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

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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) could 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 lead to the formation of particulate matter ammonium by enhancing the neutralization of nitric acid 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 highlight that the traffic-related HONO plays 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 most suffering countries from the 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 has also been found playing an important role in the evolution of haze events (Zhang et al., 2018).

Secondary aerosol can contribute up to ~70 % to the aerosol mass concentration on polluted days (Huang et al., 2014). Several reaction pathways have been proposed in the atmospheric chemistry community, such as sulfate formation via heterogeneous oxidation of SO_2 promoted by H_2O_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_2O_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 oxidized low-volatility and semi-volatile products (Bianchi et al., 2019), followed by their 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).

The HONO concentration has been measured with a wide rang from 0.18 to 9.71

ppbv at different locations, such as Beijing (Zhang et al., 2019d;Hu et al., 2002;Hendrick et al., 2014;Wang et al., 2017b), Shanghai (Wang et al., 2013;Zhang et al., 2019b), Guangdong (Hu et al., 2002;Su et al., 2008a), Hongkong (Xu et al., 2015), Shandong (Li et al., 2018), Xi'an (Huang et al., 2017b) and so on in China since 2000. More recently, modelling studies have suggested that nitrous acid (HONO) could enhance secondary aerosols formation in Beijing-Tianjin-Hebei (BTH) region (Zhang et al., 2019c), 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 modelling studies (Liu et al., 2019c;Zhang et al., 2019c) and photostationary state calculations (Wang et al., 2017b;Li et al., 2018;Huang et al., 2017b;Lee et al., 2016;Oswald et al., 2015;Zhang et al., 2019d) 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., 2008b) and photolysis of particulate nitrate were found to be the two major mechanisms with large potential of HONO formation during noontime, but the associated uncertainty may reduce their importance (Liu et al., 2019c). The heterogeneous reactions of NO_2 on ground/aerosol surfaces were proposed to be an important HONO source during nighttime (Wang et al., 2017b;Zhang et al., 2019c) and daytime in Beijing-Tianjin-

Hebei (BTH) (Zhang et al., 2019c), but it was unimportant compared with the unknown sources and the homogeneous reaction between NO and OH in Ji'an (Li et al., 2018) or compared with the traffic emission on haze days in Beijing (Zhang et al., 2019d). The traffic emission was found to be an important HONO source during nighttime and a minor daytime HONO source in BTH (Zhang et al., 2019c). However, it was proposed that direct emission of HONO from vehicles should contribute about 51.1 % (Meng et al., 2019) and 52 % of HONO source on haze days in Beijing (Zhang et al., 2019d). These results mean that more studies are 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 has 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. 39°56′31″ and Lon. 116°17′52″) 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 the main building with 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 about ToF-ACSM measurement was described in the Supplement information. 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, SO_2, CO and O_3 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 Scanning Mobility Particle Sizer (SMPS 3936, TSI), particle size magnifier (PSM, Airmodus) and 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. Multiple 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 ($P_{\mathrm{NO\text{-}OH}}$) in the atmosphere, photolysis of nitrate (P_{nitrate}) (Bao et al., 2018), nitrous acid (P_{HNO3}) and nitrophenenol ($P_{\mathrm{nitrophenol}}$) (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 ($L_{\mathrm{photolysis}}$), the homogeneous reaction with OH radical ($L_{\mathrm{HONO\text{-}OH}}$) and dry deposition ($L_{\mathrm{deposition}}$) (Liu et al., 2019c) were considered.

The HONO budget could be calculated by,

$$\frac{dc_{HONO}}{dt} = E_{HONO} + P_{HONO} - L_{HONO} + T_{vertical} + T_{horizontal} \qquad (1)$$

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 $T_{\mathrm{horizontal}}$ 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 ($F_{\mathrm{HONO}}=EI_{\mathrm{HONO}}/A$, g m^{-2} s^{-1}) and PBL height (H, m) according to the following equation,

$$E_{HONO} = \frac{a \cdot F_{HONO}}{H} \quad (2)$$

where, EI_{HONO}, is the emission inventory of HONO (g s^{-1}), A is the urban area of Beijing (m^2), α is the conversion factor ($\alpha = \frac{1\times10^{9}\cdot3600\cdot R\cdot T}{M\cdot P} = \frac{2.99\times10^{13}\cdot T}{M\cdot P}$), 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}, ppbv h^{-1}) in the troposphere was calculated by,

$$P_{HONO} = 3600 \cdot k_1 \cdot c_{precursor} \quad (3)$$

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

$$k_1 = k_2 \cdot c_{OH} \quad (4)$$

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

$$k_1 = \frac{\gamma \cdot A_S \cdot \omega}{4} \cdot Y_{HONO} \quad (5)$$

where, A_s is the surface area concentration of the reactive surface (m^2 m^{-3}), ω is the molecular mean speed (m s^{-1}), γ is the uptake coefficient of the precursor, Y_{HONO} is the yield of HONO. For ground surface, the surface area concentration is

$$A_s = \frac{\delta}{H} \quad (6)$$

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

$$\delta = \frac{f_{building} * (A_{projected} + h * P_{building})}{A_{projected}} + f_{blank} \quad (7)$$

where f_{building} (0.31) and f_{blank} (0.69) are the fraction of the projected area ($A_{\mathrm{projected}}$) of buildings and blank space, respectively; P_{building} and h are the perimeter and the height of the building, respectively. The f_{building} and P_{building} are measured from ~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 δ 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 ($L_{\mathrm{photolysis}}$), homogeneous reaction with OH radicals ($L_{\mathrm{HONO\text{-}OH}}$) and dry deposition ($L_{\mathrm{deposition}}$) (Liu et al., 2019c) were calculated according to the following equations.

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

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

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

where, J_{HONO} is the photolysis rate of HONO (s^{-1}), $k_{HONO\text{-}OH}$ is the second-order reaction rate constant between HONO and OH (6×10^{-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 ($T_{vertical}$), 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).

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

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),

$$T_{vertical} = k_{dilution}(c_{HONO} - c_{HONO,background}) \quad (13)$$

where $k_{dilution}$ is a dilution rate (0.23 h^{-1}, including both vertical and horizontal transport) (Dillon et al., 2002), c_{HONO} and $c_{HONO,background}$ 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).

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

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 the low planetary boundary layer (PBL) height, in particular, 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_4NO_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 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., 2016) 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_2O_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_2O_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 contribution of HONO to secondary aerosol formation through OH production. We simply compared the OH production via photolysis of HONO ($P_{\mathrm{OH\text{-}HONO}}=J_{\mathrm{HONO}}\times c_{\mathrm{HONO}}$) and O_3 ($P_{\mathrm{OH\text{-}O3}}=J_{\mathrm{O1D}}\times c_{\mathrm{O3}}$) 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 $P_{\mathrm{OH\text{-}HONO}}$ was always significantly higher than the $P_{\mathrm{OH\text{-}O3}}$ in winter and the maximal $P_{\mathrm{OH\text{-}HONO}}$ and $P_{\mathrm{OH\text{-}O3}}$ were $1.73\pm0.86\times10^{7}$ molecules cm^{-3} s^{-1} (2.43±1.21 ppb h^{-1}) and $1.03\pm1.06\times10^{7}$ molecules cm^{-3} s^{-1} (1.45±1.49 ppb h^{-1}), respectively (Fig. 2A). Owing to the high HONO concentration accumulated throughout the night, the maximal $P_{\mathrm{OH\text{-}HONO}}$ in winter was as about 2-6 times of that was observed in the wintertime of Colorado, USA (~0.59 ppb h^{-1}) (Kim et al., 2014), New York, USA (~0.40 ppb h^{-1}) (Kanaya et al., 2007) and Nanjing, China (0.90±0.27 ppb h^{-1}) (Liu et al., 2019b). In the period from April to June, the daily maxima of $P_{\mathrm{OH\text{-}HONO}}$ and $P_{\mathrm{OH\text{-}O3}}$ were $2.48\pm1.42\times10^{7}$ molecules cm^{-3} s^{-1} (3.48±1.99 ppb h^{-1}) and $6.51\pm4.17\times10^{7}$ molecules cm^{-3} s^{-1} (9.15±5.86 ppb h^{-1}), respectively. These results mean that the photolysis of HONO should play an important role in the initiation of the daytime HO_x and RO_x chemistry on polluted days in winter, while photolysis of O_3 becomes more important from April to June. This is consistent with the previous findings that HONO photolysis dominants 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 primary 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). We partially ascribe this to the high HONO concentration in winter Beijing. To confirm this assumption, 12 episodes in winter were chosen (Fig. 1) to uncover the connection between aerosol formation and HONO photolysis. 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 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 ($\Delta C_{OA}/C_{CO}$) as a function of the consumed HONO ($-\Delta C_{HONO}/C_{CO}$) in Fig. 2D. Except for the 4th episode that was highly affected by firework emission during the Spring Festival, $\Delta C_{OA}/C_{CO}$ showed a linear dependence on $-\Delta C_{HONO}/C_{CO}$ in winter, and the correlation coefficient was 0.75. As the meteorological condition was stagnant during these cases as indicated by the low wind speed (< 1.0 m s^{-1}, Fig. S5D), it was reasonable to ascribe the increase of OA concentration to local secondary formation initiated by OH radical and photolysis of HONO should play an important role in initiation the HO_x and RO_x chemistry. This kind of correlation could not be seen for the pollution events from April to June because the primary OH production was no longer dominated by HONO photolysis as indicated by Fig. 2D. It should be noted that oxidation of biogenic alkenes by O_3 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, $\Delta C_{nitrate}/C_{CO}$ in winter also showed good linear correlation with -$\Delta C_{HONO}/C_{CO}$ (R=0.67, Fig. S5E), suggesting that the increase of particle-phase nitrate in the daytime should also be promoted by OH radical from HONO photolysis. Interestingly, $\Delta C_{ammonium}$/CO also showed a good correlation with -$\Delta C_{HONO}/C_{CO}$ (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 HNO_3 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_2O_5 mainly contributed to nighttime nitrate (Tian et al., 2019). Although a recent work has found that daytime hydrolysis of N_2O_5 on hygroscopic aerosols is also an important source of daytime nitrate in winter Beijing (Wang et al., 2017a), the linearly correlation between $\Delta C_{nitrate}/C_{CO}$ and $\Delta C_{HONO}/C_{CO}$ at least implies that the promotion effect of HONO on nitrate formation could not be excluded. On the other hand, the correlation between $\Delta C_{sulfate}/C_{CO}$ and $-\Delta C_{HONO}/C_{CO}$ was much weaker (R=0.26), suggesting a weak connection between particle-phase sulfate and gas-phase H_2SO_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 well supported the recent modeling results that HONO could obviously promote the aerosol production in winter (Zhang et al., 2019a;Zhang et al., 2019c;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 $E_{vehicle}$ was calculated according to 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., 2019d) 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_x ratio using a low limit correlation method (Li et al., 2012). In the 2D space of HONO verse NO_x (Fig. S8), the lowest marge with $\Delta NO/\Delta NOx$ larger than 0.8 were chosen for linear correlation. The ratio of $\Delta HONO/\Delta NOx$ is 1.17±0.05%. 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., 2019d;Meng et al., 2019). Finally, several studies have measured the direct emission of HONO from vehicle exhaust. The HONO/NO_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. 1.17±0.05% was taken as the middle value which was 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_{vehicle} was calculated using the hourly NO_x emission inventory from vehicles in Beijing (Yang et al., 2019) after converted to emission flux of HONO ($F_{\mathrm{HONO}}=F_{\mathrm{NOx}}\times$ HONO/NO_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_{vehicle} using the HONO/NO_x of 1.17% was from 0.085±0.038 to 0.34±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_{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 an 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 was available for grassland soil. Three levels of water content including 25-35%, 35-45% and 45-55% were considered. The temperature dependence of F_{HONO} was calculated using the mean value of the F_{HONO} with different water content, while the low limit and upper limit of F_{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_{soil} are 0.0032±0.0027-0.013±0.014, 0.0046±0.0039-0.020±0.20 and 0.0057±0.0047-0.025±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, $c_{\mathrm{OH}}=J_{\mathrm{O1D}}\times2\times10^{11}$ molecules cm^{-3} (Tan et al., 2019). However, Tan et al. (2018) reported a larger conversion factor (4.33×10^{11} molecules cm^{-3}). Li et al. (2018) estimated the OH radical concentration considering both photolysis rate and NO_2 concentration, namely,

$$c_{OH} = \frac{4.1\times10^{9}\times(J_{O1D})^{0.83}\times\left(J_{NO_2}\right)^{0.19}\times(140c_{NO_2}+1)}{0.41c_{NO_2}^{2}+1.7c_{NO_2}+1} \quad (15)$$

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 the 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 $P_{\mathrm{NO\text{-}OH}}$ was taken as the low limit for homogeneous reaction between NO and HONO because polluted events were discussed in this work, while $P_{\mathrm{NO\text{-}OH}}$ calculated using the OH concentration ($J_{\mathrm{O1D}}\times 4.33\times 10^{11}$ molecules cm^{-3}) (Tan et al., 2018) was taken as the upper limit and $P_{\mathrm{NO\text{-}OH}}$ calculated using the OH concentration ($J_{\mathrm{O1D}}\times 2\times 10^{11}$ 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,

$$c_{OH,night} = 1\times 10^{5} + 4\times 10^{5}\times \frac{(c_{O_3}\times c_{alkenes})_{night}-(c_{O_3}\times c_{alkenes})_{night,min}}{(c_{O_3}\times c_{alkenes})_{night,max}-(c_{O_3}\times c_{alkenes})_{night,min}} \quad (16)$$

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 $P_{\mathrm{NO\text{-}OH}}$ 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 $P_{\mathrm{NO\text{-}OH}}$ (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 $P_{\mathrm{NO\text{-}OH}}$. Besides vehicle emission, power plant and industries also contribute NO emission. 40 % of NOx was from vehicle emission according to the emission inventory of NO_x 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_{NO2} (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 need to be further investigated in the future.

Photolysis of nitrate. A recent work reported the photolysis rate of nitrate ($J_{nitrate}$) in ambient $PM_{2.5}$ at a solar zenith angle of 0° (Bao et al., 2018). The $J_{nitrate}$ 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 $J_{nitrate}$. The time series of the measured nitrate concentration and the middle value of $J_{nitrate}$ 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 (γ) 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_{aerosol} in the base case. It has been found that the γ highly depends on the relative humidity (RH). The low limit bound of P_{aerosol} was calculated based on the RH dependent uptake coefficient of NO_2 on kaolinite ($\gamma_{NO2}=4.47\times10^{39}/(1.75\times10^{46}+1.93\times10^{45}RH)$, while the upper limit of P_{aerosol} was calculated according to the RH dependent γ on hematite ($\gamma_{NO2}=4.46\times10^{39}/(6.73\times10^{44}+3.48\times10^{44}RH)$) (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 γ_{NO2} on BC is 1.17×10^{-5}, with a HONO yield of 0.8 (Han et al., 2013). The light enhanced uptake γ of NO_2 (1.9×10^{-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. 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 ($\gamma_{NO2}=7.4\times10^{-7}+5.5\times10^{-8}$ 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 1×10^{-4} to 4.8×10^{-3} m^{-1} with a mean value of $1.4\pm0.5\times10^{-3}$ 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 1.5×10^{-3} to 3.85×10^{-2} m^{-1} with a mean value of $1.3\pm0.9\times10^{-2}$ m^{-1} during pollution events. The surface roughness was 3.85 calculated according to Eq. (7). The Y_{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 $P_{aerosol}$ were 0.038±0.030-0.087±0.072, 0.038±0.030-0.088±0.072 and 0.041±0.032 - 0.092±0.073 ppbv h^{-1}, respectively. The corresponding values were 0.00027±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}. Although the A_s of ground surface was higher than that of aerosol, the larger γ_{NO2} (1.17×10^{-5}) on soot particles than that on other aerosols and ground surface led to a larger production rate of HONO in this work. The $P_{aerosol}$ calculated in this work was on the same orders as soil emission, while it was lower than the $P_{aerosol}$ 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 NO_2 on different particles in this work.

It should be pointed out that HONO production from heterogeneous reaction of NO_2 on both aerosol and ground surface greatly depend on the $\gamma_{NO2,\,BET}$ and A_s. The A_s of aerosols was comparable with the modeling input. However, the small nighttime $\gamma_{NO2,\,BET}$ (10^{-8} - 10^{-7}) on dust were used in this work rather than the $\gamma_{NO2,\,BET}$ (1×10^{-6}) used in modelling 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 NO_2 on aerosols. As for heterogeneous reaction of NO_2 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}) calculated using the surface roughness and 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 NO_2 on ground surface. It should be noted that the initial uptake coefficient (γ_{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 γ_{ini} (Han et al., 2013;Liu et al., 2015). These results mean that heterogeneous reaction might not be a major HONO source. This is consistent with a recent work that found heterogeneous reaction being unimportant when compared with traffic emission during haze events in winter in Beijing (Zhang et al., 2019d).

Sinks of HONO. The loss rates of HONO by photolysis ($L_{photolysis}$), homogeneous reaction with OH radicals ($L_{HONO\text{-}OH}$) and dry deposition were calculated according to Eqs. (9)-(11). The daytime J_{HONO} varied from 1.71×10^{-5} to 1.13×10^{-3} s^{-1} on polluted days in winter, while it was in the range of 5.89×10^{-5} to 1.53×10^{-3} s^{-1} from April to June. These values are comparable to modelling results (3.9×10^{-5}-1.8×10^{-3} s^{-1}) (Gall et al., 2016). The daytime $L_{photolysis}$ were in the range of 0.03-5.23 ppb 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 $L_{HONO\text{-}OH}$ varied from 0.0049 to 0.069 ppbv h^{-1} in winter using the $k_{HONO\text{-}}$

$_{\mathrm{OH}}$ of 6×10^{-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 $L_{\mathrm{deposition}}$ 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). In the daytime, we assume a zero concentration gradient. 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×WS-0.3374 m^2 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), horizontal transport should have little influence on the daytime sources or sinks of HONO because of the short lifetime of HONO (Spataro and Ianniello, 2014). In the night, 79 % of the wind speed was lower than 1.0 m s^{-1} 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 was 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 were 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 not the major HONO source during night unlike the modelled results (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 0.25 - 1.81 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 (0.23±0.06 ppbv h^{-1}), followed by heterogeneous reactions of NO_2 on the ground surface (0.07±0.01 ppbv h^{-1}), homogeneous reaction between NO and OH (0.04±0.01 ppbv h^{-1}), emission from soil (0.014±0.005 ppbv h^{-1}), and heterogeneous reactions of NO_2 on aerosol surface (0.006±0.002 ppbv h^{-1}). $P_{\mathrm{NO\text{-}OH}}$ 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_{unknown} was 0.20±0.24 ppbv h^{-1} in February and March, while it was 0.50±0.24 ppbv h^{-1} from April to June.

The E_{vehicle} contributed 57.0±10.0% and 51.5±20.1% to the nighttime HONO sources from February to March and the rest months, respectively, even when the P_{unknown} was taken into consideration. The relative contribution of daytime E_{vehicle} decreased to 15.2±15.4% in winter and 9.7±7.8% from April to June. Thus, the daily mean fraction of the E_{vehicle} was 39.6±24.3% and 34.0±24.3% from February to March and from April to June, respectively. This means that the E_{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 or haze day HONO source (51.1 % -52 %) in Beijing (Zhang et al., 2019c;Meng et al., 2019). As pointed out in Section 3.3, E_{vechicle} was calculated based on the NO_x inventory from vehicle sector. On the other hand, NO is prone to be quickly converted to NO_2 and NO_z (including HONO, HNO_3, N_2O_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, although the diurnal curve of $P_{\text{NO-OH}}$ coincided well with that of OH concentration (Fig. S10), which means the $P_{\text{NO-OH}}$ should be mainly determined by OH concentration, 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_{vehicles} +$P_{\text{NO-OH}}$) might contribute 57.8±15 .8% and 48.6±15.9 % to the daily HONO source in winter and the rest months, respectively. Even if 40 % of NO_x was from vehicle exhaust in Beijing (He et al., 2002), traffic-related source (E_{vehicles} + 0.4$P_{\text{NO-OH}}$) might still contribute 46.9±20.5 % in winter and 39.9±20.5 % from April to June to the corresponding daily HONO source. The contribution of traffic-related source was still an important daytime source of HONO (43.9±10.6 % for E_{vehicles} +$P_{\text{NO-OH}}$, and 26.7±12.4 % for E_{vehicles} + 0.4$P_{\text{NO-OH}}$) 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_{vehicle} was obtained by using the lowest reported emission ratio of HONO/NO_x from vehicles (0.18%) (Liu et al., 2017d) rather than 1.17%, 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 NO_2 on the aerosol was calculated using the large RH-dependent uptake coefficient of NO_2 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_{vehicles} + $P_{\text{NO-OH}}$) contributed 25.7±15.8 % to the daily HONO sources in winter if all NO was assumed to be dominated by local traffic emission, while it was 14.5±15.8 % when 40 % of NO was considered as local traffic emission (He et al., 2002). Under this circumstance, the daytime P_{unknown} of HONO in winter increased to 0.83±0.36 ppbv h^{-1}, which was corresponding to 58.1±8.6 % of the HONO source. This means these assumptions might underestimate the contribution of the HONO sources. In addition, P_{ground}, P_{aerosol} and P_{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 modelling studies.

4. Conclusions and atmospheric implications.

In this work, the promotion effect of HONO on aerosol mass formation in polluted events was observed based on 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 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 modelling studies that HONO may significantly promote secondary aerosol mass formation (Zhang et al., 2019a;Zhang et al., 2019c;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) was found to be an important contributor to HONO source during polluted days in winter in Beijing. This means that HONO from the traffic-related sources can 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_z 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, the vehicles also directly emits 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 can 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 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 NO_x 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). 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_{O1D} might vary over locations and seasons due to different NO_x/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. Finally, it is necessary to quantify the contribution of traffic-related source of HONO on secondary aerosol formation based on modelling 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:

Competing interests. The authors declare that they have no conflict of interest.

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.

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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 7th and 12th 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

(D) loss rates of HONO, (E) and (F) relative contribution of each source on polluted 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_{vehicle} is calculated using the low limit of HONO/NOx from vehicles (0.18%) (Liu et al., 2017d) and the $P_{\mathrm{NO\text{-}OH}}$ is calculated using the low limit of OH concentration, while the upper limit of E_{soil}, P_{aerosol} and P_{ground} are used as described in the text.

Figures

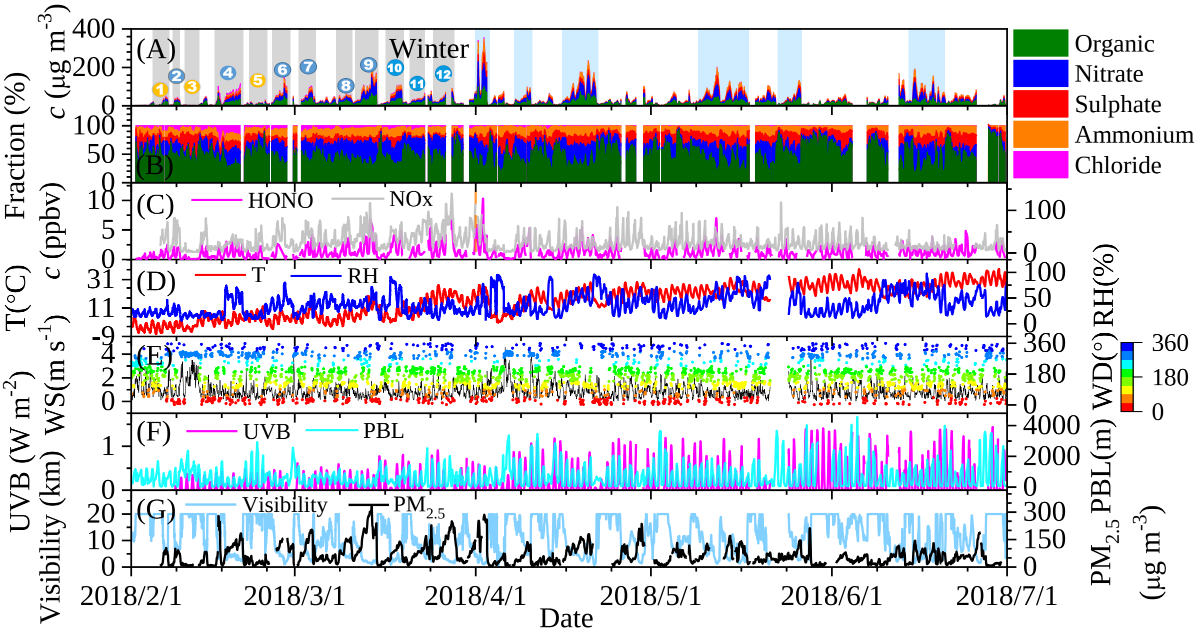
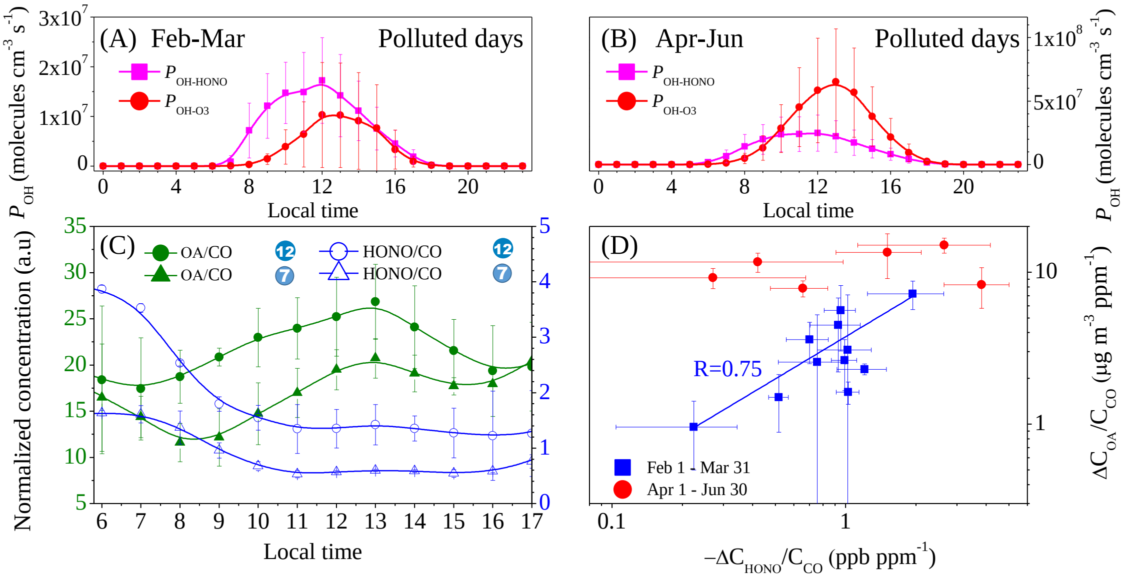


Fig. 1.



(A) Feb-Mar
Polluted days
$P_{OH-HONO}$
P_{OH-O3}
P_{OH} (molecules cm^{-3} s^{-1})
3x10^7
2x10^7
1x10^7
0
0
4
8
12
16
20
Local time
(B) Apr-Jun
Polluted days
$P_{OH-HONO}$
P_{OH-O3}
1x10^8
5x10^7
0
P_{OH} (molecules cm^{-3} s^{-1})
Local time
(C)
OA/CO
OA/CO
12
7
HONO/CO
HONO/CO
Normalized concentration (a.u)
35
30
25
20
15
10
5
6
7
8
9
10
11
12
13
14
15
16
17
Local time
5
4
3
2
1
0
(D)
R=0.75
Feb 1 - Mar 31
Apr 1 - Jun 30
0.1
1
10
$-\Delta C_{HONO}/C_{CO}$ (ppb ppm^{-1})
$\Delta C_{OA}/C_{CO}$ (μg m^{-3} ppm^{-1})

Fig. 2.

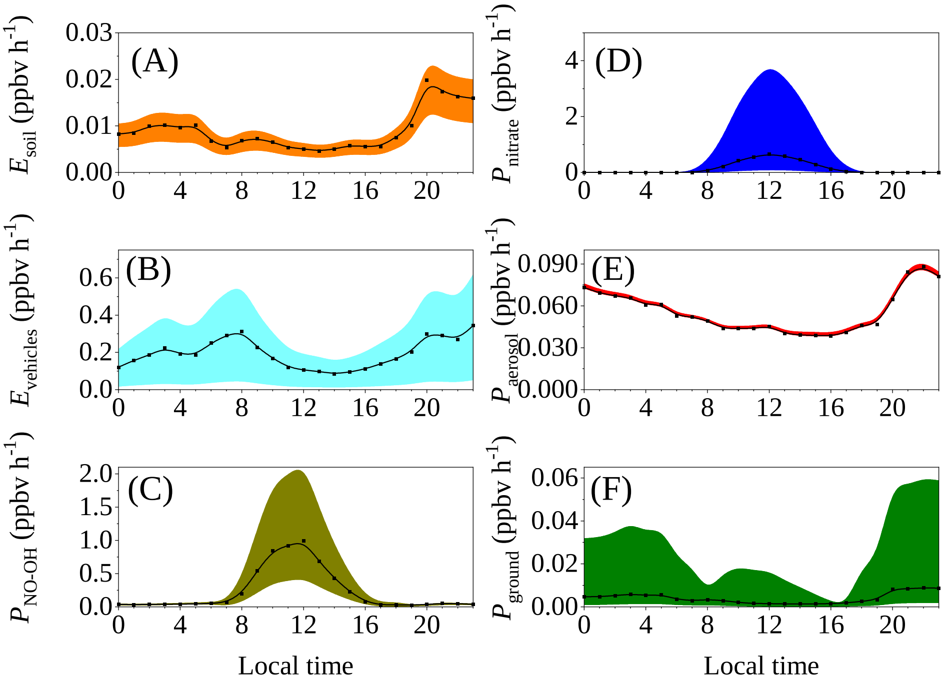
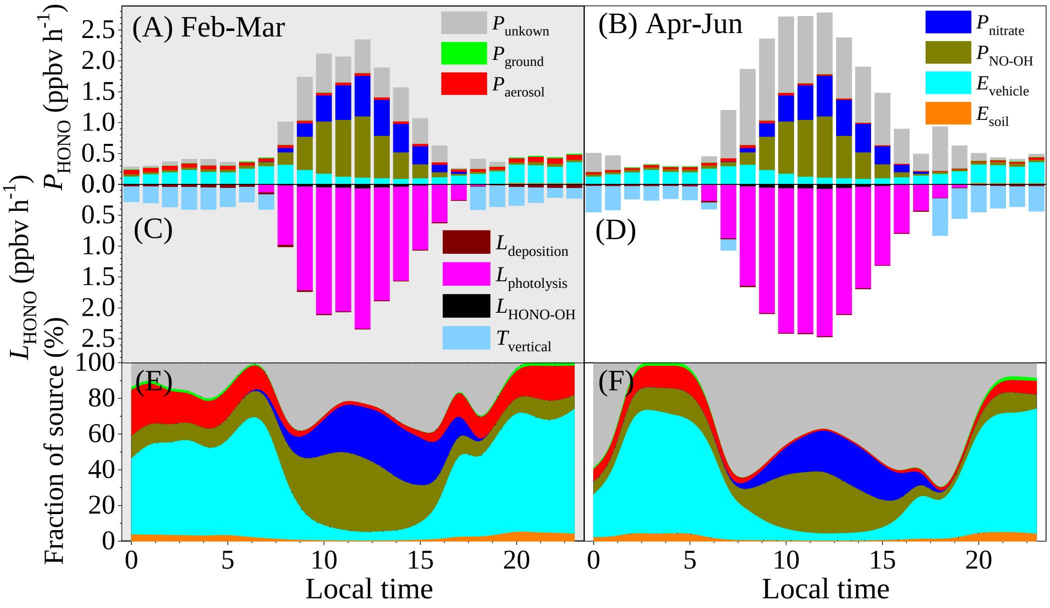

(A)
E_{soil} (ppbv h^{-1})
0.00
0.01
0.02
0.03
(B)
$E_{vehicles}$ (ppbv h^{-1})
0.0
0.2
0.4
0.6
(C)
P_{NO-OH} (ppbv h^{-1})
0.0
0.5
1.0
1.5
2.0
(D)
$P_{nitrate}$ (ppbv h^{-1})
0
2
4
(E)
$P_{aerosol}$ (ppbv h^{-1})
0.000
0.030
0.060
0.090
(F)
P_{ground} (ppbv h^{-1})
0.00
0.02
0.04
0.06
0
4
8
12
16
20
Local time
Local time

Fig. 3



(A) Feb-Mar
(B) Apr-Jun
(C)
(D)
(E)
(F)
P_{unkown}
P_{ground}
$P_{aerosol}$
$P_{nitrate}$
$P_{NO\text{-}OH}$
$E_{vehicle}$
E_{soil}
$L_{deposition}$
$L_{photolysis}$
$L_{HONO\text{-}OH}$
$T_{vertical}$
P_{HONO} (ppbv h^{-1})
L_{HONO} (ppbv h^{-1})
Fraction of source (%)
2.5
2.0
1.5
1.0
0.5
0.0
0.5
1.0
1.5
2.0
2.5
100
80
60
40
20
0
0
5
10
15
20
Local time

Fig. 4.

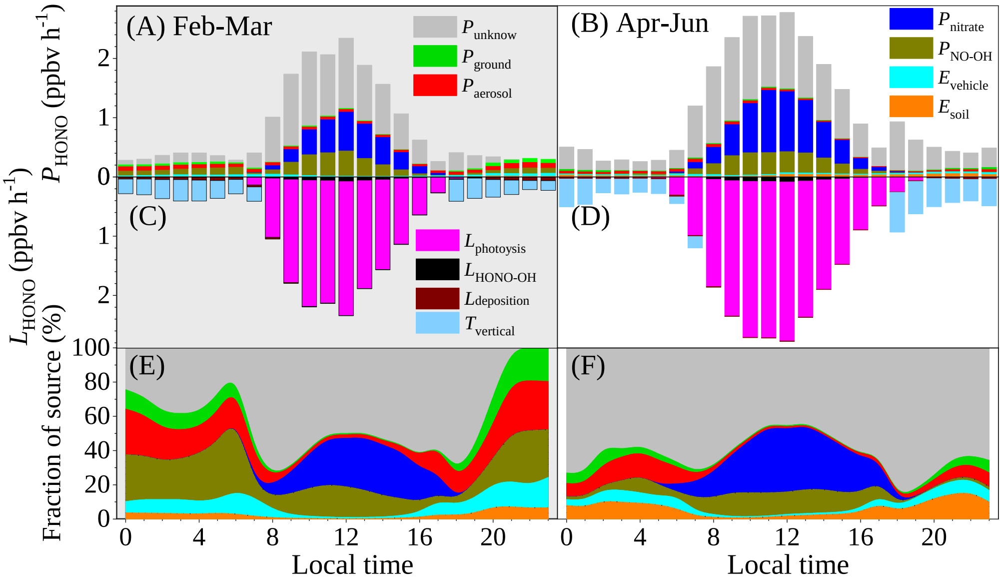

(A) Feb-Mar
(B) Apr-Jun
(C)
(D)
(E)
(F)
P_{unknow}
P_{ground}
$P_{aerosol}$
$P_{nitrate}$
P_{NO-OH}
$E_{vehicle}$
E_{soil}
$L_{photoysis}$
$L_{HONO-OH}$
$L_{deposition}$
$T_{vertical}$
P_{HONO} (ppbv h^{-1})
L_{HONO} (ppbv h^{-1})
Fraction of source (%)
0
1
2
0
20
40
60
80
100
0
4
8
12
16
20
Local time

Fig. 5.