https://doi.org/10.5194/egusphere-2023-3139
Preprint. Discussion started: 9 January 2024

Concentration and source changes of HONO during the COVID-19 lockdown in Beijing

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https://doi.org/10.5194/egusphere-2023-3139
Preprint. Discussion started: 9 January 2024

Abstract:

Nitrous acid (HONO) is an important precursor of OH radicals which affects not only the sinks of primary air pollutants but also the formation of secondary air pollutants, whereas its source closure in the atmosphere is still controversial due to a lack of experiment validation. In this study, the HONO budget in Beijing has been analyzed and validated through the coronavirus disease (COVID-19) lockdown event, which resulted in the largest changes in air pollutant emissions in the history of modern atmospheric chemistry. A home-made Water-based Long-Path Absorption Photometer (LOPAP) along with other instruments were used to measure the HONO and related pollutants from January 1, 2020 to March 6, 2020, which covered the Chinese New Year (CNY) and the COVID-19 lockdown. The average concentration of HONO decreased from 0.97 ± 0.74 ppb before CNY to 0.53 ± 0.44 ppb during the COVID-19 lockdown, accompanied by a sharp drop of NO_x and the greatest drop of NO (around 87%). HONO budget analysis suggests that vehicle emissions were the most important source of HONO during the nighttime (53%) before CNY, well supported by the decline of their contribution to HONO during the COVID-19 lockdown. We found that the heterogeneous conversion of NO_2 on ground surfaces was an important nighttime source of HONO (31%), while that on aerosol surfaces was a minor source (2%). Nitrate photolysis became the most important daytime source during the COVID-19 lockdown compared with that before CNY, resulting from the combined effect of the increase in nitrate and the decrease in NO. Our results indicate that reducing vehicle emissions should be an effective measure for alleviating HONO in Beijing.

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1. Introduction

As the most vital oxidant in the troposphere, OH radicals not only govern the sink of most trace compounds but also affect the production of secondary pollutants by initiating photochemical reactions in the atmosphere. Nitrous acid (HONO) is an important primary precursor of OH radicals (Kulmala and Petäjä, 2011; Zhang et al., 2023c). Photolysis of HONO can contribute 60% (Tan et al., 2018) and sometimes even 92% (Xue et al., 2020) to OH production in the morning. Therefore, HONO can indirectly promote the formation of both secondary aerosols (Zhang et al., 2019b) and ozone (Zhang et al., 2022a). In addition, HONO can react with histamine to form carcinogens, such as nitrosamines, after entering the human body (Farren et al., 2015). Thus, understanding the sources of HONO in the atmosphere has been a hot topic for several decades, but it is still far from closed (Jiang et al., 2022).

Intensive studies have been carried out on HONO measurements and source analysis (Liu et al., 2020c; Liu et al., 2020d; Zheng et al., 2020; Zhang et al., 2020; Xue et al., 2020; Zhang et al., 2019a; Liu et al., 2019b). The concentrations of HONO in the atmosphere range from a few ppt in remote areas (Spataro et al., 2016) to several ppb, even several tens ppb in heavily polluted areas (Liu et al., 2019b; Liu et al., 2020c; Liu et al., 2020d; Zheng et al., 2020). The sources of atmospheric HONO consist of direct emissions and secondary formation in the atmosphere. Direct emissions include vehicles, soils, indoor air, livestock farming, and biomass burning, while secondary formation includes gas-phase reaction between NO and OH radicals, photolysis of particulate nitrate, and the heterogeneous reaction of NO_2 on ground and particulate matter surfaces, including the photochemical heterogeneous reaction of NO_2.

Soil emissions, which depend on soil types, microorganisms, water content, temperature,

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and pH (Kulmala and Petäjä, 2011; Weber et al., 2015; Kim and Or, 2019), are important sources of HONO. They account for up to 80% of HONO sources, especially during fertilization in agricultural areas (Liu et al., 2019c). Biomass burning, which often occurs in the harvesting seasons of wheat/corn in summer and autumn (Zhang et al., 2019b; Sun et al., 2017; Sun et al., 2018), even contributes 17% to HONO sources (Nie et al., 2015). Vehicle emissions are considered an important source of HONO in traffic-intensive areas (Kramer et al., 2020; Li et al., 2021) ranging from 8% to 80% of HONO sources (Fu et al., 2019; Xu et al., 2015). This source is more important at nighttime compared with daytime (Zhang et al., 2016; Fu et al., 2019; Liu et al., 2020d). Recently, indoor emissions have also been proposed as a potential HONO source (Xue, 2022), which is related to the ventilation from high HONO concentrations in indoor air to low HONO concentrations in outdoor air (Zhang et al., 2019b). For example, the concentrations of HONO in urban areas increased by 0.6-0.8 ppb at night after this source was accounted for in WRF-Chem model simulations (Zhang et al., 2019a). Livestock farming is a previously overlooked source of HONO, especially in agricultural areas. This emission can account for 39-45% of HONO production in rural areas (Zhang et al., 2023a). Gas phase reaction between NO and OH, photolysis of nitrate particles, and light-enhanced conversion of NO_2 are the main sources of daytime HONO (Liu et al., 2019c; Liu et al., 2020d; Zhang et al., 2022b). The heterogeneous reaction of NO_2 on various surfaces is widely regarded as an important source of HONO (Han et al., 2016; Liu et al., 2020b). Its contribution to atmospheric HONO varied from 50% to 81% in different studies (Zheng et al., 2020; Liu et al., 2019b; Fu et al., 2019).

Although intensive studies have been performed on HONO sources, the contributions of

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different sources are still controversial (Zhou et al., 2011; Liu et al., 2014; Wu et al., 2019; Kramer et al., 2020; Meng et al., 2020). For example, some studies reported that the heterogenous reaction of NO_2 on ground surfaces was a main source of HONO, accounting for ~42% of the observed HONO in Hong Kong and the Pearl River Delta (Xu et al., 2015; Zhang et al., 2020). Vertical gradient measurements of HONO also showed that ground surfaces were the main reaction surfaces (Pusede et al., 2015). However, some other studies suggested that aerosol surfaces instead of ground surfaces were the main medium for NO_2 heterogeneous production of HONO during the day in polluted areas in Beijing and Shanghai (Liu et al., 2014; Cui et al., 2018; Meng et al., 2020). In particular, the heterogenous conversion of NO_2 to HONO on aerosol surfaces was important under heavily polluted conditions (Meng et al., 2020; Zhang et al., 2020). In contrast, some studies found that heterogeneous reaction was unimportant compared to direct emissions (Tong et al., 2016; Hao et al., 2019; Zhang et al., 2019b), accounting for only 5% to 8% of HONO sources (Kramer et al., 2020). For instance, vehicle emissions can contribute around 40%-50% to Beijing's nighttime HONO sources (Meng et al., 2020; Liu et al., 2020d). However, several studies found it to be an unimportant HONO source, with a contribution ranging from 8% to 16% (Fu et al., 2019; Zheng et al., 2020; Hao et al., 2019). It should be noted that the contribution of NO_2 heterogeneous reaction to HONO greatly depends on the choice of NO_2 uptake coefficient (γ_{NO2}), which varies from 10^{-8} to 10^{-4} in different studies (Meng et al., 2020; Liu et al., 2020b; Ge et al., 2019; Liu et al., 2015; Liu et al., 2020d). Vehicle emissions also have similar characteristics because the HONO emission rate strongly depends on the emission factor, i.e. the ratio of $HONO/NO_x$ (Kramer et al., 2020; R. Kurtenbach et al., 2001; Zhang et al., 2019c), which ranges from 0.03% to 2.1%

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(Liao et al., 2021). For other HONO sources, the relative importance is affected by many parameters, such as reaction kinetics for photolysis of nitrate, OH concentrations for homogeneous reaction between NO and OH, emission fluxes for soil emissions, and so on. Thus, the HONO budget still has a large uncertainty. In particular, it is an open question of how to prove the importance of a specific reaction pathway or a source of atmospheric HONO.

Special events taking place on large spatial scales provide us with an alternative opportunity to disclose the mysteries of the HONO budget because of obvious and potentially large changes in some of the HONO sources. During the Spring Festival in 2020, the lockdown measures during the new coronavirus disease -19 (COVID-19) pandemic led to a significant reduction in primary emissions from traffic and industries. The magnitude and speed of changes in air pollutant emissions have been considered the largest changes in the history of modern atmospheric chemistry (Kroll et al., 2020). We conducted continuous field observations of HONO and other air pollutants from January 1, 2020, to March 6, 2020, in downtown Beijing, aimed at understanding the changes in HONO concentrations and sources during the lockdown period compared to that before.

2. Experimental section

2.1 Field measurements.

Observations were carried out at the Aerosol and Haze Laboratory, Beijing University of Chemical Technology (AHL/BUCT), which has been described in our previous work (Liu et al., 2020d). Briefly, it is located on the west campus of BUCT, around 550 m from the west third-ring road of Beijing, which is a typical urban observation site. The station is on the rooftop of a 5-story building (about 18 m from the ground). HONO was measured with a homemade

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Water-based Long-Path Absorption Photometer (LOPAP, Institute of Chemistry, Chinese Academy of Sciences), which has been deployed in field observation studies (Tong et al., 2016; Chen et al., 2020) and has been proven to be a stable and credible instrument for HONO measurements (Crilley et al., 2019). The principle of this instrument is similar to that of a commercial LOPAP (QUMA). Briefly, gas-phase HONO absorbed by deionized water (≥ 18.2 MΩ) in a stripping coil reacts with N-(1-naphthyl) ethylenediamine-dihydrochloric acid (0.077 mmol L^{-1}) in an acidic solution (2 mmol L^{-1} sulfanilamide in 0.12 mol L^{-1} HCl) to form an azo dye, which is measured at 550 nm with a spectrometer equipped with a LWCC (Liquid Waveguide Capillary Cell, LWCC-3250, WPI, USA). The sampling rate was 1 L min^{-1} controlled by a flow meter and a diaphragm pump. The flow rate of absorption liquid was 0.5 ml min^{-1} controlled by a peristaltic pump. The limit of detection of the LOPAP was 0.01 ppb for a sampling duration of 60 s. The instrument was calibrated with nitrite standard solution before and after each measurement about every three weeks and calibrated by zero air every 24 hours to check zero drift. An overestimation of HONO concentration (6.7%), calibrated in control experiments with 100 ppb of NO_2 at 50% RH due to the interference of NO_2 in the sampling inlet (about 30 cm of Teflon tube), was accounted for when we calculating the HONO concentrations in this work.

A set of commercial analyzers for NO_x, SO_2, CO, and O_3 (Thermo Scientific 42i, 43i, 48i, 49i) were also available. $PM_{2.5}$ was measured using a Tapered Element Oscillating Microbalance (TEOM, Thermo Fisher Scientific, 1405). The chemical composition of non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) was measured using a Time-of-flight Aerosol Chemical Speciation Monitor (ToF-ACSM, Aerodyne). Meteorological parameters including

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temperature, RH, pressure, wind speed and direction, and ultraviolet radiation (A and B) were measured using a weather station (AWS 310 at AHL/BUCT station, Vaisala). The planetary boundary layer (PBL) height and visibility were measured using a ceilometer (CL51, Vaisala) and a visibility sensor (PWD22, Vaisala), respectively. The photolysis rate (J_{NO2}) was measured via a continuous measurement of the actinic flux in the wavelength range of 285-375 nm using a J_{NO2} filter-radiometer (2-pi-J_{NO2} radiometer, Metcon). All instruments used in the measurement as well as their detection limits are shown in Table S1.

2.2 HONO budget calculation.

Potential sources of HONO include direct emissions (vehicle emissions, soil emissions, indoor emissions, biomass combustion), the gas-phase reaction between NO and OH radicals, the photolysis of nitrate in particulate matter, and the heterogeneous reaction of NO_2 on the ground and particulate matter surfaces. The sources including vehicle emissions ($E_{vehicle}$), soil emissions (E_{soil}), the reaction of NO and OH (P_{NO-OH}), the photolysis of particulate nitrate ($P_{nitrate}$), and the heterogeneous reaction of NO_2 ($P_{aerosol}$ and P_{ground}) have been accounted for. At present, there are relatively few studies on indoor emissions. Biomass combustion is an unimportant HONO source in downtown Beijing in winter according to a previous study (Zhang et al., 2019b). Thus, these two sources are not accounted for in this work. The major sinks of HONO, including dry deposition ($L_{deposition}$), the homogeneous reaction with OH radicals ($L_{HONO-OH}$), photolysis ($L_{photolysis}$), and vertical and horizontal transport (T_{trans}), are considered.

The calculation method and details in parameterization are shown in Table 1. Briefly, the budget and estimated concentration of HONO can be calculated according to the following

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equations,

$$\frac{dC_{HONO}}{dt} = E_{soil} + E_{vehicle} + P_{NO-OH} + P_{nitrate} + P_{aerosol} + P_{ground} -$$

$$L_{photolysis} - L_{HONO-OH} - L_{deposition} - T_{trans} \quad (1)$$

$$HONO_{est,t_2} = HONO_{obs,t_1} + Sources_{t_2} - Sinks_{t_2} \quad (2)$$

where $\frac{dC_{HONO}}{dt}$ is the change rate of HONO mixing ratios (ppb h^{-1}), $HONO_{est,t_2}$ is the estimated concentration of HONO at time t_2, while $HONO_{obs,t_1}$ is the observed concentration of HONO at time t_1. The input parameters for the parameterization scheme are detailed in Table S2 (M0).

The emission rate (E_{HONO}, ppb h^{-1}) of soil and vehicle were calculated based on the emission flux (F_{HONO}, g m^{-2} s^{-1}), the PBL height (H, m), and the conversion factor (α). For vehicle emissions, according to our previous research at the same site, the emission factor (EF, $HONO/NO_x$) was selected as 1.09% (Liu et al., 2020d), which is comparable to the actual values in Hong Kong (1.2 ± 0.4% and 1.24 ± 0.35%) (Liang et al., 2017; Xu et al., 2015), Guangzhou (1.0%) (Li et al., 2012), Beijing (1.3% and 1.41%) (Zhang et al., 2019c; Meng et al., 2020), and other places. For secondary formation, the calculation of the production rate (P_{HONO}, ppb h^{-1}) is shown in Table 1, in which k_1 is the rate constant of the quasi-first order reaction (s^{-1}), $C_{precursor}$ is the concentration of the precursor (ppb). For the heterogeneous reaction of NO_2, we calculated the conversion rate in the light of Eqs. (3)-(5):

$$k_{het}^{0} = \frac{C_{HONO,corr,t_2} - C_{HONO,corr,t_1}}{\overline{C_{NO_2}} \times (t_2 - t_1)} \quad (3)$$

$$k_{het}^{co} = \frac{2 \times \left[\frac{C_{HONO,corr,t_2}}{C_{CO,t_2}} \times \overline{C_{CO}} - \frac{C_{HONO,corr,t_1}}{C_{CO,t_1}} \times \overline{C_{CO}}\right]}{(t_2 - t_1) \times \left[\frac{C_{NO_2,t_2}}{C_{CO,t_2}} + \frac{C_{NO_2,t_1}}{C_{CO,t_1}}\right] \times \overline{C_{CO}}}$$

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$$= \frac{2\times\left[\frac{C_{HONO,corr,t_2}}{C_{CO,t_2}} - \frac{C_{HONO,corr,t_1}}{C_{CO,t_1}}\right]}{(t_2-t_1)\times\left[\frac{C_{NO_2,t_2}}{C_{CO,t_2}} + \frac{C_{NO_2,t_1}}{C_{CO,t_1}}\right]} \quad (4)$$

$$k_{het} = \frac{1}{2} \times (k_{het}^{0} + k_{het}^{co}) \quad (5)$$

where k_{het} is the quasi-first-order rate constant of the transformation to HONO (s^{-1}), k_{het}^{0} and k_{het}^{co} are the reaction rate constants after uncalibrated and CO calibrated, respectively (Zhang et al., 2020). $\overline{C_{NO_2}}$ and $\overline{C_{CO}}$ are the mean concentration of NO_2 and CO from t_1 to t_2. $C_{CO,t}$ and $C_{NO_2,t}$ are mixing ratios of CO and NO_2, respectively, at the measuring time t. $C_{HONO,corr,t}$ (ppb) is the HONO concentration corrected after subtracting the primary emissions (including vehicle and soil emissions, and the HONO produced by the homogeneous reaction of NO and OH and the photolysis of nitrate) at the measuring time t according to Eq. (6):

$$c_{HONO,corr,t} = c_{HONO,t} - E_{soil,t} - E_{vehicle,t} - P_{NO-OH,t} - P_{nitrate,t} \quad (6)$$

it is worth noting that the $c_{HONO,corr}$ only accounted for vehicle exhausts in previous HONO budget studies. This may overestimate the contribution of heterogeneous reactions to HONO sources because other emission sources and homogeneous reactions should also contribute to HONO.

Meanwhile, when estimating the upper limit of the contribution of heterogeneous reactions, we take a small conversion factor (HONO/NOx) of 0.4% as the lower limit of vehicle emissions, in contrast to the normal value of 1.09% (Liu et al., 2020d). We normalize the EI_{NO_X} caused by the vehicle with the measured C_{NO_X} during the observations. This method has also been widely used in previous studies (Liu et al., 2019b; Li et al., 2018). In addition, soil emissions are calculated using the lower limit (Oswald et al., 2013). The mean value of

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k_{het} during the BCNY (before the Chinese New Year) was 0.0051 h^{-1}, while it was 0.006 h^{-1} in the COVID-19 lockdown, which are consistent with previous studies, such as Ji'nan (0.0068 h^{-1}) (Li et al., 2018) and Shanghai (0.007 h^{-1}) (Wang et al., 2013), while less than those in Shijiazhuang (0.016 h^{-1}) (Liu et al., 2020c), Kathmandu (0.014 h^{-1}) (Yu et al., 2009), and Guangzhou (0.016 h^{-1}) (Qin et al., 2009).

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230 Table 1. Summary of parameters for HONO sources and sinks

HONO formation/loss pathways	Calculations	Parameters	Reference
Soil emissions → HONO	$E_{HONO} = \alpha \times F_{HONO}/H$	$F_{HONO,soil}$	1
Vehicle emissions → HONO		$F_{HONO,vehicle} = (EI_{NOx,vehicle}/A) \times (HONO/NOx)_{vehicle}$	2
NO + OH → HONO		$k_{NO-OH} = 7.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}	3
$NO_3^- \xrightarrow{h\nu}$ HONO		$J_{NO3^-} = 8.24\times10^{-5}/3.59\times10^{-7} \times J_{HNO3,MCM}$	
$NO_2 + H_2O \xrightarrow{aerosol\ surface}$ HONO	$P_{HONO} = 3600\times k \times c_{precursor}$	$k_{het} = (\gamma_{NO2} \times A_s \times \omega/4) \times Y_{HONO}$	4
$NO_2 + H_2O \xrightarrow{ground\ surface}$ HONO		$k_{het} = (\gamma_{NO2} \times \delta \times \omega/4H) \times Y_{HONO}$	
HONO $\xrightarrow{h\nu}$ NO + OH	$L_{photolysis} = 3600\times J_{HONO} \times c_{HONO}$	$J_{HONO,MCM}$	
HONO + OH → H_2O + NO_2	$L_{HONO-OH} = 3600\times k_{HONO-OH} \times c_{HONO} \times c_{OH}$	$k_{HONO-OH} = 6\times10^{-12}$ cm^3 molecule^{-1} s^{-1}	5
HONO deposition	$L_{deposition} = (3600\times V_d \times c_{HONO})/H$	$V_d = 0.001$m s^{-1}	6
HONO transport (vertical and horizontal)	$T_{trans} = k_{dilution} \times (c_{HONO} - c_{HONO,background})$	$k_{dilution} = 0.23$ h^{-1}	7

$F_{HONO,soil}$ (soil emission flux) was calculated by the temperature-dependent HONO emission flux on grasslands with a water content of 35% to 45%. A is the urban area of Beijing, $EI_{NOx,vehicle}$ is the emission inventory of NO_x from vehicle (g s^{-1}). The calculation of the HONO emission flux, during BCNY, was based on the hourly NO_x emission inventory of Beijing vehicles ($F_{HONO}=F_{NOx} \times (HONO/NOx)_{vehicle}$), while during COVID-19, it was combined with the hourly average traffic index (www.nitrafficindex.com). The $(HONO/NOx)_{vehicle}$ was selected as 1.09% (Liu et al., 2020d). The OH concentration was estimated using the same method as in the previous study (Liu et al., 2020c). The mean photolysis frequency of nitrate (J_{NO3^-}) was normalized to the measured UV light intensity. A_s is the surface area concentration of the reaction surface (m^2 m^{-3}); ω is the average molecular velocity (m s^{-1}); γ is the uptake coefficient of the precursor, was assumed to be 2×10^{-6}; Y_{HONO} is the yield of HONO. δ is the surface roughness, in this study, we used 3.85 for our calculation (Liu et al., 2020d). c_{HONO} and $c_{HONO,background}$ is the HONO concentration at the observation site and background site, respectively.

1: (Oswald et al., 2013). 2: (Yang et al., 2019). 3: (Liu et al., 2020c). 4: (Liu et al., 2020d). 5: (Kanaya et al., 2007). 6: (Han et al., 2017b). 7: (Dillon et al., 2002).

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We further derived the uptake coefficient of NO_2 (γ_{NO2}) on both ground and particle surfaces according to Eq. (7).

$$k_{het} = \frac{\gamma_{NO2} \times A_S \times \omega}{4} \times Y_{HONO} \quad (7)$$

The calculated γ_{NO2} ranged from 1×10^{-6} to 3×10^{-6}. Therefore, we choose 2×10^{-6} to calculate the heterogeneous yield of NO_2, which is comparable with those derived in urban environments like Ji'nan (1.4×10^{-6}) (Li et al., 2018) and the laboratory experiments (10^{-7} to 10^{-6}) (Han et al., 2013; Stemmler, 2007; Han et al., 2017a) on different particles, but lower than the uptake coefficient of 10^{-5} reported in other studies (Zhang et al., 2020; Ge et al., 2019).

The OH concentration was calculated according to Eq. (8), which is based on the function of the photolysis rates (J) of O_3 and NO_2, and the NO_2 mixing ratio (C_{NO2}).

$$C_{OH} = \frac{4.1\times10^{9}\times(J_{NO2})^{0.19}\times(J_{O1D})^{0.83}\times(140C_{NO2}+1)}{0.41C_{NO2}^{2}+1.7C_{NO2}+1} \quad (8)$$

Notably, this parameterization scheme was developed based on measurements at rural sites (Ehhalt and Rohrer, 2000), where NOx concentrations were lower than in urban environments. Alicke et al. (Alicke, 2002) found that OH concentrations estimated with this scheme were in good agreement with those calculated according to a pseudo-steady state method during the pollution period in urban environments (such as Milan), although some uncertainty was expected. In our previous study (Liu et al., 2020d), we also found that the estimated OH concentrations using this method were comparable with those observed values in the North China Plain (Tan et al., 2019). Thus, daytime OH concentrations estimated using this method should be overall credible although the uncertainty is inevitable. The nocturnal OH concentration in North China generally varied from 1.0×10^5 molecules cm^{-3} (Ma et al., 2019;

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Tan et al., 2018) in winter to 5×10^5 molecules cm^{-3} in summer (Tan et al., 2017; Tan et al., 2020). We further parameterized the nocturnal OH concentrations according to atmospheric temperature to reflect the seasonal variations of OH concentration. Fig S1 summarizes the observed OH concentrations in the North China Plain. The results estimated in this study are slightly lower than those observed in Wangdu, but almost consistent with those in Beijing and Huairou. In summary, we should be optimistic about the estimation of OH concentration. Then a sensitivity analysis was performed to understand the influence of the uncertainty of OH concentration on HONO sources as discussed in Section 3.3.

The loss rate of HONO, including dry deposition ($L_{deposition}$), homogeneous reaction with OH radicals ($L_{HONO-OH}$), photolysis ($L_{photolysis}$), and vertical and horizontal transport (T_{trans}), were calculated using the equations shown in Table 1. Where J_{HONO} is the photolysis rate of HONO (s^{-1}), $k_{HONO-OH}$ is the second-order reaction rate constant between HONO and OH, V_d is the dry deposition rate of HONO, and $K_{dilution}$ is the dilution rate (including both vertical and horizontal transport). The details are described in our previous work (Liu et al., 2020c; Liu et al., 2020d).

3. Results and discussion

3.1 Air quality during observations.

Figure 1 shows the time series of the concentration and relative proportion of non-refractory components in $PM_{2.5}$, trace gases (SO_2, O_3, CO, NO, NO_2, and NO_x), and meteorological parameters (temperature, relative humidity (RH), and pressure). We divide the sampling period into two sub-periods, i.e., P1 from January 1 to January 24 (BCNY, before the Chinese New Year) and P2 from January 25 to March 6 (COVID-19 lockdown).

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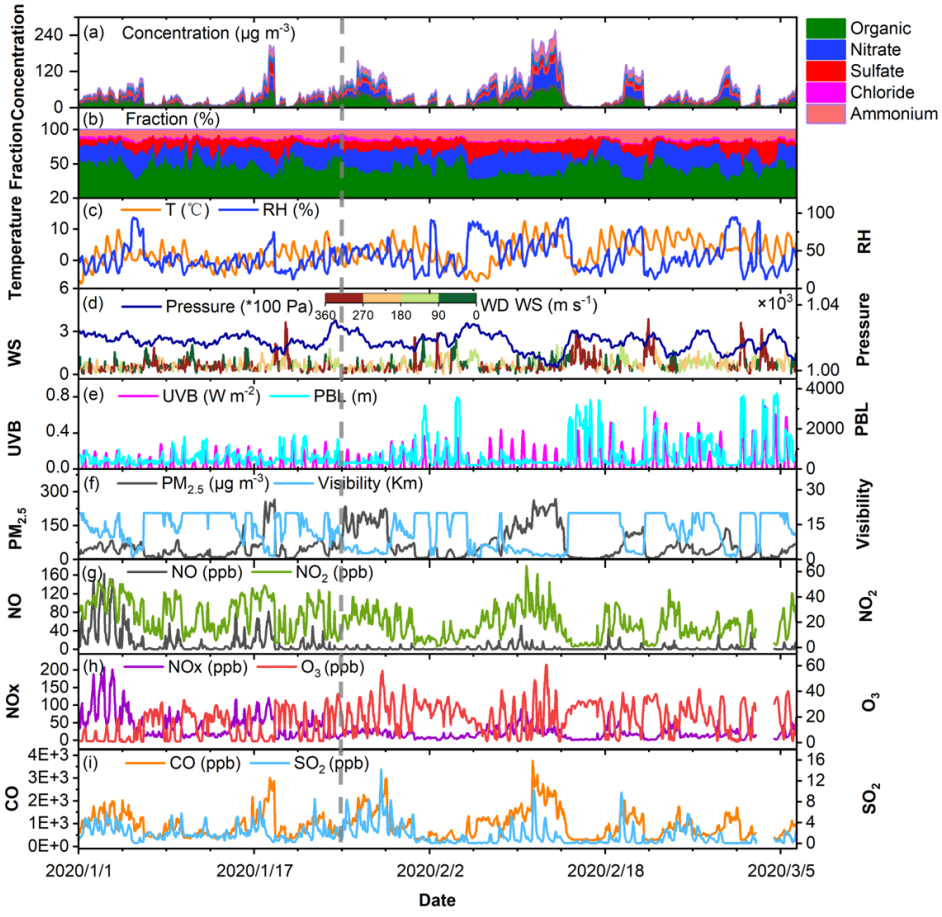

Figure 1. An overview of the measurement of the mass concentrations of the different components of non-refractory-$PM_{2.5}$ (NR-$PM_{2.5}$), the mass fraction of the individual components, $PM_{2.5}$, and meteorological parameters, NO_x (NO, NO_2), O_3, CO and SO_2 in 1-hour average from 1 January to 6 March 2020. Meteorological parameters consist of visibility, PBL heights, UVB, wind speed, wind direction, Pressure, RH, and temperature. The observations are divided into two phases (P1:2020.01.01-2020.01.24 and P2:2020.01.25-2020.03.06).

It can be seen from Fig. 1 that during P1, there was only one heavy pollution incident

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lasting one to two days, while there were two serious pollution events lasting more than two days ($PM_{2.5}$ > 75 μg m^{-3}) in the P2 stage. Table S3 summarizes the statistical results of the wind speed, $PM_{2.5}$, RH, T, HONO, trace gases, and NR-$PM_{2.5}$ for the entire measurement period. During P1, the concentration of $PM_{2.5}$ varied between 0.2-288 μg m^{-3} and the mean concentration was 47.2 ± 44.5 μg m^{-3}. In contrast, the $PM_{2.5}$ concentrations varied from 0.3 to 258 μg m^{-3} with a mean value of 69.9 ± 67.2 μg m^{-3} during P2. The concentrations of SO_2 were in the range of 0.02-8.56 ppb with a mean value of 2.09 ± 1.35 ppb in P1, while it varied from 0.01 to 14.23 ppb with the mean concentration of 1.49 ± 1.99 ppb during P2, suggesting slightly decreased contribution of coal combustion during P2 (Fig. 1i). This is similar to that reported by Cui et al (Cui et al., 2020) and Shen et al (Shen et al., 2021). The mean concentrations of NO_x decreased significantly ($P < 0.05$) from 45.35 ± 38.86 ppb in P1 to 19.44 ± 14.42 ppb in P2, dropping by about 57%. This is close to the reduction amplitude (50%) reported by Wang et al. (Wang et al., 2020a) but lower than that (76%) proposed by Lv et al (Lv et al., 2020). In particular, the NO mean concentrations dropped from 18.42 ± 29.24 ppb (ranging from 0.03 to 163 ppb) in P1 to 2.4 ± 5.46 ppb (ranging from 0.01 to 51 ppb). The average hourly concentration of NO_2 in the P1 phase was 26.9 ± 13.4 ppb, while it was 17.18 ± 11.3 ppb in P2. The NO_2 concentration dropped by about 36% from P1 to P2, which is similar to the recently reported findings (ranging from 36% to 53%) (Zhao et al., 2020; Wang et al., 2020b; Wang et al., 2021). According to the emission inventory of NO_x, traffic and industry contributed 46.7 % and 31.3% to NO_x emissions in Beijing, respectively (Zheng et al., 2014). This means the decrease in NOx concentration should be explained by both reductions in traffic and industrial emissions (Lv et al., 2020; Wang et al., 2020a; Zhao et al., 2020). In particular, traffic emissions

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during P2 should play an important role in local NO reduction. However, as the temperature and ultraviolet light irradiation increased and the NO_x concentration decreased (Kroll et al., 2020; Le et al., 2020), the average concentration of O_3 during P2 was 21.31 ± 11.73 ppb, which was significantly higher than 12.16 ± 10.79 ppb during P1. This result is similar to the 71.4% increase in O_3 in Shijiazhuang during the same period (Liu et al., 2020c). In addition, it can be seen from Fig. 1 that the change trends of $PM_{2.5}$ and CO are synchronized, which also means that both primary emissions and secondary generation contribute to the accumulation of $PM_{2.5}$ concentration (Liu et al., 2020c).

All the major components of $PM_{2.5}$, including sulfate, nitrate, ammonium, chloride, and organic aerosol, increased obviously in P2 compared to P1. Throughout the entire observation period, organic matter and nitrate dominated the composition of $PM_{2.5}$. The proportion of nitrate in inorganic salts increased to 31.2% in P2, up from 28.1% in P1. Although the sulfate concentration increased, its proportion within inorganic salts slightly decreased on haze days, going from 16.5% in P1 to 15.2% in P2. Thus, the ratio of NO_3^- to SO_4^{2-} during pollution events increased significantly from 1.76 in P1 to 2.10 in P2. This is similar to previous findings reported by Sun (Sun et al., 2020). These findings suggest that the decrease in anthropogenic emissions during the P2 period resulted in a significant reduction in gas precursors (Table S3), but it did not lead to a corresponding reduction in secondary aerosol species during periods of pollution. This is supported by the increased potential secondary aerosol formation under pollution conditions (Sun et al., 2020). For example, higher values of the SOR (sulfur oxidation ratio, molar fraction of sulfate in total sulfur including sulfate and SO_2) and NOR (nitrogen oxidation ratio, molar fraction of nitrate in total nitrogen, including nitrate and NO_2), i.e., 0.63

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and 0.34, were observed in P2 than those (0.48 and 0.14) in P1. Under stagnant weather conditions (wind speed < 2 m s^{-1}), higher temperatures and RH as shown in Table S3 might facilitate the conversion from precursors into particles (Liu et al., 2020d). The above results indicate that the air pollution dominated by secondary formation is much more serious in P2, which is supported by both the increased concentration and the greater number of pollution days in P2 than in P1, even though primary emissions decreased obviously.

3.2 Influence of Chinese New Year and the COVID-2019 epidemic event on HONO concentration in Beijing.

Figure 2 displays the time series of the HONO concentration, the HONO/NO_2 ratio, and the traffic index (www.nitrafficindex.com). In Fig. 2b, there is a significant decrease in the traffic index, indicating reduced traffic congestion during the COVID-19 lockdown (P2 period) compared to the P1 period. The HONO/NO_2 ratio is frequently used to indicate the conversion of NO_2 to HONO through heterogeneous reactions (Sun et al., 2013). A higher HONO/NO_2 indicates that the heterogeneous conversion process plays a more significant role in HONO production. However, as depicted in Fig. 2b, both the traffic index and HONO exhibit a similar decreasing trend, while the HONO/NO_2 ratio remains relatively stable. Notably, both the traffic index and the NO concentration experienced a steep decline after January 24, coinciding with a significant decrease in HONO concentration. Furthermore, as shown in Fig. S2, there is a strong correlation between HONO and NO_x in both P1 and P2. However, HONO concentration does not track $PM_{2.5}$ concentration well. These results imply that HONO might be more influenced by vehicle emissions than by heterogeneous reactions. This contrasts with prior studies that heterogeneous reactions on aerosol surfaces are the primary source of HONO in

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pollution events in Beijing (Liu et al., 2014; Cui et al., 2018; Meng et al., 2020).

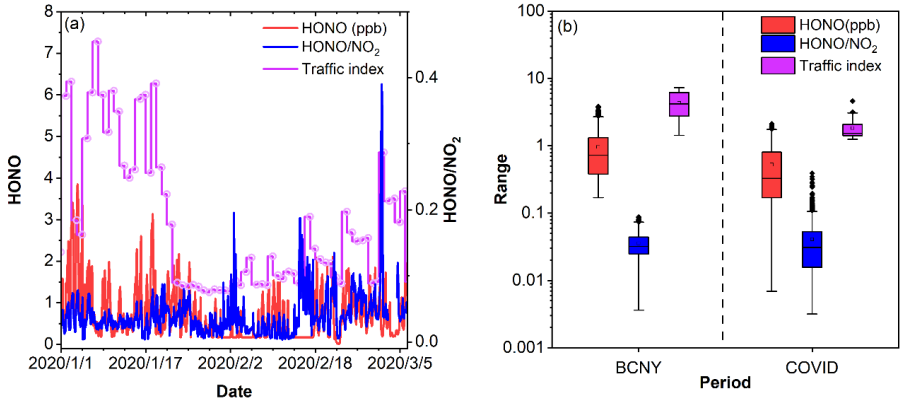

Figure 2. (**a**) Times series of HONO, traffic index, and HONO/NO_2, (**b**) Box plots of HONO, HONO/NO_2, and the traffic index in Beijing during different periods (BCNY=P1, LOCK=P2).

Table S4 summarizes the mean concentrations of HONO, NO_2, NO, and $PM_{2.5}$ over the two periods in this study as well as the data reported in previous studies. During P1, HONO concentration ranged from 0.17 to 3.85 ppb, with a mean value of 0.97 ± 0.74 ppb. This concentration is similar to previous observations, such as in Beijing, Xi'an, Jinan, Shanghai, Hong Kong, and Rome, which all ranged from 0.95 to 1.15 ppb (Acker et al., 2006; Wang et al., 2013; Xu et al., 2015; Huang et al., 2017; Liu et al., 2020d; Li et al., 2018). However, during the COVID-19 lockdown, the HONO concentration decreased to 0.53 ± 0.44 ppb, representing a drop of 45.3% compared with that in BCNY. This value is comparable to the concentrations reported in the literature for clean days in December 2016 in Beijing (0.5 ± 0.2 ppb) and in the winter of 2018 in Xiamen (0.52-0.61 ppb). At the same time, as discussed in the previous section, the NO concentration decreased by nearly 87% from BCNY to COVID-19 lockdown, and the NO_2 concentration dropped by about 36%. Consequently, we can conclude that the

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concentrations of HONO, NO, and NO_2 were the most affected pollutants during the COVID-19 lockdown period.

Figure 3 shows the diurnal curves of HONO, NO_x, NO, NO_2, HONO/NO_2, O_3, SO_2, and $PM_{2.5}$×NO_2 during P1 (BCNY) and P2 (COVID-19 lockdown). The black and red lines represent P1 and P2, respectively. HONO shows a similar trend in both periods. After sunset, HONO began to accumulate due to the attenuation of solar radiation and the development of the boundary layer, reaching maximum values of 1.41 ± 0.83 ppb and 0.92 ± 0.64 ppb around 7:00 during P1 and P2, respectively. Subsequently, due to the impact of the boundary layer and rapid photolysis, the HONO concentration gradually decreased and remained at a low level until sunset, with the corresponding minimum value of 0.43 ± 0.24 ppb and 0.27 ± 0.17 ppb at about 15:00. Similar to HONO, the NO_2 concentration shows an upward trend during the morning rush hour. Its peak appeared at 7:00 (BCNY: 31.4 ± 9.23 ppb; COVID-19 lockdown: 23.3 ± 10.74 ppb), and then dropped rapidly and remained at a low level due to photochemical processes and the development of the boundary layer. The minimum concentration occurs around 14:00 to 15:00 (BCNY: 18.17 ± 10.69 ppb; COVID-19 lockdown: 11.0 ± 7.64 ppb). After sunset, NO_2 began to increase again. It is worth noting that during BCNY, both NO_2 and NO exhibited a prominent evening peak, whereas there was no such evening peak during the COVID-19 lockdown. Thus, NO_x and NO_2 had similar changing trends, i.e., the morning peak observed in both periods with the highest mean values of 65.93 ± 50.37 ppb and 31.7 ± 21.47 ppb in BCNY and COVID-19 lockdown, respectively.

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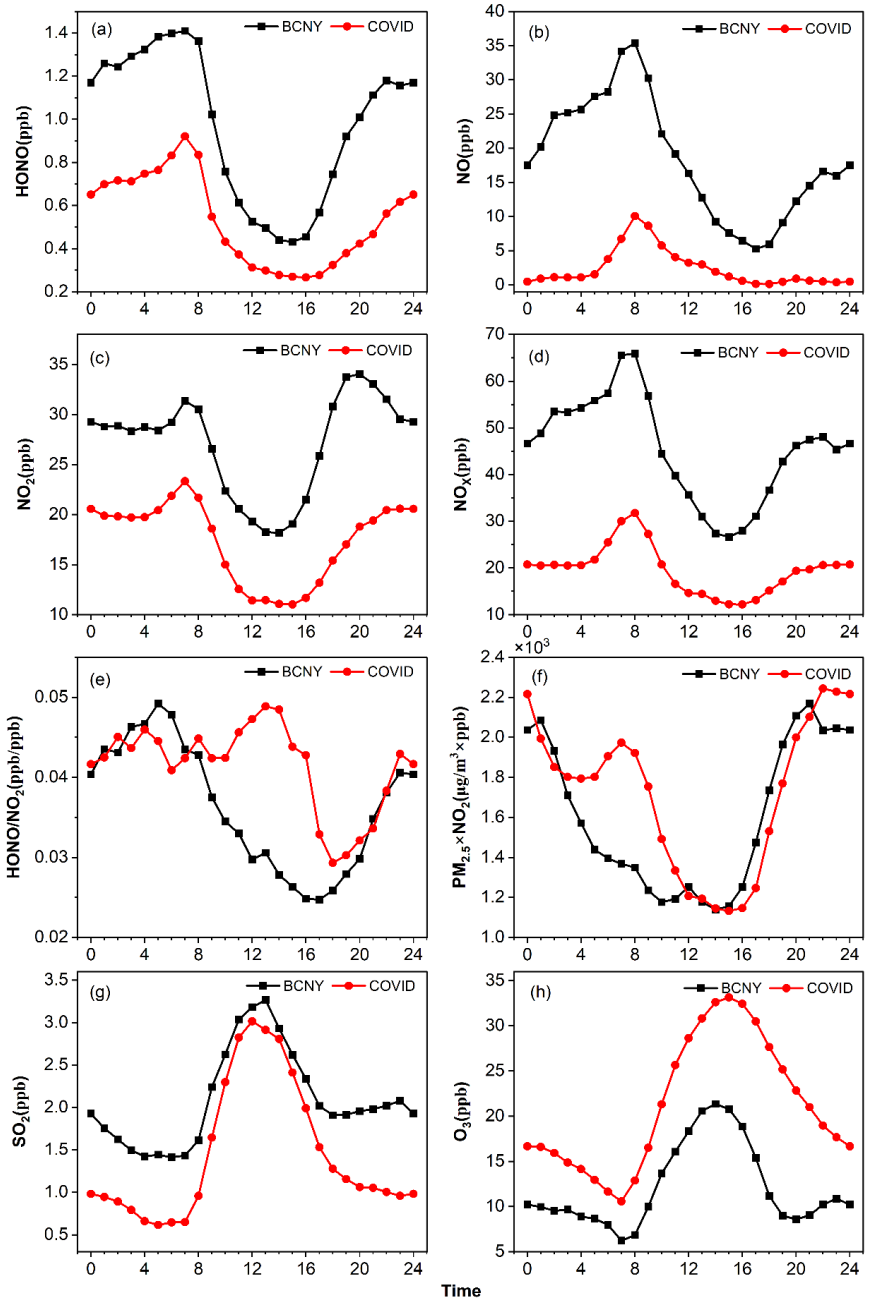

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389 **Figure 3.** Diurnal variation of HONO, NO, NO_2, NO_x, HONO/NO_2, $PM_{2.5}$×NO_2, SO_2, O_3. The

390 black lines are the diurnal curves before CNY and the red ones are during the COVID-19

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lockdown.

NO and HONO showed a similar trend in P1. They began to decline continuously after sunrise and continued to rise after sunset. The peaks of NO were 35.40 ± 43.55 ppb and 10.0 ± 12.67 ppb in P1 and P2, respectively. It is worth noting that the upward trend of NO concentration in the afternoon of the P2 stage was not obvious, as the absolute concentration of NO was very low. O_3 and HONO showed opposite diurnal curves, with the maximum O_3 concentrations occurring in the afternoon, which were 21.35 ± 9.31 ppb and 33.14 ± 10.26 ppb in P1 and P2, respectively. SO_2 and O_3 exhibited similar trends, with the maximum values in P1 and P2 were 3.26 ± 2.19 ppb and 3.01 ± 3.06 ppb at 13:00, and their lowest values were 1.41 ± 0.68 ppb and 0.62 ± 0.82 ppb at 5:00 or 6:00.

Previous studies proposed that the heterogeneous reactions of NO_2 on the aerosol surface play an important role in HONO production. Specifically, this pathway was considered the major source of HONO on polluted days (Cui et al., 2018; Meng et al., 2020; Zhang et al., 2020). $PM_{2.5}$×NO_2 can be used as an indicator for the heterogeneous reaction of NO_2 on the surface of aerosols (Cui et al., 2018). It was found that the value of $PM_{2.5}$×NO_2 in P2 (1697 ± 2142) was slightly higher than that in P1 (1583 ± 1967). In the early morning, the product of $PM_{2.5}$ and NO_2 in the P2 stage was even higher than that in the P1 stage. On the other hand, the ratio of HONO/NO_2 is usually used to evaluate the formation of HONO during the conversion of NO_2. As shown in Fig. 3, in the P1 stage, the HONO/NO_2 ratio shows a similar daily trend to HONO, which began to rise after sunset and reached a peak at night and then decreased in the early morning due to the increase of NO_2 concentrations and the photolysis of HONO. In

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the P2 stage, the variation of $HONO/NO_2$ is different from that of the P1. The $HONO/NO_2$ in the P2 period was higher than that in the P1 stage, especially in the daytime, although the values of $HONO/NO_2$ in both stages (P1: 0.036 ± 0.016; P2: 0.041 ± 0.038) were lower than that (0.052-0.080) reported by Cui et al (Cui et al., 2018). Subsequently, we further analyzed $HONO_{corr}/NO_2$ (details shown in Sect. 2.2). The $HONO_{corr}/NO_2$ attributed to secondary formation via heterogeneous reactions changed obviously after subtracting the interference of other HONO sources. As shown in Fig. S3, the daytime peak of $HONO_{corr}/NO_2$ in P2 became more prominent compared with that in Fig. 3e. At the same time, the $HONO_{corr}/NO_2$ (0.038 ± 0.035) in P1 was slightly lower than that in P2 (0.042 ± 0.034). However, the HONO concentration decreased significantly as discussed above. These results suggest that heterogeneous reactions of NO_2 on the aerosol surfaces may not be a major source of HONO because the enhanced potential of heterogeneous reactions indicated by $PM_{2.5}\times NO_2$ and $HONO_{corr}/NO_2$ in P2 contrast with the decreased HONO concentrations compared to P1. In summary, we propose that during our observation period, heterogeneous reactions of NO_2 should have a relatively minor contribution to HONO production.

3.3 Relative change of different sources to HONO budget in Beijing during different periods.

Figure 4a-f shows the diurnal variation of HONO production or emission rates for these sources at different stages, and Fig. 4g-l shows the budget of the HONO sources and sinks during P1 (BCNY) and P2 (COVID-19 lockdown). The HONO production rate via homogeneous reaction between NO and OH in the P1 period was much higher than that in the P2 period, especially during the daytime. The average rate decreased from 0.145 ± 0.189 ppb h^{-1} in the P1

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stage to 0.047 ± 0.073 ppb h^{-1} in the P2 stage. The OH concentrations increased slightly from P1 ($4.1\times10^5 \pm 5.8\times10^5$ cm^{-3}) to P2 ($6.7\times10^5 \pm 1.0\times10^6$ cm^{-3}). Therefore, the observed decrease in HONO production rate via homogeneous reaction between NO and OH should be ascribed to the substantial reduction of NO concentration as discussed above. It can be seen that the homogeneous reaction between NO and OH is indeed an important source of HONO at night. In previous studies, the nocturnal production of HONO via NO and OH was often ignored because low nighttime OH concentrations were estimated (Fu et al., 2019). However, some studies have shown that the observed nighttime OH concentrations in the Beijing urban area can also be maintained in the order of 10^5 molecules cm^{-3} in winter, which also means that the contribution of the reaction channels of NO and OH to HONO cannot be ignored. In the P1 stage, the homogeneous reaction between NO and OH accounted for 13% of the nighttime HONO sources. However, in the daytime, the homogeneous reaction between NO and OH was the most important source of HONO, which accounted for up to 51% of the daytime HONO source. This is consistent with a recent study that proposed the oxidation pathway of NO by OH is the main source of HONO (Song et al., 2023). In the P2 stage, its proportion in the night was negligible due to the dramatic decrease in NO concentration during the pandemic event, and the maximal proportion of HONO sources in the daytime was also reduced to 25%. It is worth noting that the parameterization of OH concentration will introduce uncertainty to HONO sources. Table S2 shows the sensitivity test for the HONO simulation. An increase of 10% and 200% in OH concentration in M3 and M4 results in a 24-26% change in the HONO source. It means that the accuracy of the OH measurement is important for understanding the source-sink balance of the HONO.

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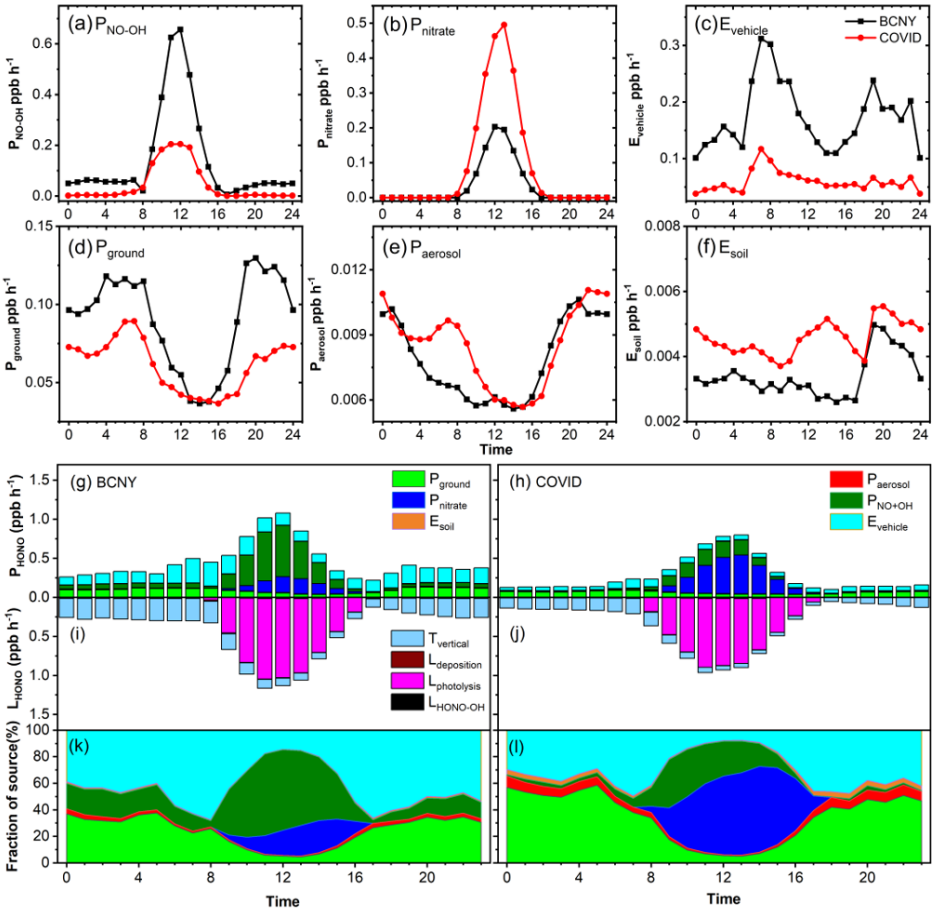

Figure 4. (**a-f**): Diurnal variations in HONO production rate from various sources. The black lines are the diurnal curves before CNY and the red ones are during the COVID-19 lockdown. (**g-l**): Variations of HONO budget. (**g,h**) Diurnal production rates of HONO; (**i,j**) loss rates of HONO (unit: ppb h^{-1}); (**k,l**) relative contributions of each source. Panels (**g**),(**i**), and (**k**) show the data from BCNY, and panels (**h**),(**j**), and (**l**) show the data from the COVID-19 lockdown.

The daytime HONO source related to photolysis of nitrate (0.223 ± 0.175 ppb h^{-1}) in the P2 stage was much larger than that (0.107 ± 0.068 ppb h^{-1}) in the P1 stage. It contributed 16%

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to the daytime HONO source in the P1 period. However, it became the most important daytime source of HONO in the P2 stage, accounting for up to 53%, as both the nitrate concentration and the light intensity increased significantly. Ye et al. (Ye et al., 2016) reported that the photolysis rate constants of nitrate particles on the surface of different materials were in the range of 6.0×10^{-6} - 3.7×10^{-4} s^{-1}. Thus, we used the lower limit value of 6.0×10^{-6} s^{-1} and the upper limit value of 3.7×10^{-4} s^{-1} for sensitivity tests (methods M9 and M10), which resulted in a change of 25% and 95% of HONO sources, respectively. The yield of soil emissions in the P2 stage is also higher than that in the P1 stage due to the temperature rise in the P2 stage because the temperature will affect the soil emission flux (Oswald et al., 2013), while the importance of this source is negligible in this study. In M15 and M16, we amplify and shrink the soil emission flux by 10 times, respectively, and the change of the simulated HONO sources was less than 5%.

The direct emission rate of HONO from vehicles in the P1 stage was much higher than that in the P2 stage. The emission rate of the P1 stage was between 0.135-0.39 ppb h^{-1}, with a mean value of 0.227 ± 0.071 ppb h^{-1}. This is comparable with the value (0.079-0.32 ppb h^{-1}) in the winter of 2018 (Liu et al., 2020d). In the P2 stage, it decreased to 0.062-0.173 ppb h^{-1}, with a mean value of 0.086 ± 0.027 ppb h^{-1}. This value is slightly higher than the lower limit of vehicle emissions of 0.013-0.076 ppb h^{-1} estimated using an emission factor of 0.18% in our previous study (Liu et al., 2020d), while it is less than the upper limit reported by Li (Li et al., 2018) in Jinan of 0.13 ± 0.06-0.53 ± 0.23 ppb h^{-1}. During the lockdown, the emission rate of HONO from vehicles was reduced by 53%-66% when compared with that before the lockdown. In the P1 period, vehicle emission was an important nighttime source of HONO. It contributed

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53% to the HONO sources, much higher than heterogeneous reactions of NO_2 on aerosol and ground surfaces (33%) (Fig. S7). In the P2 stage, due to the reduction of transport, the contribution of vehicle emissions to HONO sources decreased to 40%, while the contribution of heterogeneous reactions of NO_2 increased to 53%. This is consistent with the observed decrease in HONO concentrations. The daytime contributions of vehicle emissions to HONO sources were lower than the corresponding nighttime contributions, while it was still higher in the P1 period than in the P2 period. These results mean that vehicles should be important contributors to ambient HONO under typical emission patterns in Beijing. In the sensitivity analysis, the emission factors of 0.008 and 0.0186 were considered in methods M1 and M2, and 8% and 20% changes were found in the simulated HONO sources, respectively.

As shown in Fig. 4e, the heterogeneous reaction rate of NO_2 on aerosols did not change much between the P1 and P2 stages. The average production rate of HONO in the P1 stage was 0.007 ± 0.002 ppb h^{-1}, and it was 0.008 ± 0.002 ppb h^{-1} in the P2 stage, showing an increase of about 14%. It is worth noting that the HONO formation rate from the heterogeneous conversion of NO_2 on the surface of aerosol does not decrease, which is caused by the increase in $PM_{2.5}$ concentration along with a slight decrease in NO_2 concentration during the P2 period. If the heterogeneous transformation of NO_2 on particulate surfaces is important, especially in the case of heavy pollution, increased HONO concentrations should be expected instead of a large decrease, as observed in the P2 stage. This is consistent with the changes in $HONO_{corr}/NO_2$ and $PM_{2.5}\times NO_2$ as discussed in Sect. 3.2. For the heterogeneous transformation of NO_2 on the ground and aerosol surfaces, this source is sensitive to the uptake coefficient (γ) of NO_2. Here we assume that the upper limit of γ is 10^{-5} (M7) and the lower limit is 2×10^{-7} (M8) (Liu et al.,

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2019b; Liu et al., 2020d). As shown in Table S2, the change in simulated HONO is less than 5%. We reduced and magnified the surface area concentration (A_s) of particulate matter by a factor of 10 in M11 and M12, respectively, and the resulting change in HONO was still less than 10%, which also verifies that the heterogeneous reaction of NO_2 on aerosol surfaces may be an unimportant HONO source.

Regarding the heterogeneous reaction of NO_2 on ground surfaces, the average formation rate of HONO in the P1 stage was 0.09 ± 0.03 ppb h^{-1}, while it was 0.06 ± 0.02 ppb h^{-1} in the P2 stage. This is ascribed to the significant drop in NO_2 concentration during the COVID-19 lockdown. Fig. 4k shows that the heterogeneous reaction of NO_2 on ground surfaces is also an important nighttime source of HONO. In the P1 stage, heterogeneous reactions on both aerosol and ground surfaces explained 33% of the nighttime HONO source. In the daytime, however, the contribution of heterogeneous reactions to HONO sources dropped rapidly. In the P2 stage, the heterogeneous reaction became the most important nighttime source contributing up to 53% of HONO (Fig. S7). This can be explained by the significant decrease in NO and direct emissions of HONO from traffic. Similar to heterogeneous reactions on aerosol surfaces, we assumed that the upper limit of γ_{NO2} on ground surfaces was 10^{-5} (M5) and the lower limit was 2×10^{-7} (M6), respectively, and the changes in simulated HONO source were 40% and 9%, respectively. In M13 and M14, we set the surface roughness (δ) to 1 and 2.2 as reported in the literature, respectively (Zhang et al., 2022b; Liu et al., 2020c), and the simulated changes in HONO were less than 8%.

During the P1 and P2 periods, the mean values of $T_{vertical}$ were 0.195 ± 0.076 ppb h^{-1} and 0.102 ± 0.048 ppb h^{-1}, respectively. It was the main sink of HONO at night. The mean $L_{photolysis}$

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was 0.563 ± 0.375 ppb h^{-1} and 0.442 ± 0.324 ppb h^{-1}, respectively, which was the main daytime sink of HONO. The average loss rate of $L_{HONO\text{-}OH}$ during P1 and P2 was 0.005 ppb h^{-1} and 0.004 ppb h^{-1}, respectively. The $L_{deposition}$ was 0.009 ± 0.005 ppb h^{-1} during P1, while it was 0.004 ± 0.003 ppb h^{-1} during P2. In M17 and M18, we set the lower limit of the deposition rate (V_d) to 0.00077 and the upper limit to 0.025 (Zhang et al., 2023b), causing a change of 1% and 24% in the simulated HONO, respectively. In M19 and M20 at the same time, we set the dilution rate ($K_{dilution}$) to 0.1 and 0.44, resulting in a 12% and 19% change, respectively.

To verify these calculated sources and sinks of HONO, we further estimated the HONO concentration according to Eq. (2) and the parameters described in Sect. 2.2. Fig. S4 shows the time series of estimated HONO concentrations. The observed HONO concentrations were also shown for comparison. The estimated HONO concentrations were well correlated with the observed values from the perspective of both diurnal curves and the scattering point plot during the whole period (Fig. S5 and Fig. S6) although the estimated HONO concentrations were slightly lower than the observed values at noon as shown in Fig. S5. This means that our parametric scheme is overall reasonable but still underestimates the daytime HONO source due to some unknown daytime sources. This unknown source may be related to the photochemical reactions related to NO_2 and nitroaromatic compounds mentioned in recent studies (Liu et al., 2020a). Liu et al. have found the photoenhanced effect of the conversion from NO_2 to HONO on real urban grime and glass windows simulated in laboratory studies (Liu et al., 2019a; Liu et al., 2020b). Yang et al. also have proposed that photolysis of nitroaromatic compounds may be a daytime source of HONO (Yang et al., 2021). Considering the uncertainty of parameterization, we used Oracle Crystal Ball (version 11.1.2.4, Oracle's software for

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modeling, prediction, simulation, and optimization) (Rahmani et al., 2023) to evaluate the overall uncertainty of the parameterization through Monte Carlo simulations. The relative standard deviation is 27.2% for the HONO budget.

In summary, heterogeneous reactions of NO_2 (including ground and aerosol surfaces) contributed 33% to the nocturnal HONO sources in the P1 stage, while they increased to 53% in the P2 stage. Ground surfaces were the main interfaces for heterogeneous reactions, compared to aerosol surfaces. At the same time, vehicle emissions account for 53% and 40% of nighttime HONO sources in the P1 and P2 stages, respectively. Therefore, we can conclude that traffic-related emissions, rather than heterogeneous reactions of NO_2 were the main HONO source at night in Beijing in the typical emission patterns of air pollutants.

4. Conclusions and atmospheric implications.

During the COVID-19 pandemic at the beginning of 2020, the concentration of many air pollutants decreased significantly due to the emission reduction of factories and transportation. The average concentration of NO_x decreased by about 57%, of which NO decreased by about 87%, and NO_2 decreased by about 36%. The average concentration of HONO decreased by about 45.3% compared with those before the pandemic control. The average concentration of O_3 and $PM_{2.5}$ increased by approximately 75% and 50%, respectively.

In this study, the parameters of HONO sources were optimized. The balance of sources and sinks is well supported by a relatively high correlation between observed and estimated HONO concentrations. During the observation period, we used lockdown during COVID-19 as a disturbance factor and compared the concentration and source changes of HONO before and during COVID-19 lockdown to determine whether heterogeneous reactions on the surface

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of particulate matter and vehicle emissions were important HONO sources. We found that vehicle-related emissions were the most important nighttime HONO source in Beijing, contributing 50-60% to the nighttime HONO sources. The homogeneous reaction between NO and OH and the heterogeneous reaction of NO_2 on the aerosol surface were not important for the contribution of nocturnal HONO, accounting for 13% and 2%, respectively. The heterogeneous reaction of NO_2 on ground surfaces was also found to be an important source of HONO at night, accounting for 31% of the nighttime HONO sources. Nitrate photolysis became the most important source of HONO during the daytime compared with the situation before the pandemic control because of the combined effect of the increase in the average concentration of nitrate and the decrease in the NO concentration during the pandemic. This study confirms that reducing anthropogenic emissions can indeed reduce the concentration of HONO in the atmosphere. However, such reduction does not have a simple linear relation with the reduction in human activities, but it also depends on meteorological conditions and complex chemical transformation processes taking place in the atmosphere.

As a megacity in China, Beijing has a large population and intensive traffic emissions, as a result of frequent air pollution. Although concentrations of HONO are usually lower than those of other major pollutants, HONO efficiently triggers the formation of secondary pollutants acting as an important primary source of OH radicals. Therefore, the sources of HONO deserve to be investigated for air pollution control in Beijing. Our results suggest that motor vehicle emissions are an important HONO source, while the contribution of the heterogeneous conversion of NO_2 to HONO on the aerosol surfaces still needs to be further evaluated and, especially, the kinetic parameters on ambient aerosol should be determined. In

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future research, it is necessary to combine field observations, laboratory studies, and model simulations to quantify the contribution of traffic-related emissions to HONO, and finally obtain an accurate budget of HONO.

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Author contributions: YZ contributed to the methodology, data curation, and writing of the original draft. ZF and FZ contributed to the methodology, investigation, and data curation. CL contributed to methodology, investigation, and data curation. WW contributed to the conceptualization, investigation, reviewing, and editing the text, and supervision. XF contributed to the methodology, reviewing, and editing the text. YZ and WM contributed to the methodology, investigation, data curation, and reviewing and editing the text. ZL and CL contributed to methodology, investigation, and data curation. GZ contributed to the methodology, investigation, resources, and data curation. CY contributed to the methodology, data curation, reviewing, and editing the text. VK, FB, TP, and JK contributed to the acquisition of resources and reviewing and editing the text. MK contributed to the methodology and reviewed the text. YL contributed to the conceptualization, investigation, data curation, writing, reviewing & editing, supervision, and funding acquisition;

Competing interests: At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

Data availability: Data are available upon request to Yongchun Liu (liuyc@buct.edu.cn).

Acknowledgments: This research was financially supported by the Beijing Natural Science Foundation (8232041), Beijing National Laboratory for Molecular Sciences (BNLMS-CXXM-202011), and the National Natural Science Foundation of China (42275117 and 41931287). This research was supported in part by Hebei Technological Innovation Center for Volatile Organic Compounds Detection and Treatment in Chemical Industry (ZXJJ20220406) and the Natural Science Foundation of Hebei Province (D2023209012). The work is partially supported by Academy of Finland Flagship “Atmosphere and Climate Competence Center

https://doi.org/10.5194/egusphere-2023-3139
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(ACCC), project number 337549 and European Union's Horizon 2020 research and innovation programme under grant agreement No 101036245 (RI-URBANS) and 101056783 (FOCI) as well as Technology Industries of Finland Centennial Foundation via project "urbaani ilmanlaatu 2.0".

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