region of China (Zhang et al., 2019a; Xing et al., 2019) and Houston (Czader et al., 2015). These results imply that the role of HONO
in haze chemistry might be crucial in wintertime Beijing, while the direct evidence from observation has not been reported, yet. On the other hand, the HONO budget has been investigated via modeling studies (Liu et al., 2019c; Zhang et al., 2019b) and photostationary state calculations (Wang et al., 2017b; Li et al., 2018; Huang et al., 2017b; Lee et al., 2016; Oswald et al., 2015) at different locations. At the present time, the study of the HONO budget is still far from closed, which would require a significant effort on both the accurate measurement of HONO and the determination of related kinetic parameters for its production pathways (Liu et al., 2019c). For example, photo-enhanced conversion of NO$_2$ (Su et al., 2008) and photolysis of particulate nitrate were found to be two major mechanisms with large potential of HONO formation during noontime, but the associated uncertainty may reduce their importance (Liu et al., 2019c). Some other researches proposed that heterogeneous reactions on ground/aerosol surfaces were important during nighttime (Wang et al., 2017b; Zhang et al., 2019b) and daytime in Beijing-Tianjin-Hebei (BTH) (Zhang et al., 2019b). But the heterogeneous reaction was unimportant in Ji’an compared with the unknown sources and the homogeneous reaction between NO and OH (Li et al., 2018). In addition, the traffic emission was proposed to be an important HONO source during nighttime but not significant during daytime in BTH (Zhang et al., 2019b). However, it was proposed that direct emission of HONO from vehicles should contribute about 51.1% (Meng et al., 2019) and 52% of nighttime HONO in Beijing (Zhang et al., 2018a). These results mean that more studies is still required on the HONO budget. In particular, it is meaningful to analyze the HONO budget in polluted events for understanding the
possible influence of HONO sources on secondary pollutants formation.

In this work, we carried out comprehensive measurements at a newly constructed observation station (Aerosol and Haze Laboratory, Beijing University of Chemical Technology, AHL/BUCT Station) located in the western campus of Beijing University of Chemical Technology in downtown Beijing. We show observational evidence that HONO might have a prominent promotion effect on the secondary aerosol mass formation in winter. Traffic-related emission seems to be a vital contributor to ambient HONO during the pollution events in winter in Beijing.

2. Materials and methods

2.1 Field measurements. Field measurements were performed at AHL/BUCT Station (Lat. 39º56ʹ31ʺ and Lon. 116º17ʹ52ʺ) from February 1 to June 30, 2018. The observation station is on a rooftop of the main building, which is 550 m from the 3rd ring road in the East, 130 m from the Zizhuyuan road in the North and 565 m from the Nandianchang road in the West (Figure S1). The station is surrounded by both traffic and residential emissions, thus, is a typical urban observation site.

Ambient air was sampled from the roof of five floors (~18 m above the surface). A PM$_{2.5}$ inlet (URG) was used to cut off the particles with diameter larger than 2.5 μm before going to a Nafion dryer (MD-700-24, Perma Pure). Then a Time-of-Flight Aerosol Chemical Speciation Monitor equipped a PM$_{2.5}$ aerodynamic lens (ToF-ACSM, Aerodyne) and an Aethalometer (AE33, Magee Scientific) were connected to the manifold of aerosol sampling tube. The Reynolds number in the aerosol sampling tube was 800 with the total flow rate of 16.7 lpm and the residence time of 6.5 s. The details
Ambient air was drawn from the roof using a Teflon sampling tube (BMET-S, Beijing Saak-Mar Environmental Instrument Ltd.) with the residence time <10 s for gas-phase pollutants measurements. Trace gases including NOx, SO2, CO and O3 were measured with the corresponding analyzer (Thermo Scientific, 42i, 43i, 48i and 49i). Volatile organic compounds (VOCs) was measured using an online Single Photon Ionization Time-of-flight Mass Spectrometer (SPI-ToF-MS 3000R, Hexin Mass Spectrometry) with unit mass resolution (UMR). The principle and the configuration of the instrument has been described in detail elsewhere (Gao et al., 2013) and the Supplement information. HONO concentration was measured using a home-made Long Path Absorption Photometer (LOPAP) (Tong et al., 2016). The details are described in the Supplement information. Particle size and number concentration from 1 nm to 10 μm were measured with a Scanning Mobility Particle Sizer (SMPS 3936, TSI), a particle size magnifier (PSM, Airmodus) and a Neutral Cluster and Air Ion Spectrometer (NIAS, Airel Ltd.). Meteorological parameters including temperature, pressure, relative humidity (RH), wind speed and direction were measured using a weather station (AWS310, Vaisala). Visibility and planetary boundary layer (PBL) height were measured using a visibility sensor (PWD22, Vaisala) and a ceilometer (CL51, Vaisala), respectively.

2.2 HONO budget calculation. Several sources of ambient HONO have been identified, such as emission from soil ($E_{soil}$) (Oswald et al., 2015; Meusel et al., 2018) and vehicle exhaust ($E_{vehicle}$) (Trinh et al., 2017), production through homogeneous
reaction between NO and OH ($P_{NO-OH}$) in the atmosphere, photolysis of nitrate ($P_{nitrate}$) (Bao et al., 2018), nitrous acid ($P_{HNO3}$) and nitrophenenol ($P_{nitrophenol}$) (Sangwan and Zhu, 2018), heterogeneous reaction of NO$_2$ on aerosol surface ($P_{aerosol}$) (Liu et al., 2015) and ground surface ($P_{ground}$) (Liu et al., 2019c; Li et al., 2018; Wang et al., 2017b). However, the photolysis of HNO$_3$ and nitrophenol were excluded in this work because they were believed as minor sources (Lee et al., 2016) and their concentrations were unavailable during our observation. The removal pathways of HONO including photolysis ($L_{photolysis}$), the homogeneous reaction with OH radical ($L_{HONO-OH}$) and dry deposition ($L_{deposition}$) (Liu et al., 2019c) were considered.

The HONO budget could be calculated by,

$$\frac{dc_{HONO}}{dt} = E_{HONO} + P_{HONO} - L_{HONO} + T_{vertical} + T_{horizontal}$$  

(1)

where $\frac{dc_{HONO}}{dt}$ is the observed change rate of HONO mixing ratios (ppbv h$^{-1}$); $E_{HONO}$ represents the emission rate of HONO from different sources (ppbv h$^{-1}$); $P_{HONO}$ is the in-situ production rate of HONO in the troposphere (ppbv h$^{-1}$); $L_{HONO}$ is the loss rate of HONO (ppbv h$^{-1}$) (Li et al., 2018); $T_{vertical}$ and $T_{horizontal}$ are the vertical and horizontal transport (Soergel et al., 2011), which can mimic source or sink terms depending on the HONO mixing ratios of the advected air relative to that of the measurement site and height (Soergel et al., 2011).

The emission rate ($E_{HONO}$, ppbv h$^{-1}$) was calculated based on the emission flux ($F_{HONO}$=EI$_{HONO}$/A, g m$^{-2}$ s$^{-1}$) and PBL height ($H$, m) according to the following equation,

$$E_{HONO} = \frac{a F_{HONO}}{H}$$  

(2)

where, $EI_{HONO}$, is the emission inventory of HONO (g s$^{-1}$), A is the core urban area of
Beijing (m², with 20 km of diameter), α is the conversion factor \( \alpha = \frac{1 \times 10^9 \cdot 3600 \cdot R \cdot T}{M \cdot P} = \frac{2.99 \times 10^{13} \cdot T}{M \cdot P} \), \( M \) is the molecular weight (g mol⁻¹), \( T \) is the temperature (K) and \( P \) is the atmospheric pressure (Pa).

The production rates of HONO \( (P_{HONO}, \text{ppbv h}^{-1}) \) in the troposphere was calculated by,

\[ P_{HONO} = 3600 \cdot k_1 \cdot c_{precursor} \]  

(3)

where, \( k_1 \) is the quasi first-order reaction rate constant (s⁻¹), \( c_{precursor} \) is the concentration of precursor (ppbv). For homogeneous reaction between NO and OH,

\[ k_1 = k_2 \cdot c_{OH} \]  

(4)

where, \( k_2 \) is the second-order reaction rate constant \( (7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \) (Li et al., 2012), \( c_{OH} \) is the OH concentration (molecules cm⁻³). For heterogeneous reaction,

\[ k_1 = \frac{\gamma \cdot A_s \cdot \omega}{4} \cdot Y_{HONO} \]  

(5)

where, \( A_s \) is the surface area concentration of the reactive surface (m² m⁻³), \( \omega \) is the molecular mean speed (m s⁻¹), \( \gamma \) is the uptake coefficient of the precursor, \( Y_{HONO} \) is the yield of HONO. For ground surface, the surface area concentration is

\[ A_s = \frac{\delta}{H} \]  

(6)

where \( \delta \) is the surface roughness, which is calculated according to the mean project area, perimeter and height of the buildings in Beijing.

\[ \delta = \frac{f_{\text{building}} \cdot (A_{\text{projected}} + h \cdot P_{\text{building}})}{A_{\text{projected}}} + f_{\text{blank}} \]  

(7)

where \( f_{\text{building}} \) (0.31) and \( f_{\text{blank}} \) (0.69) are the fraction of the projected area \( (A_{\text{projected}}) \) of buildings and blank space, respectively; \( P_{\text{building}} \) and \( h \) are the perimeter and the height of the building, respectively. The \( f_{\text{building}} \) and \( P_{\text{building}} \) are measured from \( \sim 1000 \) buildings.
randomly selected on the Google Map using ImageJ software. The mean height (44.5 m) of the building in Beijing is linearly extrapolated from the literature data based on remote measurement using Light Detection and Ranging (LiDAR) sensor from 2004 to 2008 (Cheng et al., 2011). The $\sigma$ in Beijing is calculated to be 3.85, which is slightly higher than the value (2.2) used by Li et al. (2018).

As for photolysis reaction, the first-order reaction rate was

$$k_1 = J \quad (8)$$

where, $J$ is the photolysis rate to produce HONO (s$^{-1}$).

The loss rates of HONO by photolysis ($L_{\text{photolysis}}$), homogeneous reaction with OH radicals ($L_{\text{HONO-OH}}$) and dry deposition ($L_{\text{deposition}}$) (Liu et al., 2019c) were calculated according to the following equations.

$$L_{\text{photolysis}} = 3600 \cdot J_{\text{HONO}} \cdot c_{\text{HONO}} \quad (9)$$

$$L_{\text{HONO-OH}} = 3600 \cdot k_{\text{HONO-OH}} \cdot c_{\text{OH}} \cdot c_{\text{HONO}} \quad (10)$$

$$L_{\text{deposition}} = \frac{3600 \cdot v_d \cdot c_{\text{HONO}}}{H} \quad (11)$$

where, $J_{\text{HONO}}$ is the photolysis rate of HONO (s$^{-1}$), $k_{\text{HONO-OH}}$ is the second-order reaction rate constant between HONO and OH ($6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) (Atkinson et al., 2004), and $v_d$ is the dry deposition rate of HONO (0.001 m s$^{-1}$) (Han et al., 2017).

Vertical transport by advection ($T_{\text{vertical}}$), which is an important sink of HONO in the night (Gall et al., 2016; Meng et al., 2019), can be calculated according to equation (12).

$$T_{\text{vertical}} = -K_h(z, t) \frac{\partial c(z, t)}{\partial z} \frac{1}{h} \quad (12)$$

where $K_h(z, t)$ is the eddy diffusivity of heat (m$^2$ s$^{-1}$) at height $z$ (m) and time $t$, $h$ is the
height of the second layer (18 m in this study) (Gall et al., 2016). On the other hand, both the vertical and horizontal transport can be estimate according to Eq. (13),

\[ T_{\text{vertical}} = k_{\text{dilution}} (c_{\text{HONO}} - c_{\text{HONO,background}}) \] (13)

where \( k_{\text{dilution}} \) is a dilution rate (0.23 h\(^{-1}\), including both vertical and horizontal transport) (Dillon et al., 2002), \( c_{\text{HONO}} \) and \( c_{\text{HONO,background}} \) is the HONO concentration at the observation site and background site, respectively (Dillon et al., 2002).

In addition, even though all the current known sources had been considered in models, the modelled daytime HONO concentrations were still lower than the observed concentration (Tang et al., 2015; Michoud et al., 2014). Therefore, the HONO concentration could be described in equation (14).

\[
\frac{dc_{\text{HONO}}}{dt} = E_{\text{soil}} + E_{\text{vehicle}} + P_{NO\cdot OH} + P_{\text{nitrate}} + P_{\text{aerosol}} + P_{\text{ground}} + P_{\text{unknown}} - L_{\text{photolysis}} - L_{HONO\cdot OH} - L_{\text{deposition}} + T_{\text{vertical}} + L_{\text{horizontal}}
\] (14)

3. Results and discussion

3.1 Overview of the air pollution. The mass concentration of non-refractory PM\(_{2.5}\) (NR-PM\(_{2.5}\)) and HONO along with metrological parameters are shown in Fig. 1. The time series of other pollutants (SO\(_2\), CO, O\(_3\), benzene, toluene and black carbon) are shown in Fig. S2 in the Supplement information.

Similar to previous measurements (Guo et al., 2014; Wang et al., 2016), the air pollution events showed a periodic cycle of 3-5 days during the observation, as indicated by the concentration of NR-PM\(_{2.5}\) (Fig. 1A), gaseous pollutants and the visibility. During the observation period, 20-60% of hourly PM\(_{2.5}\) concentration was higher than 75 μg m\(^{-3}\) (the criterion for pollution according to the national air quality
standards) in each month (Fig. S3A). Both the frequency of severe polluted episodes and the mean mass concentration of PM$_{2.5}$ and NR-PM$_{2.5}$ were obviously higher in March than that in the rest months (Fig. 1 and S3). This can be explained by both the intensive emission during the heating season as evidenced by the high concentration of primary pollutants including CO, SO$_2$ and BC (Table S1) and the stagnant meteorological conditions supported by the low wind speed (<2 m s$^{-1}$) and planetary boundary layer (PBL) height in March (Fig. S4A).

OA and nitrate dominated the NR-PM$_{2.5}$, while their relative contribution varied significantly during the observation (Fig. 1B and Table S1). This is similar to the previously reported NR-PM$_{1.0}$ composition (Sun et al., 2015). The monthly mean fraction of OA varied from 45.9±10.2 % to 52.6±18.7 %, which was accompanied by a slight increase of sulfate from 16.0±9.1 % to 18.2±8.0 % (Fig. S4D). At the same time, the monthly mean fraction of nitrate and chloride decreased from 26.7±8.8 % to 16.7±12.8 % and from 7.7±6.1 % to 0.3±0.2 %, respectively. Ammonium showed a peak value (14.2±2.8 %) in March, then slightly decreased to 12.2±5.2 %. The intensive emission of chloride from coal combustion during heating season (Cho et al., 2008) and firework burning (Zhang et al., 2017), which was transported from Tangshan during Chinese New Year (Fig. S5A and B), led to high fraction of chloride in February and March. The decrease in nitrate and ammonium fractions from February to June should be related to the increase in temperature (Fig. S2) which was in favor of NH$_4$NO$_3$ decomposition (Wang et al., 2015). Besides the reduction of the contribution from other components, secondary formation due to increased UV light (Fig. S4C) might also
favor the increased OA fraction (Huang et al., 2014). This means that chemical
transformation in March should still be vigorous although the UV light intensity in
March is lower than in summer (Fig. S4C). It also implies other factors may compensate
the weak UV light intensity in March.

HONO, which has been recognized as the important precursor of primary OH
radical (Ren et al., 2006; Alicke et al., 2003), ranged from 0.05 to 10.32 ppbv from
February 1 to June 30, 2018 (Fig. 1C) with the mean value of 1.26±1.06 ppbv. In winter
(February and March), HONO concentration was 1.15±1.10 ppbv and comparable to
the previous results (1.05±0.89 ppbv) measured in the winter of Beijing (Wang et al.,
2017b; Hou et al., 2016), while it was slightly lower than that from April to June
(1.35±1.11 ppbv) in this work and those measured in the summer of Shanghai (2.31
ppbv, in May) (Cui et al., 2018) and Guangzhou (2.8 ppbv, in July) (Qin et al., 2009).
The mean HONO concentration in March (1.53±1.25 ppbv) was higher than that in
February and April (Fig. S3D), while was slightly higher or close to that in May and
June. Chamber studies have found that HONO is responsible for the initiation of
photosmog reactions (Rohrer et al., 2005). It is reasonable to postulate that HONO
probably play an important role in the secondary chemistry of particle formation in
March.

3.2 Possible promotion effect of HONO photolysis on aerosol formation in winter.

Oxidation of precursors by OH radicals is the main mechanism regarding to secondary
aerosol formation in the troposphere. After partially ruling out the possible influence of
PBL variation by normalizing the concentrations of all pollutants to CO (Cheng et al.,
or BC (Liggio et al., 2016), we found all secondary species including sulfate, nitrate and ammonium show obvious daytime peaks from 7:00 am to 6:00 pm (Figure S5C) (Cheng et al., 2016). The similar trends were observed after the concentrations of pollutants were normalized to BC (not shown). This suggests they might connect with photochemistry.

Photolysis of H$_2$O$_2$, HCHO, O$_3$ and HONO, and the reaction between NO and HO$_2$ are known as sources of OH radical in the atmosphere (Alicke et al., 2003; Volkamer et al., 2010; Tan et al., 2018; Tang et al., 2015). In this work, the concentration of H$_2$O$_2$, HCHO and HO$_2$ are unavailable. Thus, their contributions to OH production were not discussed here. However, it has been well recognized that the photolysis of HONO is the dominant source of OH in the dawn and dusk period (Holland et al., 2003), even contributes up to 60% of daytime OH source in winter (Spataro et al., 2013; Rohrer et al., 2005). In addition, it has been confirmed that HONO dominates the primary OH source at various locations (Tan et al., 2018; Liu et al., 2019c; Tan et al., 2017; Aumont et al., 2003). Therefore, it is meaningful to discuss the possible contribution of HONO to secondary aerosol formation through OH production. We simply compared the OH production via photolysis of HONO ($P_{OH\cdotHONO}=J_{HONO}\times c_{HONO}$) and O1D production rate from O$_3$ ($P_{O1D}=J_{O1D}\times c_{O3}$) in Fig. 2 when the PM$_{2.5}$ concentration was larger than 50 μg m$^{-3}$ and the RH was less than 90 % to understand the chemistry in pollution events. Under these conditions, local chemistry should be more important as 75 % of the wind speed was less than 1.0 m s$^{-1}$ (Fig. S6). The details about the $J_{HONO}$ and $J_{O1D}$ calculation were shown in the Supplement information and their time series were shown in Fig. S7.
On polluted days in winter, the daytime $P_{OH-HONO}$ was always significantly higher than the $P_{OH-O3}$ in winter and the maximal $P_{OH-HONO}$ and $P_{OID}$ were $1.73 \pm 0.86 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ ($2.43 \pm 1.21$ ppb h$^{-1}$) and $1.03 \pm 1.06 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ ($1.45 \pm 1.49$ ppb h$^{-1}$), respectively (Fig. 2A). Owing to the high HONO concentration accumulated throughout the night, the maximal $P_{OH-HONO}$ in winter was as about 2-6 times of that was observed in the wintertime of Colorado, USA ($\sim 0.59$ ppb h$^{-1}$) (Kim et al., 2014), New York, USA ($\sim 0.40$ ppb h$^{-1}$) (Kanaya et al., 2007) and Nanjing, China (0.90\pm0.27 ppb h$^{-1}$) (Liu et al., 2019b). In the period from April to June, the daily maxima of $P_{OH-HONO}$ and $P_{OID}$ were $2.48 \pm 1.42 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ ($3.48 \pm 1.99$ ppb h$^{-1}$) and $6.51 \pm 4.17 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ ($9.15 \pm 5.86$ ppb h$^{-1}$), respectively. Because the production of OH from photolysis of O$_3$ should be directly proportion to $P_{OID}$, these results imply that the relative importance of the photolysis of HONO compared with that of O$_3$ for initiating the daytime HO$_x$ and RO$_x$ chemistry on polluted days should be more important in winter than that from April to June. This is consistent with the previous findings that HONO photolysis dominates the primary OH source in winter of BTH (Xing et al., 2019; Tan et al., 2018), Colorado and New York City (Ren et al., 2006; Kim et al., 2014), while photolysis of O$_3$ and HCHO related reactions usually dominated OH production in summer (Alicke et al., 2003).

Oxidation of trace gas pollutants, in particular VOCs, by OH is their main removal pathway in the troposphere (Atkinson and Arey, 2003), subsequently contribute to secondary aerosol formation (Kroll and Seinfeld, 2008). A very recent work has found that oxidation of VOCs from local traffic emission is still efficient even under pollution
conditions (Guo et al., 2020). This means high HONO concentration might promote SOA formation after sunrise because HONO is an important primary OH source in the early morning. To confirm this assumption, 12 episodes in winter were further analyzed (Fig. 1). The dataset under stagnant meteorological conditions as indicated by the low wind speed (< 1.0 m s⁻¹, Fig. S5D) was analyzed to decrease the contribution of transport to the observed HONO and OA. The 1st, 3rd and 5th episodes were clean days and the other 9 episodes were typical haze events with duration above 2 days. The features of these episodes were summarized in Table S2. Fig. 2C shows the CO-normalized daytime profiles of OA and HONO in the 7th and 12th episodes as two examples. In all the selected cases, HONO exhibited quick reduction due to the photolysis after sunrise, and simultaneously, OA concentration started to increase. This is similar to the evolution of the concentration of pollutants in a typical smog chamber experiment. We further show the formation of OA (ΔC_{OA}/C_{CO}) as a function of the consumed HONO (-ΔC_{HONO}/C_{CO}) in Fig. 2D. Except for the 4th episode that was highly affected by firework emission during the Spring Festival, ΔC_{OA}/C_{CO} showed a linear dependence on -ΔC_{HONO}/C_{CO} in winter (R=0.75). This kind of correlation could not be seen for the pollution events from April to June because the relative importance of HONO photolysis in primary OH production decreased as indicated by Fig. 2D. It should be noted that oxidation of biogenic alkenes by O₃ might also contribute to OA formation. However, anthropogenic VOCs instead of biogenic VOCs dominated the wintertime VOCs in Beijing (Liu et al., 2017a). Although vehicles can emit isoprene (Zou et al., 2019), the contribution of isoprene to the observed increase of OA
concentration should be unimportant due to the low concentration of isoprene in winter (Zou et al., 2019). Therefore, it is reasonable to conclude that the increase of OA concentration in daytime might be mainly resulted from oxidation of VOCs by OH. Similar to OA, $\Delta C_{\text{nitrates/CO}}$ in winter also showed good linear correlation with $-\Delta C_{\text{HONO/CO}}$ (R=0.67, Fig. S5E), suggesting that the increase of particle-phase nitrate in the daytime should also be promoted by OH radical. Interestingly, $\Delta C_{\text{ammonium/CO}}$ also showed a good correlation with $-\Delta C_{\text{HONO/CO}}$ (R=0.61, Fig. S5E), although particle-phase ammonium should not be directly related to oxidation of NH$_3$ by OH. We explained the increased ammonium as the result of enhanced neutralization of sulfate and nitrate by NH$_3$ (Wang et al., 2018; Wen et al., 2018; Sun et al., 2018) because NH$_4^+$ was adequate to neutralize both sulfate and nitrate as shown in Fig.S8. This was consistent with the recent work which observed the important role of photochemical reactions in daytime nitrate formation, while hydrolysis of N$_2$O$_5$ mainly contributed to nighttime nitrate (Tian et al., 2019). Although a recent work has found that daytime hydrolysis of N$_2$O$_5$ on hygroscopic aerosols is also an important source of daytime nitrate in winter Beijing (Wang et al., 2017a), the linearly correlation between $\Delta C_{\text{nitrates/CO}}$ and $\Delta C_{\text{HONO/CO}}$ at least implies that the promotion effect of HONO on nitrate formation could not be excluded. On the other hand, the correlation between $\Delta C_{\text{sulfate/CO}}$ and $-\Delta C_{\text{HONO/CO}}$ was much weaker (R=0.26), suggesting a weak connection between particle-phase sulfate and gas-phase H$_2$SO$_4$. This was also consistent with the previous understanding that heterogeneous reactions of SO$_2$ were the dominant pathway for sulfate formation (Zheng et al., 2015a; He et al., 2018; Zhang
et al., 2020). Overall, this work qualitatively supported the recent modeling results that
HONO might promote the aerosol production in winter (Zhang et al., 2019a; Zhang et
al., 2019b; Xing et al., 2019; An et al., 2013) from the point of view of observation.

3.3 HONO budget in polluted events. To understand the possible sources of HONO
in polluted events in winter, the HONO budget was calculated for the events when the
PM$_{2.5}$ concentration was larger than 50 µg m$^{-3}$ and the RH was less than 90 % according
to the method described in Section 2.2.

**Vehicle emission.** The $E_{\text{vehicle}}$ was calculated in the light of Eq. (2) using the relative
emission rate of HONO to NO$_x$ and the emission inventory of NO$_x$ from vehicles. Firstly,
the ratio of HONO/NO$_x$ was calculated according to the method reported by Xu et al.
(Xu et al., 2015) and Li et al. (Li et al., 2018) from the fresh nighttime plumes which
were strictly satisfy the following criteria: 1) NO$_x$ > 45 ppb (highest 25% of NO$_x$ data);
2) $\Delta$NO/$\Delta$NO$_x$ > 0.8, with good correlation between NO and NO$_x$ (R > 0.9, P < 0.05);
3) Good correlation between HONO and NO$_x$ ($R^2>0.65$, P < 0.05); and 4) Dataset from
5:00 am to 8:00 am. The mean emission ratio of HONO to NO$_x$ was 1.8±0.5% based
on 5 fresh vehicle exhaust plumes during our observation (Table S3). This value is
higher than that in Hongkong (1.2±0.4%) (Xu et al., 2015), Beijing (1.3%) (Zhang et
al., 2018a) and Jinan (0.53±0.20%) (Li et al., 2018) using the same method, while is
comparable with the result measured in tunnel experiments (2.1%) carried out in
Beijing (Yang et al., 2014). Secondly, low HONO concentration should be companied
with high NO$_x$ and high ratio of $\Delta$NO/$\Delta$NO$_x$ if direct emission from vehicles was the
major source of HONO and the source from secondary formation was negligible in the
urban atmosphere. Therefore, we further estimated the HONO/NO\textsubscript{x} ratio using a low limit correlation method (Li et al., 2012). In the 2D space of HONO versus NO\textsubscript{x} (Fig. S8), the lowest marge with $\Delta$NO/$\Delta$NO\textsubscript{x} larger than 0.8 were chosen for linear correlation. The ratio of $\Delta$HONO/$\Delta$NO\textsubscript{x} is 1.17±0.05%. It should be pointed out that the interference from the sampling inlet overestimated 6.7 % of HONO concentration based on control experiments with 100 ppb of NO\textsubscript{2} at 50 % RH. Thus, the ratio of $\Delta$HONO/$\Delta$NO\textsubscript{x} should be 1.09±0.05% when the interference from the sampling inlet was taken into consideration. This value is lower than that estimated through empirical method discussed above, while is very close to that measured in Hongkong (1.2±0.4%) (Xu et al., 2015) and (1.23±0.35%) (Liang et al., 2017), Guangzhou (1.0%) (Li et al., 2012) and Beijing (1.3% and 1.41 %) (Zhang et al., 2018a;Meng et al., 2019). Finally, several studies have measured the direct emission of HONO from vehicle exhaust. The HONO/NO\textsubscript{x} was 0.18% from gasoline cars through chassis dynamometer tests in China (Liu et al., 2017d), while it was 0-0.95% for gasoline vehicles and 0.16-1.0 % for diesel vehicles measured under real-world driving test cycles in Japan (Trinh et al., 2017). Thus, three levels of vehicle emission factor were considered. 1.09±0.05% was taken as the middle value which is very close to the mean emission ratio (1.21) for all of these reported values in China (Li et al., 2018;Xu et al., 2015;Yang et al., 2014;Liu et al., 2017d;Gall et al., 2016;Meng et al., 2019), while 0.18% (Liu et al., 2017d) and 1.8 % were the lower limit and the upper limit, respectively.

The $E_{\text{vehicle}}$ was calculated using the hourly NO\textsubscript{x} emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO ($F_{\text{HONO}}=F_{\text{NO}_{x}} \times$
HONO/NO\textsubscript{x}) and the PBL height as described in Section 2.2. Thus, the calculated emission rate reflected the diurnal variation of both the emission inventory and the PBL height. The calculated hourly middle value of \( E_{\text{vehicle}} \) using the HONO/NO\textsubscript{x} of 1.09\% was from 0.079±0.038 to 0.32±0.15 ppbv h\(^{-1}\), which was slightly higher than the daytime emission rate of HONO in Xi’an (Huang et al., 2017b). This is reasonable when the vehicle population in Beijing is taken into consideration. The lower limit of \( E_{\text{vehicle}} \) was 0.013±0.006-0.053±0.023 ppbv h\(^{-1}\), which was close to the estimated emission rate of HONO in Jinan (Li et al., 2018). The upper limit was in the range of 0.13±0.06-0.53±0.23 ppbv h\(^{-1}\).

**Soil emission.** The emission flux of HONO from soil depends on the water content, the nitrogen nutrient content and the temperature of soil (Oswald et al., 2013). Oswald et al. (2013) measured the emission flux of HONO from 17 soil samples, including eucalyptus forest, tropical rain forest, coniferous forest, pasture, woody savannah, grassland, stone desert, maize field, wheat field, jujube field and cotton field etc. Tropical rain forest, coniferous forest and grassland are the typical plants in downtown Beijing (Huang et al., 2017a). At the same time, their emission fluxes of HONO are comparable (Oswald et al., 2013). Thus, we used the emission flux from grassland to calculate the emission rate of HONO from soil in Beijing because the temperature and water holding content dependent emission flux of HONO from grassland soil was available. Three levels of water content including 25-35\%, 35-45\% and 45-55\% were considered. The temperature dependence of \( F_{\text{HONO}} \) was calculated using the mean value of the \( F_{\text{HONO}} \) with different water content, while the low limit and upper limit of \( F_{\text{HONO}} \)
were calculated using the emission flux from 45-55% of water content and 25-35% of water content, respectively. The lower limit, the middle value and the upper limit of the $E_{\text{soil}}$ are $0.0032 \pm 0.0027$, $0.013 \pm 0.014$, $0.0046 \pm 0.0039$, $0.020 \pm 0.20$ and $0.0057 \pm 0.0047 - 0.025 \pm 0.024$ ppbv h$^{-1}$, respectively, calculated according to Eq. (2).

**Homogeneous reaction between NO and OH.** Direct measurement of OH concentration was unavailable in this work, while several methods were used to estimate the ambient OH concentration. In winter in Beijing, it has been found that the OH concentration is linearly correlated with $J_{O1D}$, that’s, $c_{OH} = J_{O1D} \times 2 \times 10^{11}$ molecules cm$^{-3}$ (Tan et al., 2019). However, Tan et al. (2018) reported a larger conversion factor (4.33$x10^{11}$ molecules cm$^{-3}$). Li et al. (2018) estimated the OH radical concentration considering both photolysis rate and NO$_2$ concentration, namely,

$$c_{OH} = \frac{4.1 \times 10^9 \times (J_{O1D})^{0.83} \times (J_{NO2})^{0.19} \times (140 + 1) \times (140 + 1)}{0.41c_N^{2} + 1.7c_{NO2} + 1}$$  (15)

Overall, the estimated OH concentrations according to Eq. (15) were comparable with that estimated by Tan et al. (2019) (Fig. S10C). The method for the photolysis rates calculation were shown in SI and the time series of the photolysis rates were shown in Fig. S7. On polluted days, high concentration of NO$_2$ resulted into lower OH concentrations estimated using the Eq. (15). Therefore, the corresponding $P_{NO-OH}$ was taken as the low limit for homogeneous reaction between NO and HONO because polluted events were discussed in this work, while $P_{NO-OH}$ calculated using the OH concentration ($J_{O1D} \times 4.33 \times 10^{11}$ molecules cm$^{-3}$) (Tan et al., 2018) was taken as the upper limit and $P_{NO-OH}$ calculated using the OH concentration ($J_{O1D} \times 2 \times 10^{11}$ molecules cm$^{-3}$) (Tan et al., 2019) was the middle value. In the night, OH concentration usually varied...
from 1.0×10^5 molecules cm\(^{-3}\) (Li et al., 2012; Tan et al., 2018) in winter to 5×10^5 molecules cm\(^{-3}\) in summer (Tan et al., 2017). The nighttime OH concentration was estimated linearly correlated with the product of nighttime O\(_3\) concentration and alkenes concentration, namely,

\[
c_{OH,night} = 1 \times 10^5 + 4 \times 10^5 \times \frac{(c_{O_3} \times c_{alkenes})_{night} - (c_{O_3} \times c_{alkenes})_{night,min}}{(c_{O_3} \times c_{alkenes})_{night,max} - (c_{O_3} \times c_{alkenes})_{night,min}}
\]

The time series of OH concentration calculated using different methods was shown in Fig. S11. Thus, the lower limit, the middle value and the upper limit of P\(_{NO-OH}\) were 0.007±0.019-0.43±0.26, 0.026±0.053-0.99±0.79 and 0.028±0.053-2.14±1.71 ppbv h\(^{-1}\), respectively, calculated according to Eqs. (3) and (4). The calculated middle value of P\(_{NO-OH}\) (with mean daytime value of 0.49±0.35 ppb h\(^{-1}\)) was comparable with these estimated values by Li et al. (2018) (0.4 ppb h\(^{-1}\)) and Huang et al. (2017b) (0.28 ppb h\(^{-1}\)). It should be noted that measured NO concentration was used to calculate the P\(_{NO-OH}\).

Besides vehicle emission, power plant and industries also contribute NO emission. 40 % of NOx was from vehicle emission according to the emission inventory of NOx in Beijing (He et al., 2002).

It should be noted that OH concentration was estimated based on J\(_{O1D}\) (Tan et al., 2019; Tan et al., 2018) or J\(_{O1D}\) and J\(_{NO_2}\) (Li et al., 2018). As discussed in Section 3.2, HONO was an important primary OH source in the daytime. Unfortunately, it could not be parameterized for calculating OH concentration because the measured or modelled OH concentration was unavailable in this work. This might underestimate the early daytime OH concentration, subsequently, the contribution of homogeneous reaction of NO with OH to HONO source. This needs to be further investigated in the future.
Photolysis of nitrate. A recent work reported the photolysis rate of nitrate \( (J_{\text{nitrate}}) \) in ambient PM\(_{2.5}\) at a solar zenith angle of 0° (Bao et al., 2018). The \( J_{\text{nitrate}} \) varied from 1.22×10^{-5} to 4.84×10^{-4} s\(^{-1}\) with the mean value of 8.24×10^{-5} s\(^{-1}\). These values were further normalized according to the zenith angle and UV light at our observation station to calculate the low limit, the upper limit and the middle \( J_{\text{nitrate}} \). The time series of the measured nitrate concentration and the middle value of \( J_{\text{nitrate}} \) were shown in Fig. 1 and Fig. S7, respectively. Therefore, the corresponding daytime lower limit, the middle value and the upper limit of HONO from photolysis of nitrate were 0.0011±0.0021-0.096±0.092, 0.0072±0.0021-0.66±0.092 and 0.042±0.082-3.86±0.008 ppbv h\(^{-1}\), respectively, calculated in the light of Eqs. (3) and (8).

Heterogeneous reactions of NO\(_2\) on aerosol and ground surface. The production of HONO from heterogeneous reactions of NO\(_2\) on aerosol surface was calculated according to Eqs. (3) and (5). The aerosol surface concentration was measured with a SMPS. The uptake coefficient (\( \gamma \)) of NO\(_2\) on different particles varied from 5×10^{-9} to 9.6×10^{-6} (Ndour et al., 2009; Underwood et al., 2001; Underwood et al., 1999), while it was recommended to be 1.2×10^{-8} (Crowley et al., 2010), which was used to calculate the \( P_{\text{aerosol}} \) as the base case. It has been found that the \( \gamma \) highly depends on the relative humidity (RH). The low limit bound of \( P_{\text{aerosol}} \) was calculated based on the RH dependent uptake coefficient of NO\(_2\) on kaolinite \( (\gamma_{\text{NO2}}=4.47 \times 10^{39}/(1.75 \times 10^{46} + 1.93 \times 10^{45}\text{RH})) \), while the upper limit of \( P_{\text{aerosol}} \) was calculated according to the RH dependent \( \gamma \) on hematite \( (\gamma_{\text{NO2}}=4.46 \times 10^{39}/(6.73 \times 10^{44} + 3.48 \times 10^{44}\text{RH})) \) (Liu et al., 2015). Heterogeneous reaction of NO\(_2\) on black carbon (BC) was also considered in the
night. The surface area concentration of BC was calculated according to its specific area (87 m$^2$ g$^{-1}$) (Su et al., 2018) and the measured mass concentration. The $\gamma_{\text{NO}_2}$ on BC is $1.17 \times 10^{-5}$, with a HONO yield of 0.8 (Han et al., 2013). The light enhanced uptake $\gamma$ of NO$_2$ ($1.9 \times 10^{-6}$) on mineral dust was further parameterized (Ndour et al., 2008) after normalized to the solar radiation intensity in Beijing.

The contribution of heterogeneous reaction of NO$_2$ on ground surface was calculated similar to that on mineral dust. The same kinetics for heterogeneous reaction of NO$_2$ on aerosol surface were used to calculate the nighttime contribution of ground surface (Zhang et al., 2016; Aumont et al., 2003). A recent work observed a significant enhancement of NO$_2$ and HONO formation by UV light on the real urban grime (Liu et al., 2019a). Thus, RH dependent kinetic data measured on urban grime ($\gamma_{\text{NO}_2}=7.4 \times 10^{-7}+5.5 \times 10^{-8}$ RH) was used to calculate the daytime upper limit for heterogeneous uptake of NO$_2$ on the ground surface. The $A_s$ of aerosols varied from $1 \times 10^{-4}$ to $4.8 \times 10^{-3}$ m$^{-1}$ with a mean value of $1.4 \pm 0.5 \times 10^{-3}$ m$^{-1}$ during pollution events. This value is comparable with that used in modeling studies (Zhang et al., 2016; Aumont et al., 2003). The $A_s$ of ground surface which was calculated according to Eq. (6) and (7) varied from $1.5 \times 10^{-3}$ to $3.85 \times 10^{-2}$ m$^{-1}$ with a mean value of $1.3 \pm 0.9 \times 10^{-2}$ m$^{-1}$ during pollution events.

The surface roughness was 3.85 calculated according to Eq. (7). The $Y_{\text{HONO}}$ was set to 0.5 because of the hydrolysis reaction of NO$_2$ (Liu et al., 2015), while it was 0.8 for light enhanced reaction (Liu et al., 2019a; Ndour et al., 2008) and on BC (Han et al., 2013).

The lower limit, the middle value and the upper limit of $P_{\text{aerosol}}$ were
The corresponding values were
0.0027±0.00017-0.0020±0.0012, 0.0014±0.00095-0.0089±0.006 and 0.0025±0.0023-
0.060±0.032 ppbv h⁻¹ for $P_{ground}$. The $P_{aerosol}$ calculated in this work was much lower
than that estimated by Huang et al. (Huang et al., 2017b) because different calculation
methods have been used. In their work, the production rate of HONO was estimated
based on the conversion rate (Huang et al., 2017b), whilst it was calculated based on
the measured aerosol surface area concentration and uptake coefficient of NO₂ on
different particles in this work. In addition, the calculated $P_{aerosol}$ was 2-4 orders of
magnitude lower than other sources due to the very small $\gamma_{NO₂}$ on particle surface.

It should be pointed out that HONO production from heterogeneous reaction of
NO₂ on both aerosol and ground surface greatly depend on the $\gamma_{NO₂, BET}$ and $A_s$. The $A_s$
of aerosols is comparable with the modeling input. However, the small nighttime $\gamma_{NO₂, BET}$
(10⁻⁸ - 10⁻⁷) were used in this work rather than the $\gamma_{NO₂, BET}$ (1×10⁻⁶) used in
modeling studies (Zhang et al., 2016; Aumont et al., 2003; Gall et al., 2016). This leads
to a lower production rate of HONO from heterogeneous reaction of NO₂ on aerosols.

As for heterogeneous reaction of NO₂ on ground surface, besides the small $\gamma_{NO₂, BET}$
used in this work, the $A_s$ of ground surface (0.0015 to 0.0385 m⁻¹), which was calculated
using the surface roughness and the PBL height, was also significantly lower than the
fixed value of 0.3 m⁻¹ in modeling studies that might overestimate the contribution of
HONO production from heterogeneous reaction of NO₂ on ground surface. It should be
noted that the initial uptake coefficient ($\gamma_{ini}$) was parameterized in this work. This will
overestimate the contribution of heterogeneous reaction of NO$_2$ to HONO source because the steady-state uptake coefficient is usually one order of magnitude lower than $\gamma_{ini}$ (Han et al., 2013; Liu et al., 2015). These results mean that heterogeneous reaction should be unimportant for HONO source in Beijing.

**Sinks of HONO.** The loss rates of HONO by photolysis ($L_{\text{photolysis}}$), homogeneous reaction with OH radicals ($L_{\text{HONO-OH}}$) and dry deposition were calculated according to Eqs. (9)-(11). The daytime $J_{\text{HONO}}$ varied from $1.71 \times 10^{-5}$ to $1.13 \times 10^{-3}$ s$^{-1}$ on polluted days in winter, while it was in the range of $5.89 \times 10^{-5}$ to $1.53 \times 10^{-3}$ s$^{-1}$ from April to June. These values are comparable to modeling results ($3.9 \times 10^{-5}$-$1.8 \times 10^{-3}$ s$^{-1}$) (Gall et al., 2016). The daytime $L_{\text{photolysis}}$ were in the range of 0.03-5.23 ppbv h$^{-1}$ and 0.25-7.10 ppb h$^{-1}$ in winter and the rest months, respectively. It was the major sink of HONO in the daytime. The $L_{\text{HONO-OH}}$ varied from 0.0049 to 0.069 ppbv h$^{-1}$ in winter using the $k_{\text{HONO-OH}}$ of $6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 2004) and the middle value of OH concentrations. It was from 0.0050 to 0.085 ppbv h$^{-1}$ from April to June. The $L_{\text{deposition}}$ was in the range of 0.004-0.056 ppbv h$^{-1}$ in winter and 0.004-0.030 ppbv h$^{-1}$ from April to June, calculated according to Eq. (11).

As pointed in Section 2.2, vertical transport by advection is an important nocturnal sink of HONO (Gall et al., 2016). In this work, the vertical distribution of HONO concentration is unavailable. Recently, Meng et al. (2019) measured the vertical distribution of HONO in Beijing in December, 2016. The concentration of HONO showed nearly flat profiles from ground level to 240 m in pollution events after sunset, while negative profiles of HONO were observed in pollution events during night (Meng
et al., 2019). The nighttime concentration gradient was 0.0047±0.0025 ppb m⁻¹ derived from the nighttime dataset (Meng et al., 2019). Because the daytime vertical gradient of HONO concentration is unavailable in Beijing, we do not calculate the daytime vertical transport. On the other hand, the eddy diffusivity of heat in urban environment was measured in New Delhi, Indian (Yadav et al., 2003). Using their dataset with the wind speed lower than 2.0 m s⁻¹, we derived the relationship between the $K_h$ and the wind speed (WS) ($K_h=0.9389\times WS-0.3374$ m² s⁻¹). The nighttime $T_{vertical}$ changed from 0.15 to 0.37 ppbv h⁻¹ in winter, while it was from 0.12 to 0.68 ppbv h⁻¹ according to Eq. (12) from April to June. Because the wind speed was usually lower than 1.0 m s⁻¹ in pollution events (Fig. S6), the contribution of horizontal transport to the daytime HONO sources or sinks decreased because of the short lifetime of HONO. In the night, 79 % of the surface wind speed was lower than 1.0 m s⁻¹ on pollution days when the PM$_{2.5}$ concentration was larger than 50 μg m⁻³ and the RH was less than 90 % in winter, thus the air masses from suburban areas should have influence on the sources and sinks of HONO in Beijing. If the HONO concentration at background is zero, the vertical and horizontal transport rate of HONO varied from 0.17 to 0.61 ppbv h⁻¹ which is calculated in the light of Eq. (13) on haze days in winter and from 0.15 to 0.74 ppbv h⁻¹ in pollution events from April to June. These values are is higher than that calculated according to Eq. (12). Because the background HONO concentration was unavailable, we only considered the nighttime transport calculated according to Eq. (12) in the following section.

**Comparison among different HONO sources.** Fig. 3 summarizes the diurnal patterns
of each sources with different parameterizations during the pollution events from February to March. The black dots and lines mean the middle values, while the shadow indicates the corresponding lower bound and upper bound. In the nighttime, vehicle and soil emission, and homogeneous reaction between NO and OH were the important sources of HONO. In the daytime, however, photolysis of nitrate and homogeneous reaction between NO and OH dominated the sources of HONO. Heterogeneous reactions of NO$_2$ on aerosol surface and ground surfaces were unimportant compared with other sources because of the very low uptake coefficient compared with modeling studies (Zhang et al., 2016; Aumont et al., 2003).

Fig. 4A-F shows the HONO budget estimated using the middle values among these parameters during the polluted events. The mean production rate of HONO varied in the range of 0.16 - 1.76 ppbv h$^{-1}$ from these identified sources, while the corresponding loss rate was from 0.21 to 2.34 ppbv h$^{-1}$ during the polluted events in winter. The main loss of HONO was the photolysis during the daytime (1.74± 0.44 ppbv h$^{-1}$), whereas it was vertical transport in the nighttime (0.28±0.08 ppbv h$^{-1}$). Direct emission from vehicles exhaust was the largest nighttime source of HONO (0.22±0.06 ppbv h$^{-1}$), followed by homogeneous reaction between NO and OH (0.04±0.01 ppbv h$^{-1}$), emission from soil (0.014±0.005 ppbv h$^{-1}$), heterogeneous reactions of NO$_2$ on the ground surface (0.006±0.002 ppbv h$^{-1}$) and heterogeneous reactions of NO$_2$ on aerosol surface (0.0005±0.0001 ppbv h$^{-1}$). $P_{NO-OH}$ and $P_{nitrate}$ dominated the daytime HONO production, with daytime mean values of 0.49±0.35 ppbv h$^{-1}$ and 0.34±0.23 ppbv h$^{-1}$, respectively. As shown in Fig. 4, these six sources still underestimated the daytime
sources of HONO. The $P_{\text{unknown}}$ was $0.25\pm0.24$ ppbv h$^{-1}$ in February and March, while it was $0.50\pm0.38$ ppbv h$^{-1}$ from April to June.

The $E_{\text{vehicle}}$ contributed $57.3\pm17.9\%$ and $33.9\pm15.2\%$ to the nighttime HONO sources from February to March and the rest months, respectively, even when the $P_{\text{unknown}}$ was taken into consideration. The relative contribution of daytime $E_{\text{vehicle}}$ decreased to $12.6\pm14.3\%$ in winter and $9.3\pm8.4\%$ from April to June. Thus, the daily mean fraction of the $E_{\text{vehicle}}$ was $40.5\pm27.5\%$ and $24.3\pm17.7\%$ from February to March and from April to June, respectively. This means that the $E_{\text{vehicle}}$ dominates the nighttime HONO source during the polluted events in Beijing, which is consistent with the previous result that vehicle emission was the major nighttime HONO source ($51.1\%$ - $52\%$) in Beijing (Zhang et al., 2019b; Meng et al., 2019). As pointed out in Section 3.3, $E_{\text{vehicle}}$ was calculated based on the NOx inventory from vehicle sector. On the other hand, NO is prone to be quickly converted to NO$_2$ and NO$_3$ (including HONO, HNO$_3$, N$_2$O$_5$, PAN and organonitrate etc) by O$_3$, HO$_2$, RO$_2$ and OH in the atmosphere. It is reasonable to assume that local traffic emission dominates the ambient NO source in the urban environment. Thus, homogeneous reaction between NO and OH in the atmosphere could also be related to vehicle exhaust. As shown in Fig.3, the diurnal curve of $P_{\text{NO-OH}}$ coincided well with that of OH concentration (Fig. S10). This means the $P_{\text{NO-OH}}$ should be mainly determined by OH concentration. However, the $P_{\text{NO-OH}}$ should still reflect the indirect contribution of traffic related emission to HONO source because the ambient NO concentration was used to calculate the $P_{\text{NO-OH}}$. Traffic-related HONO sources ($E_{\text{vehicles}} + P_{\text{NO-OH}}$) might contribute $59.3\pm20.7\%$ and $36.2\pm14.4\%$ to
the daily HONO source in winter and the rest months, respectively. Even if 40 % of NOx was from vehicle exhaust in Beijing (He et al., 2002), traffic-related source 

\[(E_{\text{vehicles}} + 0.4P_{\text{NO-OH}})\] might still contribute 48.1±24.3 % in winter and 29.6±16.2 % from April to June to the corresponding daily HONO source. The contribution of traffic-related source was still an important daytime source of HONO (42.3±10.3 % for \(E_{\text{vehicles}} + P_{\text{NO-OH}}\), and 24.4±11.3 % for \(E_{\text{vehicles}} + 0.4P_{\text{NO-OH}}\)) on polluted days in winter.

As shown in Fig. 3, uncertainties existed when calculating each HONO source. To further understand the role of traffic emission, we also estimated the lower limit of the traffic-related contribution as follows: 1) the lower limit of \(E_{\text{vehicle}}\) was obtained by using the lowest reported emission ratio of HONO/NOx from vehicles (0.18%) (Liu et al., 2017d) rather than 1.09%, which was the empirical value calculated based on the field measurement in Fig. S7; 2) the lower limit for homogeneous reaction between NO and OH radical was calculated according to the method by Li et al. (2018); 3) the upper limit of the emission rate from soil was estimated using the emission flux of HONO with low water content (Oswald et al., 2013); 4) the upper limit of HONO production rate from heterogeneous reaction of NO2 on the aerosol was calculated using the large RH-dependent uptake coefficient of NO2 on hematite (Liu et al., 2015) rather the value recommended by Crowley et al. (Crowley et al., 2010); 5) the upper limit for heterogeneous reaction on ground surface was calculated using the RH-dependent kinetic data measured on urban grime (Liu et al., 2019a). As shown in Fig. 5, traffic-related source \((E_{\text{vehicles}} + P_{\text{NO-OH}})\) contributed 38.0±15.6 % to the daily HONO sources in winter if all NO was assumed to be dominated by local traffic emission, while it was
31.5±17.5 % when 40 % of NO was considered as local traffic emission (He et al., 2002). Under this circumstance, the daytime $P_{\text{unknown}}$ of HONO in winter increased to 1.06±0.36 ppbv h$^{-1}$, which was corresponding to 63.2±10.1 % of the HONO source. This means these assumptions might underestimate the contribution of the HONO sources. In addition, $P_{\text{ground}}$, $P_{\text{aerosol}}$ and $P_{\text{nitrate}}$ could be also partially related to traffic emission of NO$_x$ (Lee et al., 2016; Tan et al., 2017). These results mean that the contribution of traffic-related emission might be larger than our estimation in this work. Therefore, our work at least suggests that traffic related emission should be a very important HONO source in winter Beijing although more work is required based on comprehensive modeling studies.


In this work, we observed the good correlation between the growth of OA and nitrate mass concentration and the consumed HONO from early morning to noon during the polluted days in winter. This suggests that HONO might promote aerosol mass formation in polluted events in Beijing. This promotion effect could be related to OH production from photolysis of HONO on aerosol formation followed by oxidation process of the corresponding precursors. Our observation supports well the recent modeling studies that HONO may significantly promote secondary aerosol mass formation (Zhang et al., 2019a; Zhang et al., 2019b; Xing et al., 2019; An et al., 2013).

Based on budget analysis calculations, traffic-related sources (direction emission and conversion of NO from vehicle emission) should be an important contributor to HONO source during polluted days in winter in Beijing. This means that HONO from the
traffic-related sources might have an important role in aerosol mass formation in the atmosphere.

Vehicle population in China is increasing very quickly (Liu et al., 2017b; Wang et al., 2011). Thus, the negative influences of the vehicle emission on air quality will increase especially in populous metropolitan areas (Yang et al., 2019; Guo et al., 2020), such as Beijing and Shanghai, if targeted pollution control technologies are not applied. It has been estimated that the vehicles emission accounted for over 40% of total urban NO\(_x\) emissions in Beijing (He et al., 2002). In the atmosphere, NO\(_x\) involves very complicated reaction network, from which finally leads to aerosol mass formation and production of ozone in VOC limited environment. At the same time, reactions of NO\(_x\) also leads to some reactive NO\(_x\) species (Seinfeld and Pandis, 2006). In particular, HONO is an important precursor of OH, which governs the conversion of primary pollutants to secondary pollutants in the atmosphere. Besides indirect production of HONO from NO, vehicles also directly emit HONO as discussed in this work. Even if the low limit of emission factor was used to calculating the HONO source from the vehicles, the traffic-related emission should still be an important source of HONO in winter Beijing. Therefore, this work implies that mitigation of HONO and NO\(_x\) emission from vehicles might be an effective way to reduce secondary aerosol mass formation and can have a positive effect on severe haze events in wintertime Beijing.

It should be pointed out that we only considered O\(_3\) and HONO when discussing the sources of OH. Other sources such as HO\(_2\) (and RO\(_2\)) with NO, ozonolysis of alkenes and photolysis of OVOCs might also contribute to OH radicals in the
atmosphere (Tan et al., 2018). In the future it will be vital to comprehensively analyze OH sources and to quantify the role of HONO in secondary aerosol mass formation although photolysis of HONO is the major primary OH source in winter. On the other hand, as discussed in Section 3.3, uncertainties about the HONO budget might originate from the emission factors, OH concentration, and reaction kinetics and so on. The source of HONO from vehicles was calculated based on the emission inventories, which should have a significant bias (Squires et al., 2020). For example, the emission flux of NOx calculated using the emission inventory from Yang et al. (2019) is as 2.4±0.5 times as the reported emission flux reported by Squires et al. (2020). In addition, the exact height of vertical mixing of HONO was assumed to be the same as the PBL height, this might underestimate the contribution of vehicle, soil and heterogeneous reaction on ground surface. To take the next step, it is required to measure the emission factors from vehicle exhaust under real road conditions in the future. When calculating the OH concentration, the factor between OH concentration and $J_{\text{OH}}$ might vary over locations and seasons due to different NOx/VOCs ratio (Holland et al., 2003). Direct measurements of OH concentration would be helpful for decreasing the uncertainty of both OH sources and HONO budget analysis. The importance of vehicle emission to HONO source also needs to be further confirmed during special periods such as Chinese New Year when vehicle emission reduces obviously in the future. Finally, it is necessary to quantify the contribution of traffic-related source of HONO on OH production and secondary aerosol formation based on modeling studies in the future.
Data availability. The experimental data are available upon request to the corresponding authors.

Supplement. The supplement related to this article is available online at:

Author information

Author contributions. YL, WW and MK designed the experiments. YL wrote the paper and performed HONO budget analysis. YZ, CL, WW, YC, MG and XW carried out HONO measurement. ZF, FZ, JC, WD and KD did aerosol composition measurements. BC and JK did particle size measurements. YW, BH and YW analyzed meteorological data analysis. CY, FB, JK, TP, HH, MG and MK revised the manuscript.

Acknowledgements:

This research was financially supported by the National Natural Science Foundation of China (41877306), the Ministry of Science and Technology of the People’s Republic of China (2019YFC0214701), Academy of Finland via Center of Excellence in Atmospheric Sciences (272041, 316114, and 315203) and European Research Council vShandong Universityia ATM-GTP 266 (742206), the Strategic Priority Research Program of Chinese Academy of Sciences and Beijing University of Chemical Technology.

References:


Fu, G. Q., Xu, W. Y., Yang, R. F., Li, J. B., and Zhao, C. S.: The distribution and trends of fog and haze in the North China Plain over the past 30 years, Atmos. Chem. Phys., 14, 11949-11958, 10.5194/acp-14-11949-2014, 2014.


Tong, S., Hou, S., Zhang, Y., Chu, B., Liu, Y., He, H., Zhao, P., and Ge, M.: Exploring the nitrous acid (HONO)
formation mechanism in winter Beijing: direct emissions and heterogeneous production in urban and suburban areas, Faraday Discuss., 189, 213-230, 10.1039/c5fd00163c, 2016.


Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., Wang, X., and Wang, T.: Fast heterogeneous N2O5 uptake and ClNO2 production in power plant and industrial plumes observed in the nocturnal...
residual layer over the North China Plain, Atmos. Chem. Phys., 17, 12361-12378, 10.5194/acp-17-12361-2017, 2017c.


Figure captions

Fig. 1. An overviewed measurement of non-refractory-PM$_{2.5}$ (NR-PM$_{2.5}$), HONO, NOx, PM$_{2.5}$ and meteorological parameters from Feb. 1 to July 1, 2018. (A) the mass concentration of different components of PM$_{2.5}$, (B) the mass fraction of individual component, (C) HONO and NOx concentration, (D) temperature and RH, (E) wind speed and wind direction, (F) UVB and PBL height and (G) visibility and PM$_{2.5}$ concentration during observation. We consider the period before Apr. 1 as winter. During the winter period, 12 cases are selected and numbered, including three clean cases (1, 3, and 5, marked in yellow) and the rest 9 pollution episodes (marked in blue).

Fig. 2. Contribution of HONO to OH production and correlation between OA and HONO concentration. Diurnal production rates of OH from photolysis of HONO and O$_3$ on polluted days with PM$_{2.5}$ concentration larger than 50 $\mu$g m$^{-3}$ and RH less than 90 % (A) from Feb 1 to Mar 31, (B) from Apr 1 to Jun 30; (C) Daytime variation of OA/CO and HONO/CO concentration for the 7$^{th}$ and 12$^{th}$ episodes and (D) correlation of the daytime OA/CO increased and consumed HONO/CO.

Fig. 3. Diurnal pattern of HONO sources calculated with different parameterizations. The low bound, the middle value, and upper bound of (A) soil emission calculated based on 45-55%, 35-45% and 25-35% of water content, (B) vehicle emission with relative emission factor to NOx of 0.18%, 1.17±0.05% and 1.8 %, (C) production from reaction between NO and OH, whose concentration estimated using Xu (Xu et al., 2015), (Tan et al., 2019)

Fig. 4. The budget of HONO (A) and (B) Diurnal production rates of HONO, (C) and
days with PM$_{2.5}$ concentrations higher than 50 μg m$^{-3}$ and RH less than 90 %. The left column shows the data from February 1 to March 31) and the right one shows the data from April 1 to June 30.

**Fig. 5.** (A)-(B) Diurnal production rates and (C)-(D) diurnal loss rates of HONO; (E)-(F) relative contribution of HONO sources on polluted days with PM$_{2.5}$ concentrations higher than 50 μg m$^{-3}$ and RH less than 90 %. The $E_{\text{vehicle}}$ is calculated using the low limit of HONO/NOx from vehicles (0.18%) (Liu et al., 2017d) and the $P_{\text{NO-OH}}$ is calculated using the low limit of OH concentration, while the upper limit of $E_{\text{soil}}$, $P_{\text{aerosol}}$ and $P_{\text{ground}}$ are used as described in the text.
Fig. 1.
Fig. 2.
Fig. 3
Fig. 4.
Fig. 5.